

MODELLING OF CARBON SINK CAPACITY OF THE BLACK SEA

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ABSTRACT

MODELLING OF CARBON SINK CAPACITY OF THE BLACK SEA

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The concentration of carbon dioxide in the atmosphere is constantly increasing due to human activities and results in global warming. Since Industrial Revolution 30 and 25 percentages of the anthropogenic atmospheric carbon dioxide are taken up by the forests and by the oceans respectively. Carbon dioxide is rising faster than biosphere can tolerate and the rest of the carbon dioxide which can not be hold, continues to accumulate and causes further heating of the atmosphere. The carbon sink capacity of the oceans declined from 30 percent to 25 percent within the last five decades due to increased sea surface temperatures and changes in the related dynamics. In this thesis, it is aimed to investigate the CO₂ system and to evaluate the carbon sink capacity of the Black Sea. Three sources of data are used: i) R/V Knorr 2001 and 2003 Black Sea cruises seawater carbonate chemistry data sets related with air-sea exchange, physical mixing ii)The dataset of meteorological variables such as mean sea level pressure, 10 meter wind speed and hydrological parameter such as sea surface temperature iii) the dataset of partial pressure of CO₂ in the atmosphere. These datasets are utilized to set a

model allowing evaluating CO₂ fluxes. The calculated results for air-sea CO₂ fluxes indicate that for 2001 early summer time Black Sea acted as a sink for atmospheric CO₂ and for 2003 early spring time the Black Sea acted both as a sink and a source for atmospheric CO₂. The developed CO₂ model will be a guidance to understand how atmospheric processes interact with the processes in the ocean. Also the outcomes of this thesis will help Turkey to get information which is necessary for defining internal strategy to reduce CO₂ emission.

Keywords: Climate Change, Atmosphere-Sea Interaction, Carbon Flux, Seawater Carbonate System, Black Sea

ÖZ

KARADENİZ'İN KARBON TUTMA KAPASİTESİNİN MODELLENMESİ

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Yüksek Lisans, Yer Sistem Bilimleri Bölümü

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Antropojenik aktivitelerden dolayı atmosferik karbondioksit konsantrasyonu giderek artmaktadır ve küresel ısınmaya sebep olmaktadır. Endüstriyel devrimden bu yana okyanuslar atmosferik karbondioksitin %25'ini; okyanuslar da %30'unu tutmaktadır. Karbondioksitin artış hızı biyosferin tolere edebileceğinden daha da hızlıdır ve yutaklarca tutulamayan karbondioksit atmosferde birikerek atmosferin daha da ısınmasına sebep olmaktadır. Son 50 yıl içinde okyanusların karbondioksiti tutma kapasitesi artan deniz suyu sıcaklıkları ve ilgili dinamiklerdeki değişiklikler sebebiyle %30'dan %25'e düşmüştür. Bu tezde Karadeniz'in karbondioksit sistemi incelenerek karbon tutma kapasitesi hesaplanmaya çalışılmıştır. Bu amaçla üç veri seti kullanılmıştır: i) R/V Knorr 2001 ve 2003 Karadeniz seferlerinden elde edilen atmosfer deniz etkileşimi ve fiziksel karışım ile bağlantılı olan karbonat kimyası veri seti, ii) Deniz seviyesi basıncı, 10 metre rüzgar hızı ve deniz suyu sıcaklığı gibi parametreleri içeren meteorolojik veri seti. iii) Atmosferik karbondioksitin kısmı basıncını içeren dataseti. Bu datasetleri kullanarak atmosfer-deniz karbondioksit akısını değerlendirmek

amacıyla bir model kurulmaya çalışılmıştır. Hesaplanan atmosfer-deniz karbondioksit akıları sonuçları Karadeniz'in 2001 seferi sırasında atmosferik karbondioksit için bir yutak olduğunu, 2003 seferi sırasında ise hem bir yutak hem de bir kaynak olduğunu göstermiştir. Hazırlanan bu karbondioksit modeli atmosferik süreçlerin okyanuslardaki süreçlerle nasıl bir etkileşimde olduğunu anlamak için bir rehber olacaktır. Ayrıca tez sonucunda elde edilen veriler Türkiye'nin karbondioksit salınımı azaltmada izleyeceği içsel stratejiler için de bir kaynak oluşturacaktır.

Anahtar Kelimeler: İklim Değişikliği, Atmosfer-Deniz Etkileşimi, Karbon Akısı, Deniz Suyu Karbonat Sistemi, Karadeniz

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LIST OF ABBREVIATIONS

ECMWF	The European Centre for Medium-Range Weather Forecasts
fCO ₂	Fugacity of Carbon Dioxide
GHG	Green House Gases
IPCC	Intergovernmental Panel on Climate Change
NOAA	National Oceanic and Atmospheric Administration
pCO ₂	Partial Pressure of Carbon Dioxide
S	Salinity
Sigma _t	Density
SST	Sea Surface Temperature
T	Temperature
TA	Total Alkalinity
TCO ₂	Total Dissolved Inorganic Carbon
Ω _{ar}	Aragonite Saturation State
Ω _{ca}	Calcium Saturation State

CHAPTER 1

1. INTRODUCTION

1.1. The Climate System and Green House Gases (GHGs)

The incoming solar radiation powers the climate system, the physical-chemical features of the atmosphere and also the life on the Earth (Trenberth and Stepaniak, 2004). Approximately 30% of the solar radiation is reflected back to the atmosphere or scattered, the remaining 70% of the radiation is absorbed by the atmosphere, the land and the ocean at the surface and this radiation heats the atmosphere and the planet (Ramanathan and Feng, 2009). For the balance of absorbed incoming solar energy, the Earth must radiate back the same amount of energy to the space (Trenberth and Stepaniak, 2004). Since the Earth's surface is cooler than the sun, the emitted thermal radiation is in the form of infrared radiation which represents long wavelengths in radiation spectrum (Le Treut et al., 2007). This thermal radiation is absorbed and re-emitted by the Green House Gases (GHGs) (Ramanathan and Feng, 2009).

The major greenhouse gases are water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), ozone (O_3), nitrous oxide (N_2O), sulfur hexafluoride (SF_6), hydrofluorocarbons (HFC), perfluorocarbons (PFC) & chlorofluorocarbons (CFC) and the concentrations of three important GHGs and changes in their concentrations since pre-industrial times were represented in Table 1.1 (IPCC Reports, 2007 and 2013).

Table 1.1. Changes in Green House Gases Concentration between 1750 – 2011 (Source: IPCC Reports 2007 and 2013)

GH G	Life Time (year)	Concentration before Industrial Revolution	Concentration (2005)	1750-2005 Increase	Concentration (2011)	1750-2011 Increase
CO ₂	50-200	278 ppm	379 ppm	% 35	391 ppm	% 40
CH ₄	12	715 ppb	1774 ppb	% 148	1803 ppb	% 150
N ₂ O	120	270 ppb	319 ppb	% 18	324.2 ppb	% 20

Carbon dioxide (CO₂) has a small fraction in the atmosphere [e. g. 404 ppm (February 2016) (Dlugokencky and Tans, 2016)], however, CO₂ is more abundant than other trace gases such as methane (CH₄), halocarbons and nitrous oxide (N₂O) in the atmosphere therefore it is accepted to be the second most significant greenhouse gas next to water vapor (Heinze et al., 2015) and the most significant anthropogenic driving factor for climate change (Myhre et al., 2013).

The greenhouse effect of CO₂ is related to its molecular structure: the rotational and vibrational movements of gaseous CO₂ molecules interact with the thermal radiation emitted by the Earth's surface and thus heat the lower layers of the atmosphere (Barret, 2005).

Through the Earth's greenhouse effect described above, life becomes livable (Le Treut et al., 2007) because if the Earth was a black body, the temperature of the surface temperature would be -19°C which is much colder than annual average global mean temperature (14°C) (Trenberth and Stepaniak, 2004).

1.2. Carbon Cycle

1.2.1. The Global Carbon Cycle

The global carbon cycle is comprised of a group of carbon reservoirs, which are linked through the carbon flux in the Earth System and the domains of the global carbon cycle can be classified by their turnover time scales: The first is the fast domain which represents the quick turnovers and it includes the atmosphere, the ocean, surface ocean sediments, vegetation, soil and freshwaters; the second is the slow domain which includes large carbon stocks in rocks and sediments (Ciais et al., 2013). The carbon exchange between the fast and slow domain occurs through volcanic emissions of CO₂, chemical weathering, erosion and formation of sediment on the seafloor (Sundquist, 1986). The turnover time is at least 10000 years for the slow domains, several years for the atmosphere, decades to millennia for the other fast domains and the natural exchange fluxes between the two domains of the carbon cycle are comparatively small (<0.3 PgC yr⁻¹, 1 Pg C=1 Gt C=10¹⁵ g C) and thus can be considered constant in time over the last several centuries (Ciais et al., 2013).

In Figure 1.1, it was represented that the atmosphere is a small fraction of the carbon reservoirs and it corresponds to a mass of approximately 829 PgC and CO₂ is the dominant source for the atmospheric reservoir and CH₄ and CO are the other important carbon sources for the atmospheric pool. It was shown in Figure 1.1 that the terrestrial biosphere includes carbon in the form of organic compounds in vegetation (450 to 650 PgC), in the form of dead organic matter in litter and soils 1500 to 2400 PgC in permafrost soils (~1700 PgC) and also in fossil fuel reservoirs as gas (383 to 1135 PgC), oil (173 to 264 PgC) and coal (446 to 541 PgC).

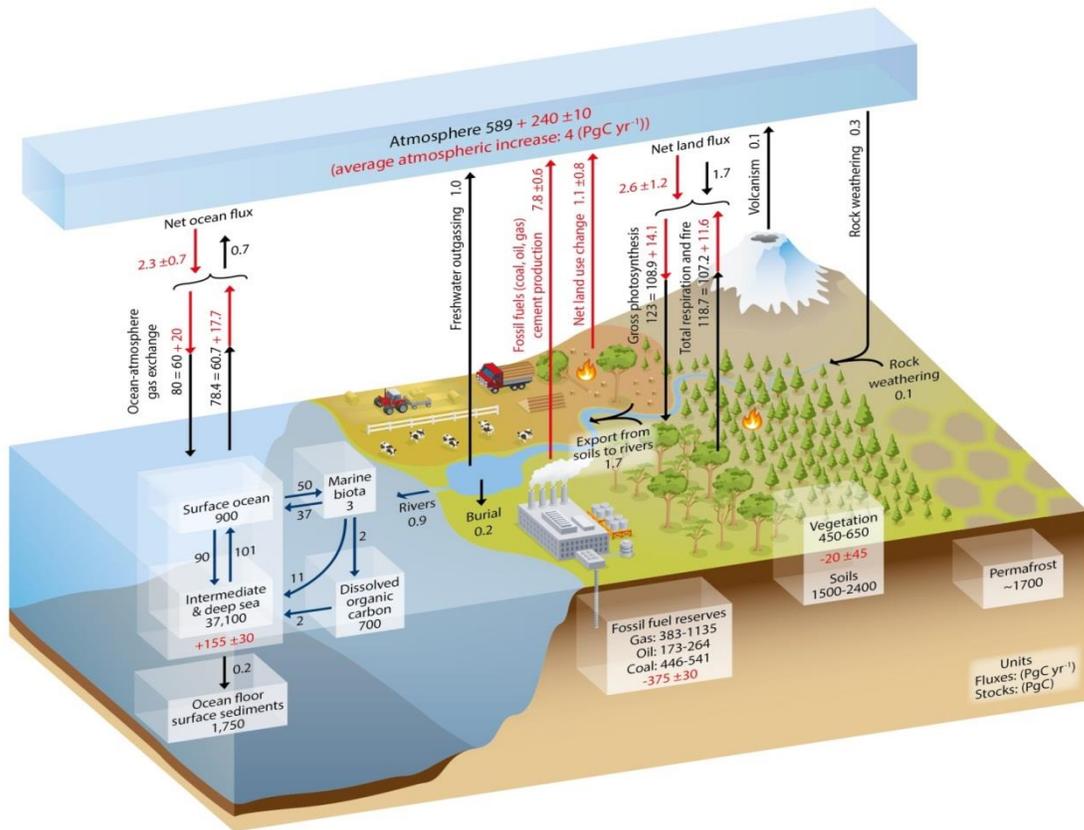


Figure 1.1. Simplified global carbon cycle. Numbers indicate the carbon stocks in PgC. Black numbers and arrows represent reservoir mass and fluxes estimated for the time prior to the Industrial Era. Red arrows and numbers represent anthropogenic fluxes for the 2000-2009 time period. The fossil fuel reserves are obtained from GEA (2006); the sediment storage represents the sum of 150 PgC of the organic carbon in the mixed layer (Emerson and Hedges, 1988) and 1600 PgC of the deep-sea sediments to neutralize fossil fuel carbon dioxide (Archer et. Al., 1998). The change in the air-sea flux was calculated from the difference in atmospheric partial pressure of carbon dioxide since 1750 (Sarmiento and Gruber, 2006). The atmospheric inventories were calculated using a conversion factor of 2.12 PgC per ppm (Prather et al., 2012). Source: (Ciais et al., 2013).

In the oceanic reservoir, carbon is mainly found as Dissolved Inorganic Carbon (DIC, ~38000 PgC) in surface ocean (900 PgC), in intermediate and deep sea (37100 PgC) (Figure 1.1). The ocean has carbon also in the form of Dissolved Organic Carbon (DOC, ~700 PgC) which has a turnover time of 1000 years (Hansell et al., 2009), and in marine biota, which comprises mainly phytoplankton and other microorganisms (~3 PgC), with a turnover time of days to a several weeks (Ciais et al., 2013). It was demonstrated in Figure 1.1 that the major part of the carbon in the ocean is stored in intermediate and deep waters.

Before the Industrial Era, the fast domain was almost at a steady state, however, since the Industrial Era because of fossil fuel extraction and their usage, a serious amount of carbon has transferred to the fast domain from slow domain, consequently resulted in a human-induced modification in the global carbon cycle (Figure 1.1).

1.2.2. The Oceanic Carbon Cycle

By this time, the oceans have captured approximately 155 ± 30 PgC from atmosphere, which is equal to roughly 25% of the total amount of carbon dioxide released to the atmosphere through human activities (555 ± 85 PgC) since pre-industrial times (Rhein et al., 2013). Gruber et al., (2009) found a global oceanic uptake rate of 1.9 PgC yr^{-1} by using the difference in partial pressure of CO_2 across the air water interface with combination of riverine input for the time period of 1995-2000 and Takahashi et al. (2009) estimated the global oceanic uptake rate 2.0 PgC yr^{-1} which is normalized to the year 2000.

The main processes which control the ocean carbon cycle are: solubility pump; biological pump, and biological counter pump (Le Quere and Metzl, 2003).

The solubility of carbon dioxide is the function of temperature, pressure and salinity and there is an inverse relation between the solubility of CO_2 and temperature (Al-Anezi et al., 2008). This solubility effect results in outgassing in the equatorial region

where the cold deep water is transferred to surface layer by upwelling and heated by the atmosphere and conversely this effect provides CO₂ uptake at mid-latitudes and high latitudes where surface waters are transported by the currents and this process is called as solubility pump (Le Quere and Metzl, 2003).

Temperature is also a significant factor for solubility of CO₂ in surface waters that the concentration of CO₂ is approximately 2000 μmol kg⁻¹ in warm low latitude surface waters however in cold high latitude waters it is around 2100 μmol kg⁻¹ because of elevated solubility at lower temperatures (Zeebe and Wolf-Gladrow, 2008).

Biological carbon uptake generally takes place in the surface waters (in the euphotic layer), where phytoplankton by the photosynthesis produces biomass which is consumed by other organisms on higher trophic levels (Heinze et al., 2015). This process also depends on the availability of light and nutrients (phosphate, nitrate, silicic acid and micronutrients such as iron) for the organisms to grow (Denman et al., 2007). The dead tissues of the marine plankton either stay in the water as dissolved organic carbon (DOC) or they aggregate into particulate organic carbon (POC) which sinks into deeper layers, and the sinking process of POC removes carbon from surface waters and stores it in the deep layer where it has no interaction with the atmosphere for decades to centuries and deep waters which have high amount of carbon are transferred back to the surface by physical mechanisms (Le Quere and Metzl, 2003). Both DOC and POC return back to dissolved inorganic carbon through degradation (Le Quere and Metzl, 2003) and the whole cycle of carbon which includes export production and physical transport of carbon is defined as biological pump (Hansell et al., 2009).

The formation of CaCO₃ by marine organisms through shell and skeleton building, is a significant source of CO₂ to the surrounding seawater and in turn a source for the atmospheric CO₂ (Frankignoulle et al., 1994). During the formation of CaCO₃, CO₂ is released in the surface waters therefore this process counters the biological pump and it is defined as the biological counter pump (Le Quere and Metzl, 2003). Generally, CaCO₃ particles reach the seafloor before they dissolve and the deep layers are

undersaturated with respect to CaCO_3 and the rest of the particles penetrate the marine sediment and they either redissolve or accumulate within the sediment (Denman et al., 2007).

1.3. Carbon Dioxide in the Atmosphere

The variations in earlier CO_2 concentrations in the atmosphere can be deduced from the measurements of air composition entrapped in the ice cores from Antarctica (Lüthi et al., 2008). The strong correlation between the atmospheric CO_2 and the temperature during eight glacial cycles was confirmed by the measurements in Antarctica (Petit et al., 1999; Siegenthaler et al., 2005; Jouzel et al., 2007; Lüthi et al., 2008). The concentration of atmospheric CO_2 varied between ~180 parts per million (ppm) and ~280 ppm during glacial and interglacial periods (Figure 1.2).

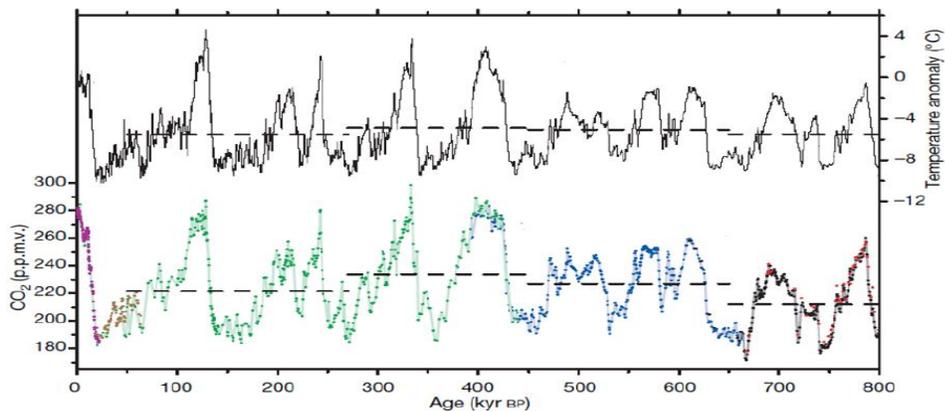


Figure 1.2. Compilation of CO_2 records obtained from drillings in Antarctica and temperature anomaly over the past 800 kyr. (Source: Lüthi et al., 2008)

Since the industrial era (1750), the concentration of atmospheric CO_2 has increased from about 277 ppm in 1750 (Joos and Spahni, 2008) to 404 ppm in 2016

(Dlugokencky and Tans, 2016) For the first time, the concentration of CO₂ in the atmosphere has passed the critical 400 ppm threshold level and the increase trend of atmospheric CO₂ continued (Figure 1.3).

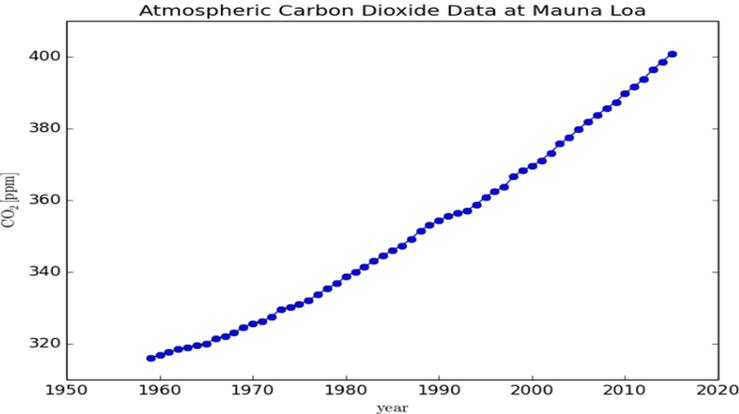


Figure 1.3. Annual mean atmospheric carbon dioxide data at Mauna Loa Observatory, Hawaii. (Source:Tans and Keeling, 2016)

The main reason of high levels of atmospheric CO₂ was primarily caused by fossil fuel emissions and secondly by anthropogenic land use change activities (IPCC, 2013). The Representative Concentration Pathways (RCPs) developed by the Intergovernmental Panel on Climate Change (IPCC) showed that the rise of atmospheric CO₂ concentration will continue beyond 2100 and the level of the concentration will be 421 ppm for RCP2.6 (very low forcing level), 538 ppm for RCP4.5 (stabilization scenario), 670 ppm for RCP6.0 (stabilization scenario) and 936 ppm for RCP8.5 (very high baseline emission scenario) according to the model simulations by 2100 and the continuous increase in emissions of greenhouse gases will lead to further warming and severe consequences for all elements of the climate system which includes the atmosphere, water cycle, cryosphere, ocean, global carbon cycle and furthermore even

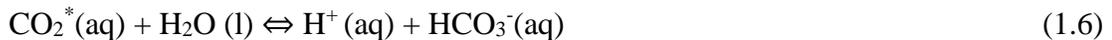
if the emissions are restricted, the effects of the climate change will persist (IPCC, 2013).

1.4. Carbonate System in Seawater

Dissolved inorganic carbon (TCO₂) is found in four forms in seawater: aqueous form (CO₂ (aq)), carbonic acid (H₂CO₃), bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions and the reactions of CO₂ when it dissolves in seawater and combines with water were shown in Equations 1.1, 1.2, 1.3 and 1.4:



where (g), (l) and (aq) represent the state of the species, a gas, a liquid or in aqueous solution respectively and since it is difficult to discriminate the species CO₂ (aq) and H₂CO₃ (aq) it is common to combine the concentrations of CO₂ (aq) and H₂CO₃ (aq) and to use these sum as the concentration of a hypothetical species, CO₂^{*}(aq) and when rearranging the equations in terms of this species Equations 1.5 and 1.6 are obtained:



The equilibrium equations between the concentrations of the different species were shown in Equations 1.7, 1.8 and 1.9:

$$K_0 = [\text{CO}_2^*] / f(\text{CO}_2) \quad (1.7)$$

$$K_1 = [\text{H}^+][\text{HCO}_3^-] / [\text{CO}_2^*] \quad (1.8)$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-] \quad (1.9)$$

where, K₀ is the solubility coefficient of CO₂ in seawater; K₁ and K₂ are the first and second dissociation constants of the carbonic acid which are functions of temperature,

pressure and salinity, $f(\text{CO}_2)$ represents the fugacity of CO_2 in the gas form and brackets indicate total stoichiometric concentrations of the chemical species (Dickson et al., 2007).

In seawater carbonate system, there are only four measurable parameters: total alkalinity (TA), total inorganic carbon (TCO_2), pH and either partial pressure of CO_2 ($p\text{CO}_2$) or $f(\text{CO}_2)$ and from two of these parameters, together with the temperature, salinity, pressure, abundances of other components of seawater and the suitable equilibrium constants, the other two parameters of the carbonate system in seawater can be determined (Lewis and Wallace, 1998).

1.4.1. Total Alkalinity and Total Dissolved Inorganic Carbon

Alkalinity can be basically defined as the ability of seawater to resist pH changes upon addition of acid (Sabine et al., 2004). Equation 1.10 represents all the constituents of total alkalinity in seawater where $[\text{H}^+]_F$ represents the free concentration of hydrogen ion and ellipses indicate minor acid and base species which can be safely neglected, and Equation 1.11 shows the components of the total inorganic carbon where CO_2^* represents hypothetical species (Dickson et al., 2007).

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \\ & + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] + \dots \\ & - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \dots \end{aligned} \quad (1.10)$$

$$\text{TCO}_2 = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1.11)$$

TA and TCO_2 are conservative parameters of seawater chemistry in the context of mixing and changes in pressure and temperature however changes in salinity and several biogeochemical processes such as calcium carbonate precipitation or production of particulate organic matter by marine organisms can alter the TA in the oceans (Wolf-Gladrow et al., 2007). Entrance of CO_2 from the atmosphere increases the concentration of TCO_2 while TA is not affected and also respiration and photosynthesis result in the same condition however TA maybe altered through nutrient release and

uptake.

1.4.2. Partial Pressure and Fugacity of CO₂

The partial pressure of CO₂ (pCO₂) represents the product of mole fraction of CO₂ in dry air [xCO₂ (dry)] and total pressure and the fugacity of CO₂ [f(CO₂)] indicates the fugacity of CO₂ in air which is in equilibrium with the water. f(CO₂) in air is approximately 0.3% less than the pCO₂ due to nonideality of CO₂, at pressure levels of the order of 1 atm (Weiss, 1974). f(CO₂) was represented in Equation 1.12, where x(CO₂) is the mole fraction of CO₂, R is the universal gas constant, T is temperature and V is the volume of CO₂ (Lewis and Wallace, 1998).

$$f(\text{CO}_2) = x(\text{CO}_2) \cdot p \cdot \exp \left[\frac{1}{RT} \int_0^p V(\text{CO}_2) - RT/p' \, dp' \right] \quad (1.12)$$

1.4.3. pH, Revelle Factor and Omega

pH represents the hydrogen ion concentration in seawater (Equation 1.13) and Equation 1.14, where [H⁺]_F represents the free hydrogen ion concentration, gives the total hydrogen ion concentration (Dickson et al., 2007).

$$\text{pH} = -\log[\text{H}^+] \quad (1.13)$$

$$[\text{H}^+] = [\text{H}^+]_F + [\text{HSO}_4^-] \quad (1.14)$$

The Revelle factor (Equation 1.15) represents the percentage change in f(CO₂) or in pCO₂ arising from a 1% change in total dissolved inorganic carbon at constant alkalinity and it is a function of temperature, salinity and the total alkalinity and total dissolved inorganic carbon:

$$\text{Revelle Factor} = (dp\text{CO}_2/d\text{TCO}_2) / (p\text{CO}_2 / \text{TCO}_2) \quad (1.15)$$

and the value of the Revelle factor changes approximately between 8 and 20 (Lewis and Wallace, 1998). Warm tropical and subtropical waters have generally low Revelle Factors and cold high latitude waters have high values of Revelle Factor and the carbon uptake capacity of oceans has an inverse relation with Revelle Factor which indicates that oceans with lower Revelle Factor have more capacity to take up anthropogenic

carbon dioxide and also the higher Revelle values in the North Pacific nearsurface waters when compared to North Atlantic waters, which is located at the comparable latitudes, are attributed to lower alkalinity values ($\sim 100 \mu\text{mol kg}^{-1}$) (Sabine et al., 2004).

Omega shows the saturation state of oceans regarding inorganic precipitation and dissolution of calcium carbonate (Tyrrell et al., 2008). Aragonite (Ar) and calcite (Ca) are the two most observed forms of CaCO_3 in the ocean therefore omega is calculated with respect to calcite and aragonite (Chierici and Fransson, 2009).

Equation 1.16 shows the calculation of omega where K_{sp} represents the state of dissolution at equilibrium.

$$\Omega = \frac{[\text{CO}_2^-] \cdot [\text{Ca}^{2+}]}{K_{sp}} \quad (1.16)$$

The values of $\Omega < 1$ indicate undersaturated conditions where CaCO_3 dissolution may occur, whereas the values of $\Omega > 1$ indicate saturated conditions where CaCO_3 precipitation may occur (Tyrrell et al., 2008).

1.5. Carbon Dioxide Exchange between Atmosphere and Seawater

The difference between the partial pressure of CO_2 in seawater and partial pressure of CO_2 in the atmosphere ($\Delta p\text{CO}_2 = [(p\text{CO}_2)_{sw} - (p\text{CO}_2)_{air}]$) regulates the CO_2 flux magnitude and direction across the sea surface for instance, when $(p\text{CO}_2)_{air}$ is larger than $(p\text{CO}_2)_{sw}$, $\Delta p\text{CO}_2$ becomes negative and seawater takes up the atmospheric CO_2 (Takahashi et al., 2009) and the net air-sea CO_2 flux is calculated using the Equations 1.16:

$$F = k \propto \Delta p\text{CO}_2 \quad (1.16)$$

where k represents gas transfer velocity (ms^{-1}), which is a function of 10 meter wind speed (u_{10}) (ms^{-1}), and Schmidt number (Sc); α is the solubility coefficient of CO_2 in seawater ($\text{mol/m}^3\text{atm}^{-1}$).

Wind speed, precipitation, heat flux, sea ice and surfactants are the other controls on the gas exchange rate between sea surface and the atmosphere (Denman et al., 2007) and the rate of gas exchange is well correlated with the wind speed (Wanninkhof and McGillis, 1999; Nightingale et al., 2000). Huge amount of anthropogenic CO₂ is taken up by Antarctic Intermediate Water as a consequence of low atmospheric CO₂ concentration and strong winds which increases gas transfer (Sabine et al., 2004).

Surface (pCO₂)_{sw} is affected by physical and chemical processes such as changes in temperature, salinity and inorganic carbon speciation, by biological processes (photosynthesis and oxidation), transport process (mixing and advection of water masses which have different CO₂ concentrations) and CO₂ flux between air and sea (Park et al., 2010). Results of the study for the northern North Atlantic surface waters published by Peng et al. in 1987 showed that (pCO₂)_{sw} has the lowest value in summer time and highest value in winter time and this variation in concentration of (pCO₂)_{sw} was mainly attributed to high biological activity in surface mixed layer in summer and upward transfer of CO₂ rich deep water by convective mixing in winter.

1.6. Oceans under High Atmospheric/ Anthropogenic CO₂ and Ocean Acidification

Cumulatively from the beginning of the industrial age, the ocean is estimated to have taken up approximately 25 to 30% (Rhein et al., 2013) of total anthropogenic CO₂ emissions however the oceanic uptake has several crucial consequences: it results in pH reductions and modifications in vital chemical processes which are as a whole referred to as ocean acidification (Doney et al., 2009). The rate of change in ocean pH may be faster than at any time in the last 300 million years and due to this modification in seawater chemistry, the capacity of the ocean to uptake the atmospheric CO₂ diminishes (IGBP, 2013). The carbon uptake capacity of ocean is reduced because of decrease in solubility, increase in vertical stratification and decrease in formation of water mass which ventilates thermocline, intermediate and deep water (Arora et al., 2013). From planktonic coccolithophores and pteropods and other molluscs, to echinoderms, corals,

coralline algae and many other marine organisms will be directly affected by the ocean acidification since it will be more difficult for some species to utilize carbonate to build skeletons and shells, under high CO₂ conditions which cause a decrease in CO₃²⁻ concentration (Doney et al., 2014). Results of the study published by Beaufort et al. in 2011 showed that as partial pressure of CO₂ increases calcification decreases and affects coccolithophores mass and this pattern is valid for past forty thousand years and today's ocean.

The average ocean surface pH has decreased by 0.1 units, from about 8.21 to 8.10 and a further decrease in pH units is expected if atmospheric CO₂ concentrations increase to a level of 800 ppm as in the scenario developed by IPCC (Orr et al., 2005).

1.7. General Characteristics of the Black Sea

1.7.1. Oceanographic Characteristics of the Black Sea

The Black Sea, located between latitudes of 41° to 46°N and longitudes of 28° to 41.5°E, is semi-enclosed basin with a narrow opening to the Aegean basin of the Eastern Mediterranean through the Bosphorus and Dardanelles Straits and the Sea of Marmara (Fig. 1.4.). The Black Sea with a maximum depth of about 2200 m involves discharges from three largest rivers of Europe: Danube, Dniepr and Dienstr and it is the World's largest anoxic basin and a more complex ecosystem structure than the mesotrophic Aegean Sea and the oligotrophic Mediterranean Sea (Oğuz and Jilan, 2005; Oğuz and Tuğrul, 2009).



Figure 1.4. The Black Sea and its Bathymetry

The water balance of the Black Sea was studied by Ünlüata et al. (1989) and it was shown that there is a positive water balance in which the sum of precipitation $Q_p \sim 300 \text{ km}^3 \text{ yr}^{-1}$ and runoff $Q_r \sim 350 \text{ km}^3 \text{ yr}^{-1}$ is more than evaporation $Q_e \sim 350 \text{ km}^3 \text{ yr}^{-1}$. The contribution from Danube itself is about $210 \text{ km}^3 \text{ yr}^{-1}$ water and from Dniestr and Dniestr about a total of $60 \text{ km}^3 \text{ yr}^{-1}$ water is delivered into the same area, and the rest is dispersed around the basin (Oğuz and Tuğrul, 2009). The variations in the water budget of the Black Sea was studied by Oguz (2009) and it was shown that the sum of river discharge and precipitation stays constant at about $550 \text{ km}^3 \text{ yr}^{-1}$ and evaporation is steady at $300 \text{ km}^3 \text{ yr}^{-1}$.

The characteristics of the surface waters change seasonally and described by a temperature of $5\text{-}6^\circ\text{C}$ and salinity of 18.5-18 in winter and $\sim 25^\circ\text{C}$ and salinity of 18 in summer time (Oğuz and Jilan, 2005). Between the oxic surface and anoxic deep layers

the suboxic zone is defined with boundaries related to the densities of sigma \sim 15.6 and 16.2 (Tuğrul et al., 1992) and the existence of a constant pycnocline between the brackish upper layer and the saltier deep waters hinders ventilation of deep layer below 100–150 m depth (Oğuz and Tuğrul, 2009).

The cold intermediate layer (CIL) is located below the surface layer and described as a layer where temperature reaches the minimum (e.g. lower than 8°C) and the thickness of CIL changes seasonally and regionally from 25 m to 100 m (Oguz et al., 1993). The mixing of CIL and the Bosphorus outflow derives the deep water formation in the Black Sea (Murray et al., 1991). The deepest layers of the Black Sea is almost uniform and described by $T\sim 9.0^{\circ}\text{C}$ and $S\sim 22.32$ and almost 87% of the waters of the Black Sea are anoxic (Oğuz and Jilan, 2005).

The upper layer circulation in the Black Sea, which is driven by wind and buoyancy, is defined as the Rim current around the periphery, an interior cell which consists of two or more cyclonic gyres, and a set of quasi-stable/recurrent anticyclonic eddies on the coastal part of the Rim current (Figure 1.5). Eddies interact among each other and also with meanders and filament of the Rim current constantly and also over the northwestern shelf the effect of the Danube outflow dominates the circulation (Oguz et al., 1995; Oğuz et al., 2002).

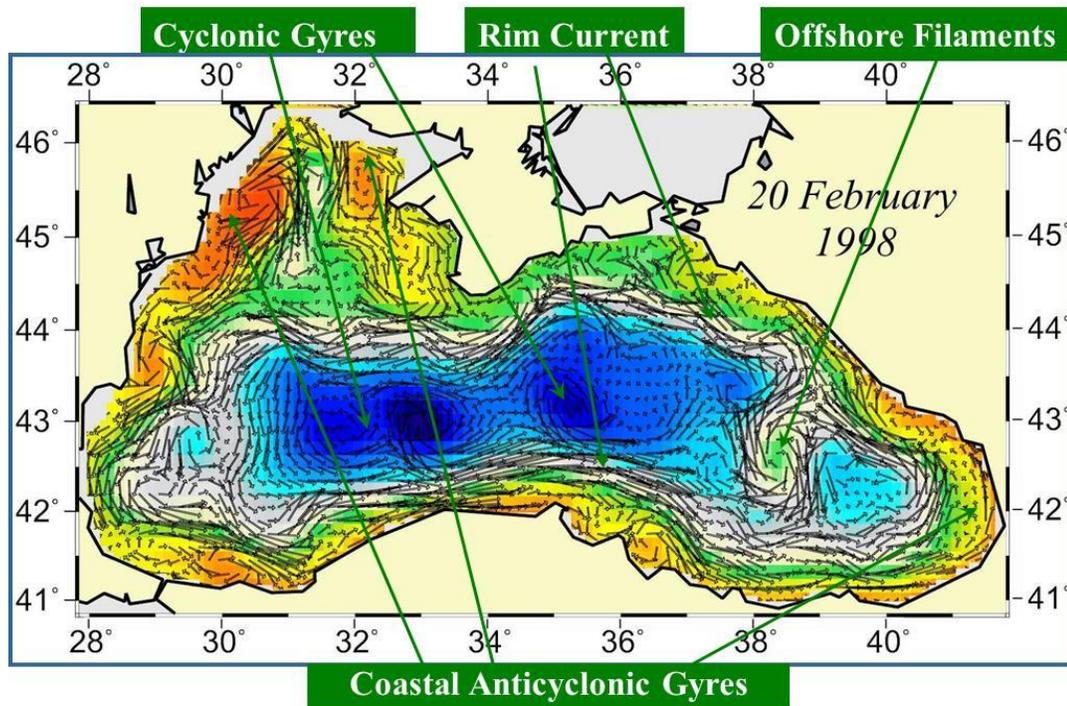


Figure 1.5. Circulation Patterns of the Black Sea (Source: Oğuz et al., 2002).

1.7.2 Black Sea Climate System

The North Atlantic Oscillation (NAO) represents the variation in sea level pressure between the Icelandic Low and the Azores High systems and affects the precipitation and temperature over the North Atlantic region and Europe (Marshall et al., 2001). Since the winter time is dynamically more active, the strongest variation occurs in the cold seasons (Linderholm et al., 2007). The positive phase of NAO is related to higher than normal surface pressures around south of 55°N and deeper than normal pressure throughout the Arctic to increase the meridional pressure gradient (Hurrell and Deser, 2009) and the negative phase of NAO implies a weakened pressure gradient. During the winter times when the NAO index is high, a strong pressure gradient occurs over the North Atlantic and results in warmer and wetter weather conditions in northern

Europe and drier and colder conditions in eastern-southeastern Europe and opposite conditions occur when NAO has negative index (Hurrell, 1995).

After the examination of hydro-meteorological and biogeochemical data, Oğuz et al. (2006) have shown that NAO is an important forcing for the Black Sea together with the East Atlantic- West Russia (EAWR) climate systems and there is a strong relation between the NAO index and the climatic variations over the Black Sea which results in relatively colder and drier winters during the positive phase of NAO, and vice versa for the negative phase of NAO.

The change in sea surface temperature (SST) is well correlated with the NAO index (Figure 1.6). Figure 1.6.a. represents that there has been a cooling phase up to 1910, then a 1°C warming between 1910 and 1970, a 1.5°C cooling next 20 years and a strong warming after 1995. Figure 1.6.a represents the variations in the SST of the Black Sea through the period 1877 and 2010. There is a continuous gradual winter warming after 1995 (Oğuz 2009; Küçükavşar, 2013).

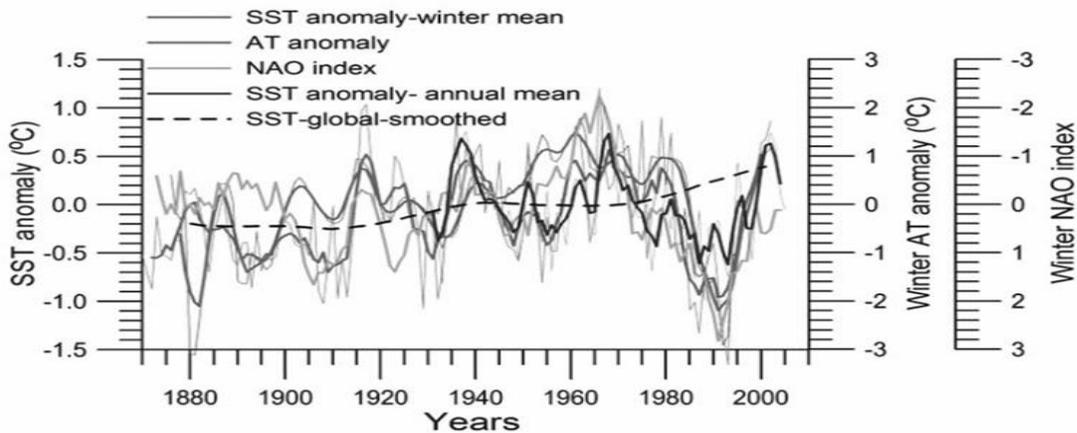


Figure 1.6. Long term variations in the Black Sea winter mean and annual mean sea surface temperature anomalies, the winter mean air temperature anomaly, and the winter mean NAO index. (Source: Oguz, 2009)

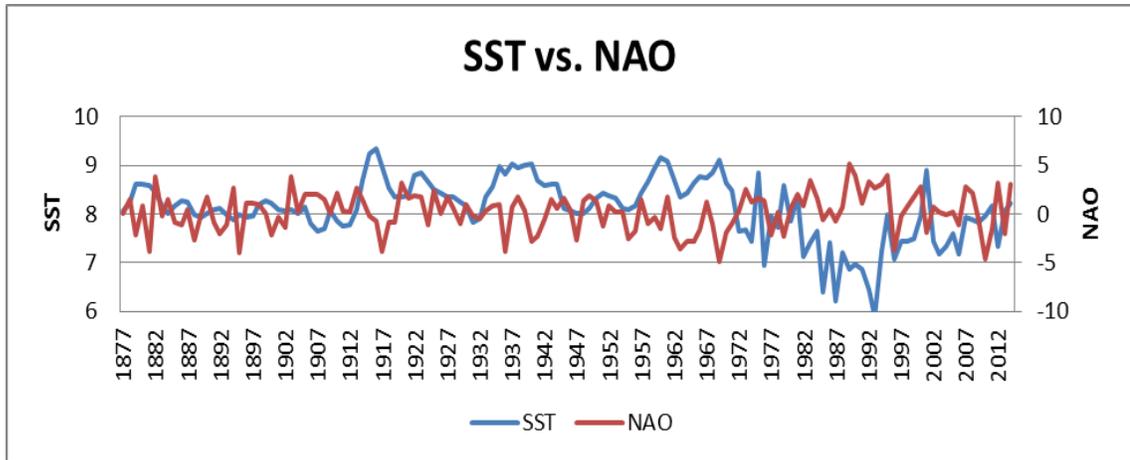


Figure 1.7. Black Sea Sea Surface Temperature (SST) data in the period of 1877-2012 with the fitted values from regression analysis on coastal east-west SST averages from 1970 to 2012 and combined with Oğuz et al, 2006 analysis and shown by NAO Index.

(Source: Oğuz et al., 2006; Kucukavsar, 2013)

The general atmospheric circulation in the Black Sea region is mainly affected by the Azores and Siberian high pressure areas and the Asian low pressure areas and therefore in winter time northeastern winds with speeds of $7-8 \text{ ms}^{-1}$ are dominant and eastern winds with speed of $5-7 \text{ ms}^{-1}$ are effective only in the southeastern part of the region and in summer time northwestern winds are observed with speed of $2-5 \text{ ms}^{-1}$ in the coastal areas and $3-5 \text{ ms}^{-1}$ offshore (Arkhipkin et al., 2014).

The Black Sea has been accompanied with major changes in the hydro-meteorological properties in relation to changes in large-scale atmospheric systems over the Eurasia in the recent decades (Oguz et al., 2006), in this context the climate change and variability have therefore played a major role on the Black Sea ecological changes in spite of difficulty of substantiating their relative contributions with respect to the other drivers.

1.8. Carbon Cycle and Budget of the Black Sea

Carbonate system of the Black Sea was investigated by Hiscock and Millero (2006) and they have shown that the total alkalinity (TA) values in surface waters ($\sim 3500 \mu\text{mol kg}^{-1}$) represent higher values than typical oceanic values because of low salinity and high alkalinity from rivers (Dyrssen, 1986) and TA decreases with depth until sigma-theta reaches 16.2, then increases within the anoxic/sulphide zone where sigma is >16.2 and this increase represents a strong correlation with the increase in salinity, phosphate and silicic acid concentrations in the water column. Hiscock and Millero (2006) calculated total inorganic carbon from measured pH and TA and showed the correlation between TA and TCO_2 in anoxic waters and this correlation indicates that the increase in TA and TCO_2 is proportional to hydrogen sulfide release.

Results of the study published by Bianchi et al. in 2009 indicated that photosynthesis is one of the most significant factors for the immense CO_2 uptake. Therefore phytoplankton are very important for the carbon cycle since they consume carbon dioxide in the water and reduce the level of carbon dioxide in the atmosphere (Falkowski, 2012).

Coccolithophores are the most permanent and the strongest components of the annual phytoplankton composition in the Black Sea ecosystem (Oğuz and Merico, 2006) and next to North Atlantic Ocean, the Black Sea is the second most important area for coccolithophore blooms in the context of continuity, spatial and temporal extent (Çokacar et al., 2004). Coccolithophores act as both source and sink for atmospheric CO_2 : when they form their calcium carbonate shells they release CO_2 and the fugacity of CO_2 increases and during the photosynthesis they consume CO_2 (Buitenhuis et al., 2001).

1.9. Purpose and Objectives of the Present Study

Since pre-industrial times, the oceans have absorbed nearly 25% of anthropogenic CO_2 (Rhein et al., 2013) thus the role of the oceans in tolerating the climate change through

carbon uptake is very significant. Climate change is a global problem and some regions are more vulnerable to the climate change such as the Black Sea. In this context, it is crucial to understand how the Black Sea responds to the increased levels of anthropogenic CO₂ in the atmosphere. However the carbon sink capacity of the Black Sea has never been analyzed until present time and CO₂ exchange and carbonate system in the Black Sea were poorly documented.

For this purpose, early summer (May-June) data (inorganic carbon components) of year 2001 and spring (April) data of year 2003 of R/V Knorr cruises were examined along with the atmospheric variables. The features of the components in the carbonate system of the Black Sea were defined. The correlations between the elements of the carbonate system were examined. The variations of CO₂ system and how this system interacts with the atmospheric parameters were mainly discussed in the context of solubility pump.

The outcomes of this study are important to define the CO₂ uptake/sink capacity of the Black Sea and to see how the components of the Earth System interact with each other (e.g. atmosphere and the Black Sea surface waters).

CHAPTER 2

2. MATERIALS AND METHOD

Hydrophysical data (temperature, salinity, density) and data related to the Black Sea carbonate system (provided by Friederich et al.,) and nutrients (provided by Tuğrul et al., and IMS) were obtained from two R/V Knorr research cruises to the Black Sea in May-June 2001 and April 2003. Data on meteorological parameters were obtained from ECMWF (European Centre for Medium-Range Weather Forecasts)-ERA Interim (Dee et al., 2011) and atmospheric CO₂ data were extracted from NOAA (National Oceanic and Atmospheric Administration) (Dlugokency et al., 2015). The missing components of the carbonate system for the selected stations were derived and then the layers of the Black Sea were investigated for the selected stations in the context of seawater carbonate system. Finally, the carbon dioxide flux at the seawater and atmosphere interface was calculated.

2.1. Data Collection and Extraction

2.1.1. In-situ Pump Profiling System-CTD and Nutrient Data

The R/V Knorr 2001 cruise consisted of two legs in the western Black Sea and was conducted from 20 May to 10 June, 2001. The locations of stations occupied in the Leg 1 and Leg 2 were shown in Figures 2.1 and 2.2 respectively. The R/V Knorr 2003 cruise was conducted from April 15 to May 15, 2003 and it was composed of three legs. The first leg (Leg 7) was from 15 April to 25 April, 2003 and only the data of this leg was used in the present study. The locations of stations in Leg 7 were shown in Figure 2.3.

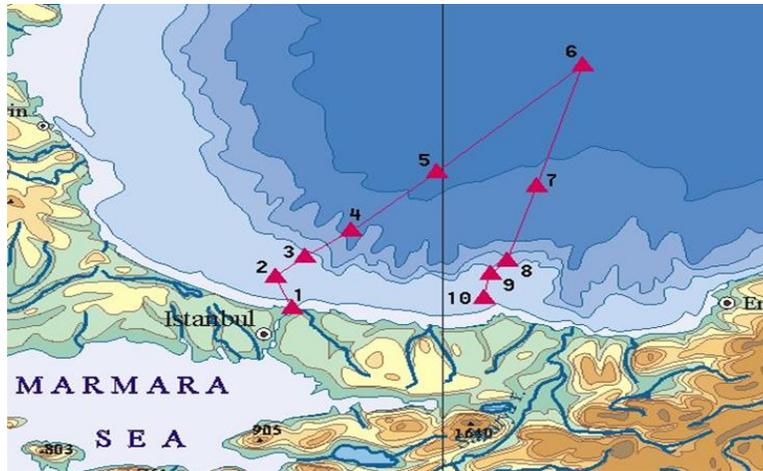


Figure 2.1. Stations of Leg 1 of The R/V Knorr 2001 Cruise (Downloaded from the WEB1¹)



Figure 2.2. Stations of Leg2 of The R/V Knorr 2001 Cruise. (Downloaded from the WEB2²)

¹ <http://www.ocean.washington.edu/cruises/Knorr2001/Leg1Crop.jpg>

² <http://www.ocean.washington.edu/cruises/Knorr2001/Leg2Crop.jpg>

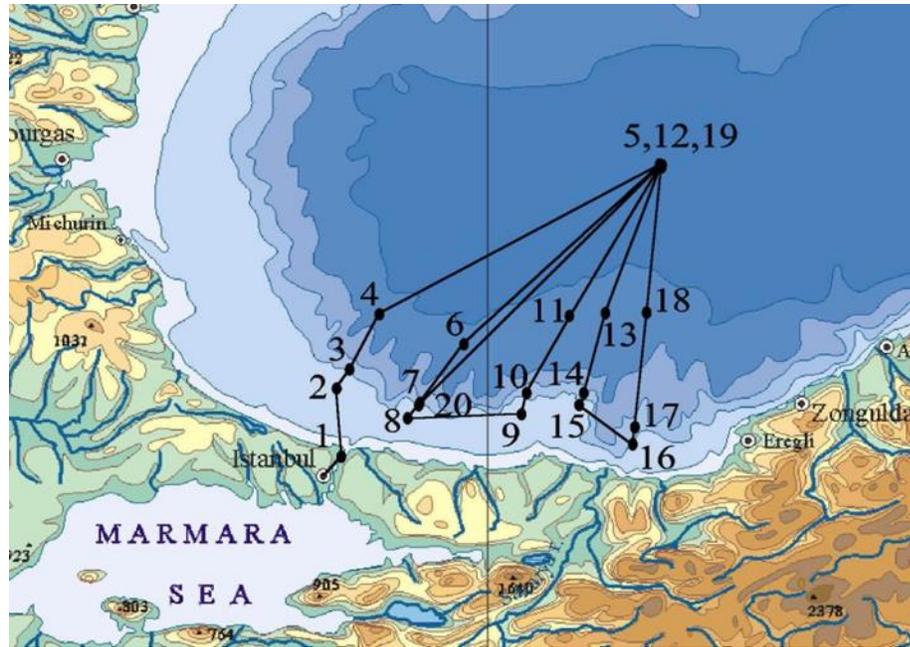


Figure 2.3. Stations of Leg 7 of The R/V Knorr 2003 Cruise (Downloaded from the WEB3³)

The data of pump profiling system for stations 3,5,6,7,9 and 10 of Leg 1, for stations 2,3,12,13 of Leg 2 (2001 cruise) and stations 3,4,6,12,13,14,17,18 and 20 of Leg 7 (2003 cruise) included pressure, temperature, salinity, density (σ_t), mole fraction of CO_2 ($x\text{CO}_2$), total dissolved inorganic carbon data (TCO_2) and also phosphate (PO_4) and silicate (Si) data. The date and locations of the selected stations were listed in Table 2.1. The data of these cruises are available at: WEB4⁴ and WEB5⁵.

³ http://www.ocean.washington.edu/cruises/Knorr2003/station_locations/charts/charts.html

⁴ www.ocean.washington.edu/cruises/Knorr2001

⁵ www.ocean.washington.edu/cruises/Knorr2003

Table 2.1. Dates and Coordinates of the Selected Stations for R/V Knorr 2001 and 2003
Cruises in the Black Sea

Cruise	Station	Leg	Date	Latitude	Longitude
Knorr 2001	Station 3	Leg 1	24 th of May	41.50	29.25
Knorr 2001	Station 5	Leg 1	25 th of May	41.97	29.94
Knorr 2001	Station 6.1	Leg 1	26 th of May	42.50	30.76
Knorr 2001	Station 6.2	Leg 1	28 th of May	42.50	30.76
Knorr 2001	Station 7	Leg 1	29 th of May	41.88	30.50
Knorr 2001	Station 9	Leg 1	29 th of May	41.48	30.50
Knorr 2001	Station 10.1	Leg 1	30 th of May	41.45	30.26
Knorr 2001	Station 10.2	Leg 1	31 st of May	41.50	30.25
Knorr 2001	Station 2	Leg 2	2 nd of June	42.50	30.77
Knorr 2001	Station 3	Leg 2	4 th of June	44.12	30.91
Knorr 2001	Station 12	Leg 2	7 th of June	44.28	32.25
Knorr 2001	Station 13	Leg 2	8 th of June	42.50	30.77
Knorr 2003	Station 3	Leg 7	15 th of April	41.58	29.16
Knorr 2003	Station 4	Leg 7	16 th of May	41.83	29.34
Knorr 2003	Station 6	Leg 7	18 th of May	41.70	29.83
Knorr 2003	Station 12	Leg 7	21 st of May	42.50	31.00
Knorr 2003	Station 13	Leg 7	21 st of May	41.83	30.69
Knorr 2003	Station 14	Leg 7	22 nd of May	41.48	30.54
Knorr 2003	Station 17	Leg 7	23 rd of May	41.34	30.83
Knorr 2003	Station 18	Leg 7	23 rd of May	41.83	30.91
Knorr 2003	Station 20	Leg 7	24 th of May	41.44	29.58

2.1.2. Wind, Mean Sea Level Pressure and Sea Surface Temperature Data

ERA Interim is a global atmospheric reanalysis, which has a spectral resolution of T255 (~80 km) and 60 vertical levels (from the surface up to 0.1 hPa), was produced by the ECMWF and it goes back to 1979 and it is constantly updated (Dee et al., 2011). For the present study, the data of the cruise dates and nearest cruise locations were

extracted. The parameters of ERA Interim are available at: WEB6⁶ and 10 meter wind data components, mean sea level pressure data and sea surface temperature data were retrieved from ERA-Interim with 0.125 degree resolution (~14 km). The extracted data was in GRIB (Gridded Binary) format.

2.1.3. Atmospheric Carbon Dioxide Data

NOAA constructs a two dimensional matrix which includes time and latitude from 90°S to 90°N with intervals of 0.05 sine and using this database NOAA constructs a time averaged meridional distribution for any specified latitude band. And this database was constructed for Green House Gases (GHGs) at marine boundary layer. For CO₂ the period begins January 1, 1979 and ends when current year weekly air samples from global network are delivered to NOAA. The database is available at: WEB7⁷. The partial pressure of CO₂ data were obtained from NOAA Greenhouse Gas Marine Boundary Layer (MBL) Reference dataset (Dlugokency et al., 2015). The partial pressure of CO₂ data of the cruise sine latitudes were extracted from this database. The database is in text format and the unit of the partial pressure of CO₂ in atmosphere is $\mu\text{mol mol}^{-1}$.

2.2. Methodology

2.2.1. Derivation of Necessary Parameters for the Black Sea Carbonate System

Potential temperature (θ) values were not available in the pump profiling data of 2001 cruise therefore θ values were calculated for the stations in 2001 through the R package seacarb (function θ , Gatusso et al., 2015) which is used for the derivation of parameters of the seawater carbonate system.

The available xCO₂ data were converted to partial pressure of CO₂ using the R package

⁶ <http://apps.ecmwf.int/datasets/data/interim-full-daily/levtype=sfc/>

⁷ <http://www.esrl.noaa.gov/gmd/ccgg/mbldata.php>

seacarb (function $x2pCO_2$, Gattuso et al., 2015) and then pCO_2 values were converted to the fugacity of CO_2 by the same R package (function $p2fCO_2$, Gattuso et al., 2015). After evaluating pCO_2 data, the CO2SYS Matlab program (Lewis and Wallace, 1998), which calculates the state of the carbonate system of water samples when relevant input is provided, was run for pCO_2 and TCO_2 . The pH scale was chosen as seawater scale and the dissociation constants of Mehrbach et al. (1973) reformulated by Dickson and Millero (1987) were selected. Default nutrient values in the program were used in the absence of nutrient data. The other parameters of the seawater carbonate system, pH and TA were obtained as the outputs of the program. Also Revelle Factor and omega aragonite (Ω_{ar}) and omega calcite (Ω_{ca}) values of the Black Sea were calculated by the CO2SYS Matlab program to see CO_2 uptake capacity of the Black Sea and the saturation level with respect to $CaCO_3$. Thus, all the components of the seawater carbonate system became available to estimate the CO_2 fluxes and carbon sink capacity of the Black Sea.

2.2.2. Carbonate System Analysis of the Surface, Intermediate and Deep Layers of the Black Sea

The Black Sea is a multi-layer system; therefore in order to be able to see the characteristics of different water masses, the water column were classified as surface mixed layer, intermediate layer and deep layer. For this purpose, strong gradients of temperature (thermocline) and density (pycnocline) and salinity (halocline) were analyzed from temperature, density and salinity profiles which include all the available data from the selected stations.

Afterwards, the correlations between the parameters, such as Salinity vs Alkalinity and Salinity vs TCO_2 were obtained for each layer in the Black Sea. The open source python library Scipy (Jones et al, 2001) was used to calculate the correlation coefficients (r) and coefficient of determination (r^2). All the plottings in the present study were done using python open source matplotlib library (Hunter, 2007).

2.2.3. Calculation of the Carbon Dioxide Fluxes between the Surface Waters of the Black Sea and the Atmosphere

The carbon dioxide fluxes at the seawater-air interface were calculated using Matlab program (provide by Diana RUIZ PINO personal contact). The data files (latitude, longitude, mean sea level atmospheric pressure, sea surface temperature, salinity, ten meter wind speed, fugacity of CO₂ in seawater and partial pressure of CO₂ in atmosphere) were organized to build the input files required by the program. The corresponding output data files (flux data) were used to evaluate the CO₂ exchange between seawater surface and atmosphere for the Black Sea. Atmospheric pCO₂ or fCO₂ (almost same values for all stations and extracted from NOAA Greenhouse Gas Marine Boundary Layer (MBL) Reference data bank), pCO₂ or fCO₂ in the surface mixed layer and ΔpCO₂ and/or ΔfCO₂, which is the difference between the air and ocean partial pressure or fugacity, were also listed within the same table (See Chapter 3). Three different windspeed dependent models were used to calculate gas the transfer velocity (k) and they were represented in Equations 2.1, 2.2 and 2.3. Wanninkhof's approach (Wanninkhof, 1992) is represented by W92 Wanninkhof and McGillis's approach (Wanninkhof and McGillis, 1999) is represented by W-Mc99 and Ho et al.'s approach (Ho et al., 2006) is represented by Ho06.

$$k (W92)=0.312*u(10)^2*(Sc/660)^{-0.5} \quad (2.1)$$

$$k (W-Mc99)=0.0283*u(10)^3*(Sc/660)^{-0.5} \quad (2.2)$$

$$k (Ho06)=0.266*u(10)^2*(Sc/600)^{-0.5} \quad (2.3)$$

In Equations 2.1, 2.2 and 2.3 u(10) indicates 10 meter wind speed (ms⁻¹) and Sc represents Schmidt number. Schmidt number was calculated according to W92 for all three gas transfer velocity models. Equation 2.4 shows the calculation of Sc where A represents coefficients for a third order polynomial fit for temperature dependence of the Schmidt number (A0=2073.1, A1=-125.62, A2=3.6276, A3=-0.043219) and SST represents Sea Surface Temperature.

$$Sc=A0+A1*SST+A2*SST^2+A3*SST^3 \quad (2.4)$$

CHAPTER 3

3. DATA ANALYSIS, RESULTS and DISCUSSION

3.1. Spatial Data Analysis for Multi-Layer Black Sea System

All the stations used in the present study are located in the western Black Sea. R/V Knorr 2001 cruise was conducted in late May and early June while R/V Knorr 2003 cruise was conducted in April and May. The coastal stations of R/V Knorr 2001 cruise were represented by stations 3, 9, 10 (Leg1) and the open basin stations were represented by stations 6, 5, 7 (Leg1) and by stations 2, 3, 12, 13 (Leg 2). The stations of R/V Knorr 2003 cruise used in the present study were 3, 4, 6, 12, 13, 14, 17, 18, 20 and they were all defined as open basin stations.

The water column was separated into three layers: surface mixed, deep and intermediate layer according to the vertical changes in salinity, temperature and sigma-theta profiles. The surface mixed layer is located above the thermocline where the temperature is almost constant representing the homogeneous water body. Mixed Layer Depth (MLD) changes (deepens or shallows) from the coastal to open seas, from season to season, and it is influenced by the physical dynamical features of the water bodies. For example, it is shallow in the open central stations where cyclonic eddies are observed and it is deeper in the coastal areas where the Rim Current and anticyclonic eddies are observed (Figure 3.1, 3.2 and 3.3).

Below the mixed layer, Cold Intermediate Layer (CIL) is located (the minimum temperature layer less than 8°C) and the CIL was more clearly observed during 2003 cruise and took place within the depth range of 50-100m (Figure 3.1). In the Black Sea, water masses having sigma-theta values higher than 16.2 kg/m³ indicate the deep layer

(Tuğrul et al., 1992) where the temperature, salinity and sigma-theta gradients are low and also TCO₂ and TA concentrations are almost constant. The layer of strong temperature, salinity and sigma-theta gradient were defined as intermediate layer which is located between the surface mixed layer and the deep layer.

Considering all stations data; the surface mixed layer ranged from surface to ~20 m for 2001 data and for 2003 data it ranged from surface to ~40 m. The shallowest deep water layer was formed at ~117 m for 2001 data. For both 2001 and 2003 cruises, the data were available down to 190m.

The stations were also sub-divided into different groups, regarding the similarities in their salinity, temperature and sigma-theta profiles. The locations of the stations (as being coastal or open basin station) were also taken into account. In this context, three groups of stations were defined for 2001: The first group includes the stations 6.1 (Leg1), 6.2 (Leg1), 2 (Leg2) and 13 (Leg2); the second group includes stations 9 (Leg1) and 10.1 (Leg1) and the third group includes stations 10.2 (Leg1) and station 3 (Leg2). The rest of the stations were investigated individually. The stations in 2003 were also separated into three groups namely: the first group with the stations 3, 14 and 20; the second group with the stations 13 and 18; and the third group with the stations 6 and 4.

3.2. Characterization of the Black Sea Waters

3.2.1. Physical Characteristics of the Black Sea Waters

The Black Sea is a multi-layer system. There is a strong vertical salinity gradient in the water column due to large input of freshwater from rivers (mainly flowing to northwest shelf) at the surface and input of Mediterranean origin saline waters through the Bosphorus. The resulting permanent pycnocline (due to the changes in temperature and sharp changes in salinity) prevents exchanges of dissolved constituents between the surface mixed layer and deeper waters, setting up a multilayer system (Yılmaz, 2002).

Deep water contains high concentrations of H_2S , since O_2 is consumed within the surface layer and mainly within the intermediate layer by the degradation of the sinking organic matter. Temperature, salinity and density (Sigma-theta) profiles for selected stations for both 2001 and 2003 R/V Knorr cruises showed these specific characteristics (Figure 3.1, 3.2 and 3.3).

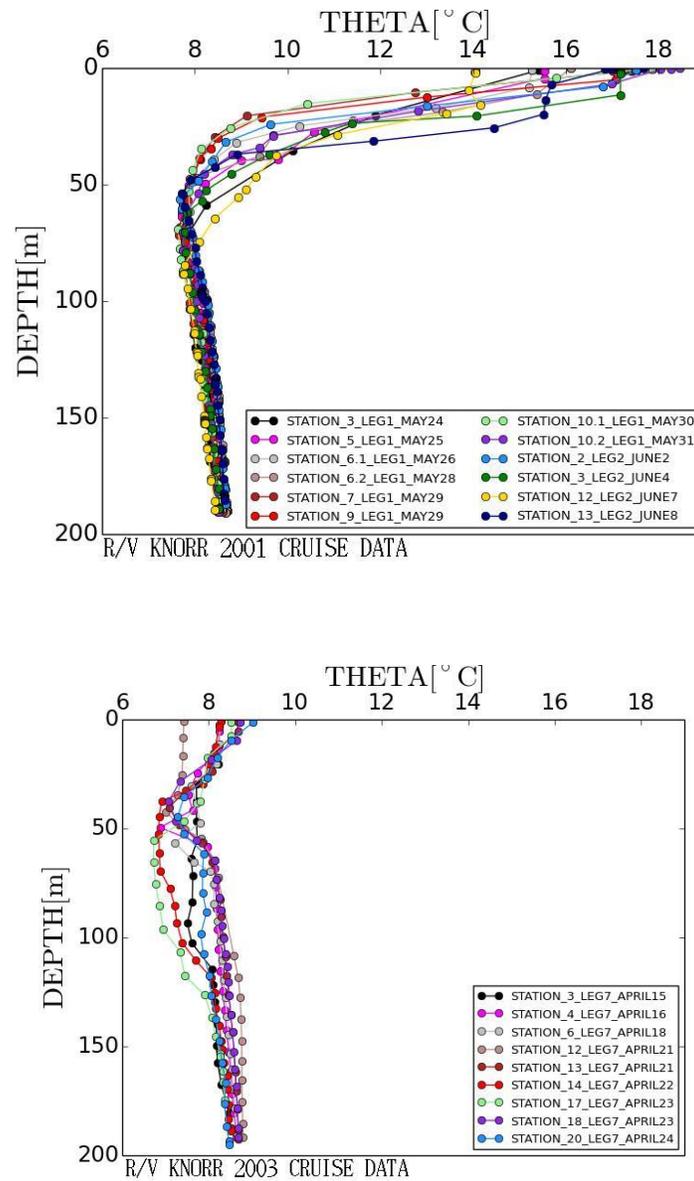


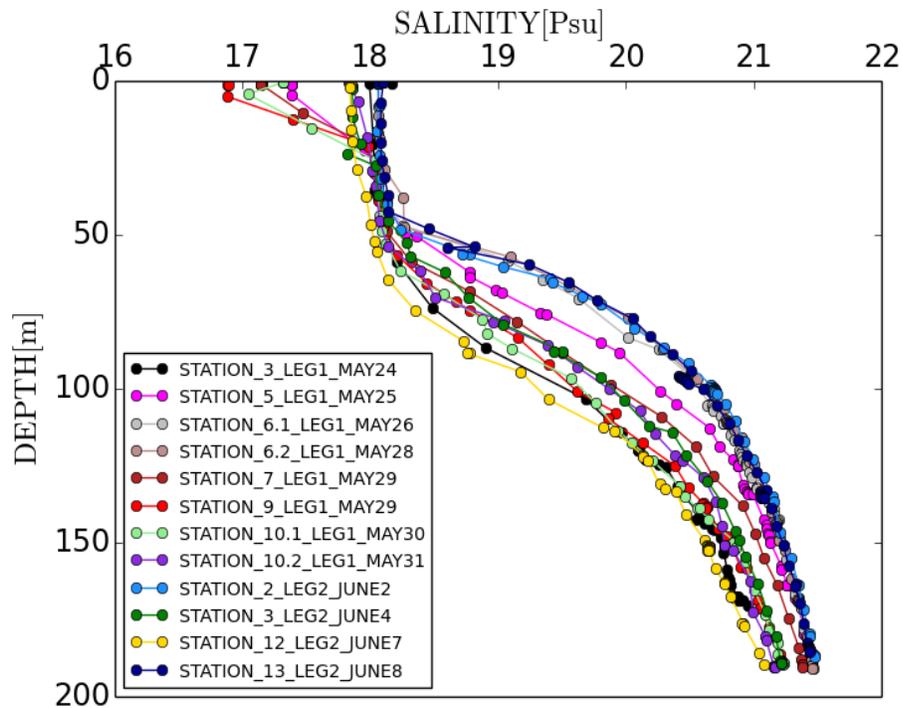
Figure 3.1. Vertical distribution of Temperature (Theta, °C) in the Black Sea for R/V Knorr 2001 and 2003 cruises

Figure 3.1 presented that seawater temperature stayed almost constant in the surface mixed layer for every station. For 2001 R/V Knorr cruise data seawater temperature ranged in ~ 14 and 18.5°C and considering 2003 R/V Knorr cruise data, seawater temperature varied between ~ 7.3 and $\sim 9^{\circ}\text{C}$ in the surface mixed layer of the Black Sea. For both 2001 and 2003 cruises data, the gradient in seawater temperature was minimum in deep layer of the Black Sea and it fluctuated between 8.5°C and 9°C .

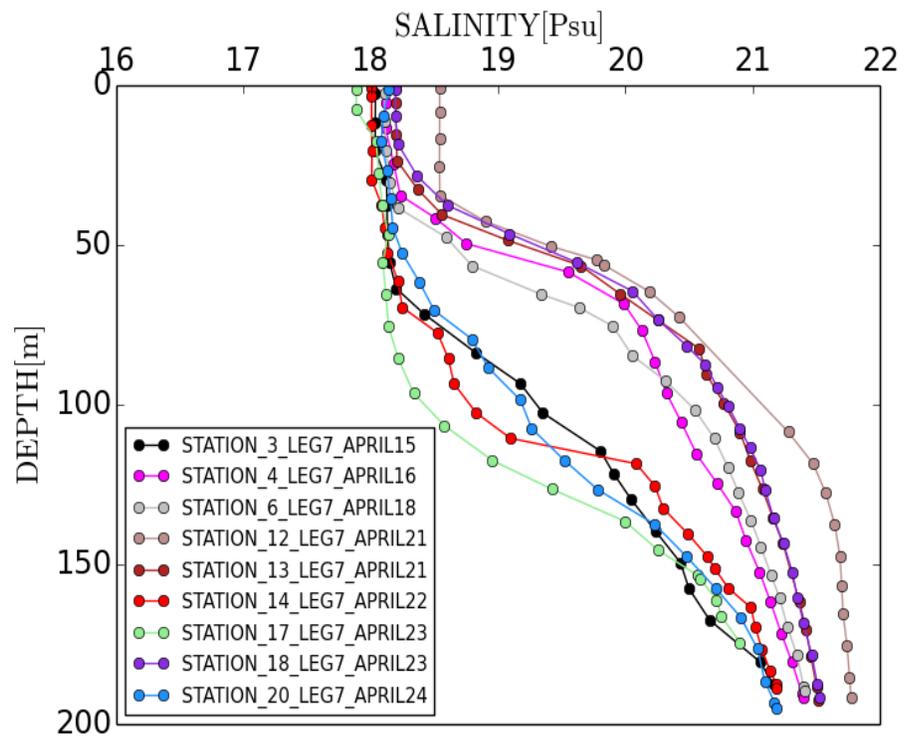
It was shown in Figure 3.2 that salinity varied between 17 and 18.5 in the surface mixed layer for 2001 and for 2003 cruise salinity varied between 18 and 18.5 and these values were almost half that of open ocean (Goyet et al., 1991). In deep layer salinity values increased to 21.5 and stayed almost constant for both of the datasets. Due to the freshwater input from rivers (especially the Danube, Dniester, Dnieper, Don and Kuban), the salinity values are low in the surface waters compared to the deep water salinity values and this situation results in permanent stratification in the water column with respect to salinity and thus density (Murray et al., 2007).

Regarding the sigma-theta (σ_t) profiles in Figure 3.3, it is shown that the surface mixed layer sigma-theta values were less than the other layers because of low salinity and high temperature. For 2001 R/V Knorr cruise, sigma-theta varied between ~ 11.5 kg/m^3 and 13 kg/m^3 and for 2003 Knorr R/V cruise sigma-theta varied between ~ 13.8 kg/m^3 and ~ 14.5 kg/m^3 in the surface mixed layer. $\sigma_t \sim 16.2$ kg/m^3 indicates the upper boundary of permanent halocline in the Black Sea. In this context, the sigma-theta values were greater than 16.2 in deep layer for both of the datasets and deep water sigma-theta values stabilized around 16.5 kg/m^3 . Density is mainly affected by salinity therefore an increase in salinity also results in increase in density (Murray et al., 2007).

Profiles of the hydrophysical parameters (Figure 3.1, 3.2 and 3.3) demonstrated that due to strong mixing in the surface mixed layer, the values of the parameters were almost unvaried for every station. The variation in the parameters was smallest in deep layer and more homogenous and uniform values were found in the deep layer of the Black Sea.

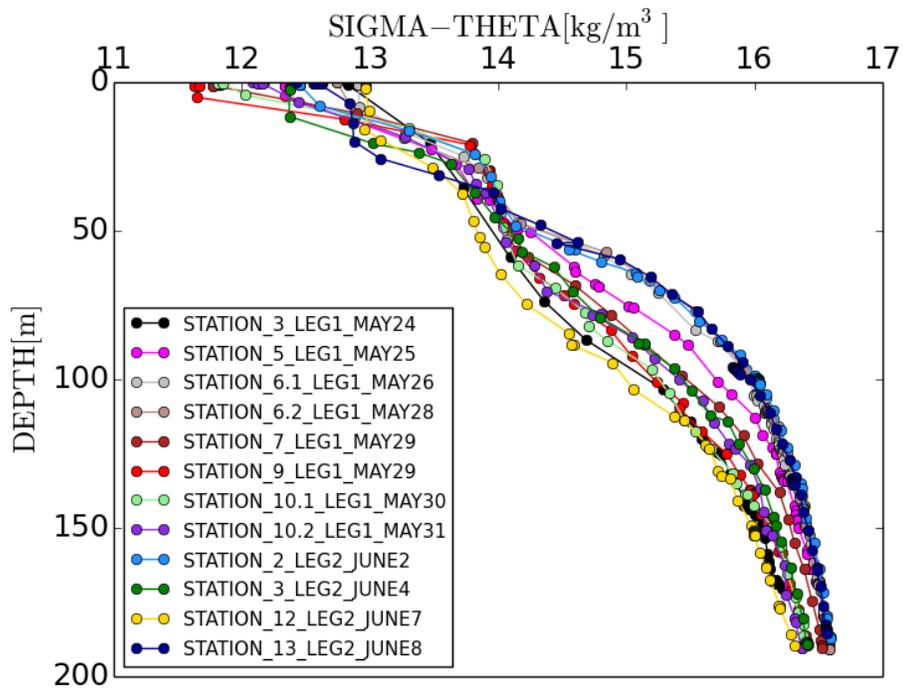


R/V KNORR 2001 CRUISE DATA

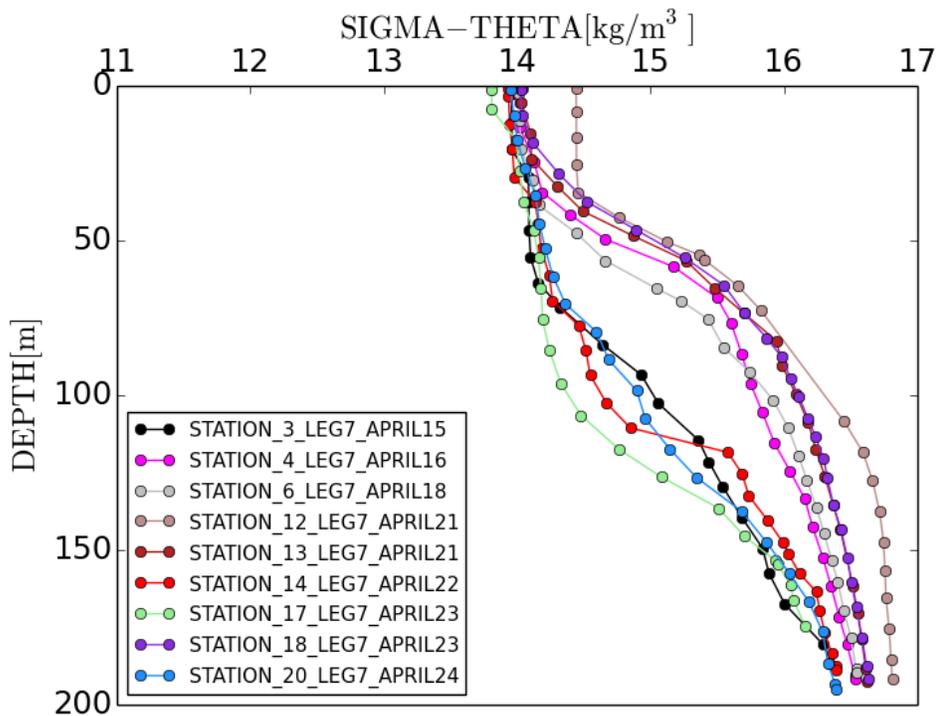


R/V KNORR 2003 CRUISE DATA

Figure 3. 2. Vertical distribution of Salinity (psu) in the Black Sea for R/V Knorr 2001 and 2003 cruises



R/V KNORR 2001 CRUISE DATA



R/V KNORR 2003 CRUISE DATA

Figure 3.3. Vertical distribution of Sigma-theta (kg/m³) in the Black Sea for R/V Knorr 2001 and 2003 cruises

3.2.2. Vertical Distribution of pH, TA, TCO₂ and Variations

The oceanic CO₂ buffer capacity is mainly controlled by temperature, the distribution of TCO₂ and TA. Generally as SST increases, the relative amount of carbon dioxide in the atmosphere increases and as carbonate alkalinity increases the carbon dioxide amount in the atmosphere decreases (Omta et al., 2011). Therefore the distributions of pH, TA and TCO₂ were investigated for all layers (surface mixed layer, intermediate layer and deep layer).

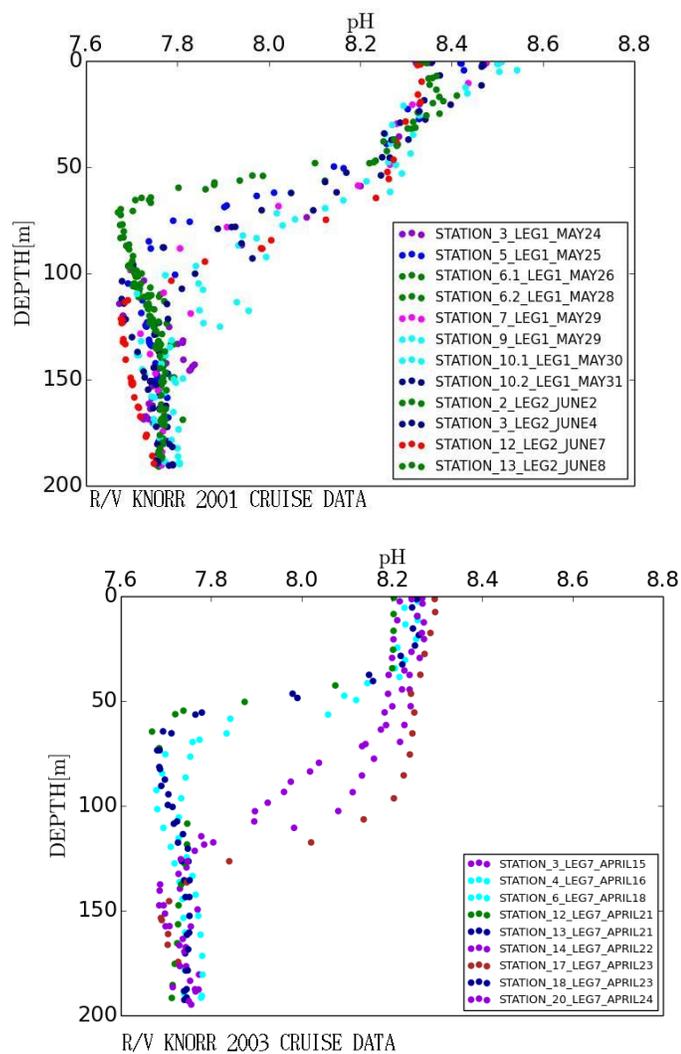


Figure 3.4. Vertical distribution of pH for 2001 and 2003 R/V Knorr cruise data

The pH values in the surface layer ranged from ~ 8.3 to 8.6 in 2001 cruise data. 2003 surface pH data ranged from ~8.2 to 8.3. For both of the data, pH in deep water of the Black Sea stabilized at~7.7 to 7.8 (Figure 3.4). The mean surface pH value for 2001 data is %2.3 higher than 2003 mean surface pH data. The decrease in pH values below the surface mixed layer for both of the datasets is attributed to the strong bacterail degradation in the intermediate layer (Çoban-Yıldız et al., 2006).

The calculated pH values range from 7.9 to 8.2 in 2005 for the global oceans and the lower pH values are found in the upwelling regions in the Tropical Pacific and in the Arabian and Bering Seas and higher values are found in the polar and subpolar regions of high photosynthetic production (Takahashi et al., 2014).

Figure 3.5 indicated that for both 2001 and 2003 data, TA first slightly decreased with depth from the surface to approximately 75 m and then it started to increase. Results of the study published by Hiscock and Millero in 2006 represented that the increase in TA values in the Black Sea was the result of bacterial anaerobic respiration of organic matter to bicarbonate and concurrent reduction of sulfate to hydrogen sulfide. This increase correlated well with the increase in salinity and sigma-theta. In 2001, the significantly high TA values (~3350 $\mu\text{mol/kg}$) were found in the surface layer when compared to 2003 surface layer data. As a result of riverine input which has high TA and low salinity, very high TA values in the surface waters of the Black Sea are observed (Dyrssen, 1985, 1986).

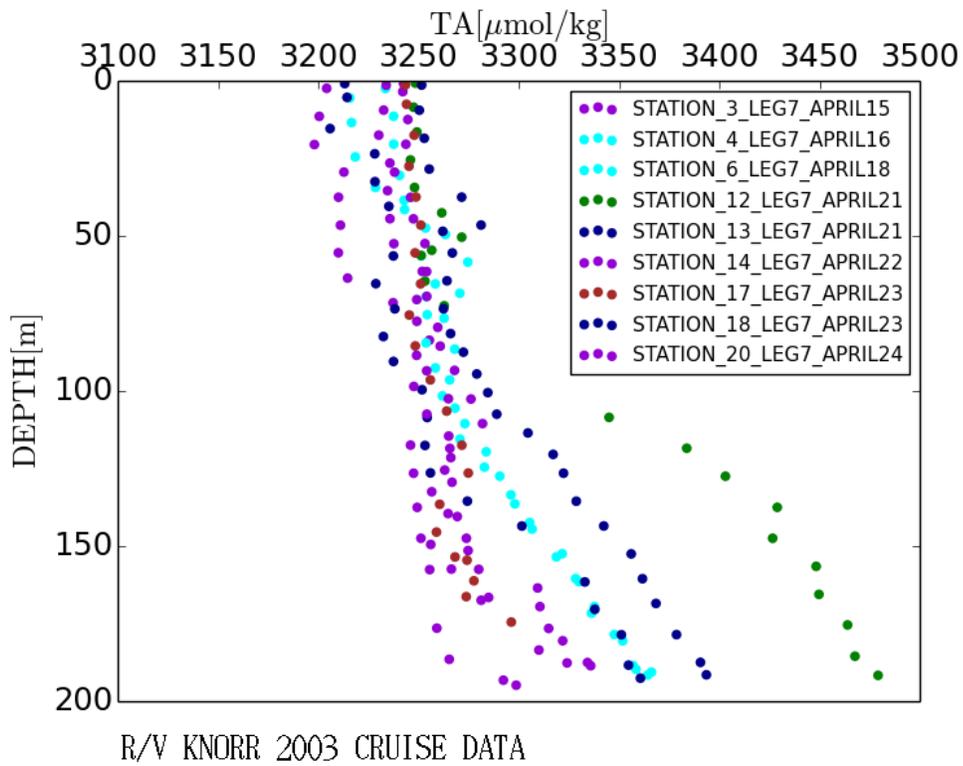
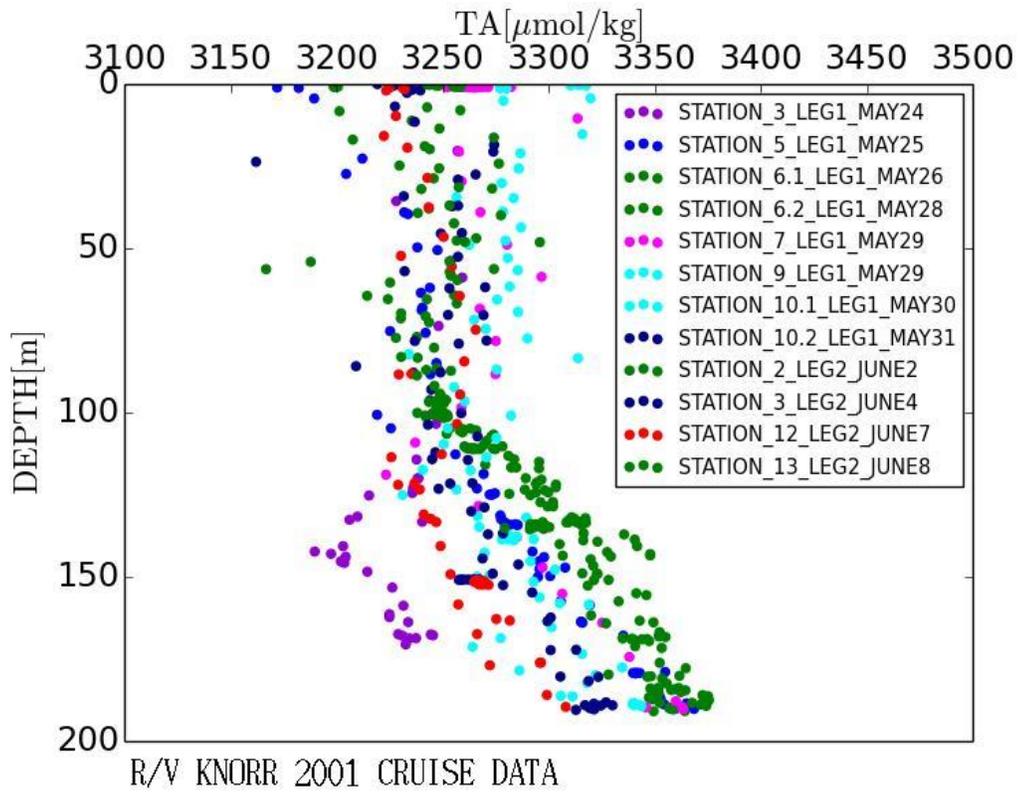


Figure 3.5. Vertical distribution of TA for 2001 and 2003 R/V Knorr cruise data

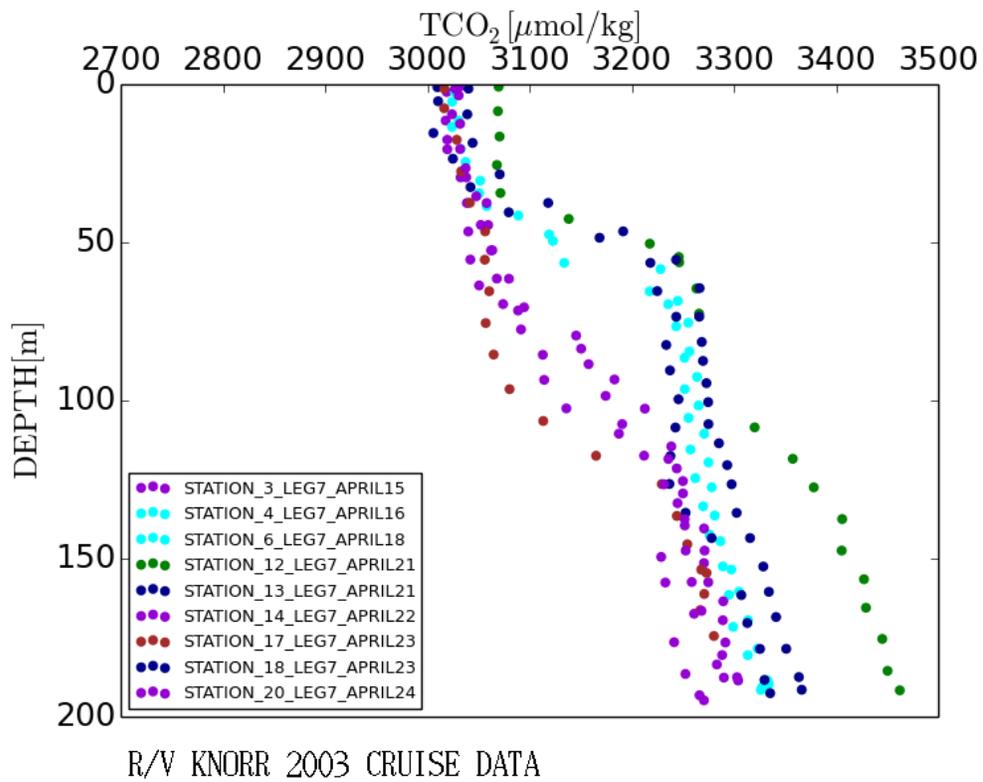
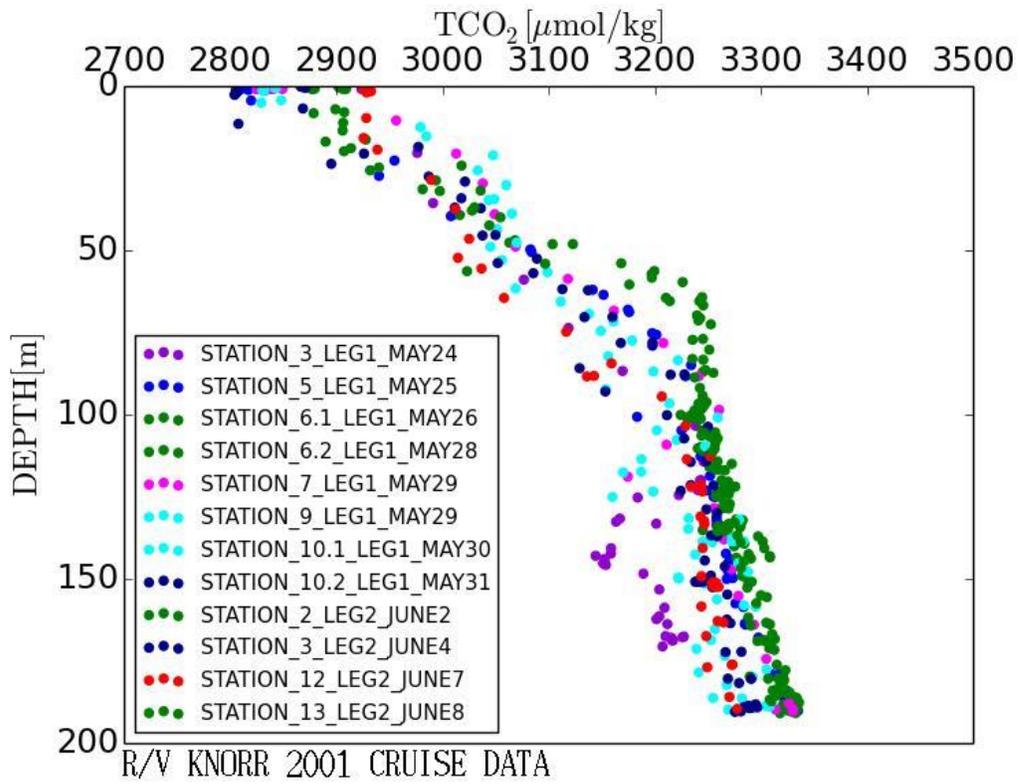


Figure 3.6. Vertical distribution of TCO₂ for 2001 and 2003 R/V Knorr cruise data

It was demonstrated in Figure 3.6 that TCO_2 values increase below the surface mixed layer for both 2001 and 2003 data. This increase was accepted as the indicator of oxidation of organic material by oxygen under the photic zone (in the oxycline) (Hiscock and Millero, 2006).

For 2003 data, the highest pH in the surface water was in the station 17; the highest TCO_2 and lowest pH values were in station 12 and also station 3 and highest TA was in station 18. The lowest TCO_2 value in 2003 surface water data was in station 13 and the lowest TA value was in station 3 (Table 3.1).

As seen in Table 3.2; the highest TA and pH values in the surface mixed layer were found in Station 10.1 for 2001 data and the highest TCO_2 value was found in Station 12. The lowest pH value was both in station 3 (Leg 1) and station 12; the lowest TCO_2 value was found in station 3 (Leg 2) and the lowest TA value was found in station 5.

When all the available data is analyzed it is seen that the highest values of TA and TCO_2 are found in deep water of the Black Sea.

Table 3.1. Minimum and maximum values of pH, TA and TCO₂ (2003 R/V Knorr Cruise Data)

Cruise	Location	Station	Water Layer	pH Min / Max	TCO₂ (μmol kg⁻¹) Min / Max	TA (μmol kg⁻¹) Min / Max
2003	open	3	Surface Mixed Layer	8.20 / 8.21	3018 / 3019	3198 / 3204
			Intermediate Layer	7.73 / 8.20	3038 / 3261	3210 / 3281
			Deep Layer	7.77	3288 / 3290	3321 / 3324
2003	open	4	Surface Mixed Layer	8.22 / 8.23	3024	3215 / 3216
			Intermediate Layer	7.72 / 8.21	3037 / 3270	3218 / 3296
			Deep Layer	7.76 / 7.78	3276 / 3327	3305 / 3366
2003	open	6	Surface Mixed Layer	8.25	3026 / 3032	3233 / 3237
			Intermediate Layer	7.67 / 8.22	3051 / 3278	3240 / 3290
			Deep Layer	7.72 / 7.74	3281 / 3334	3298 / 3358
2003	open	12	Surface Mixed Layer	8.20	3068 / 3071	3246 / 3249
			Intermediate Layer	7.76 / 8.07	3138 / 3266	3251 / 3271
			Deep Layer	7.71 / 7.74	3320 / 3462	3345 / 3479
2003	open	13	Surface Mixed Layer	8.24 / 8.25	3006 / 3025	3205 / 3228
			Intermediate Layer	7.68 / 8.22	3042 / 3245	3228 / 3262
			Deep Layer	7.72 / 7.74	3236 / 3335	3253 / 3360
2003	open	14	Surface Mixed Layer	8.26 / 8.27	3030 / 3032	3242 / 3244
			Intermediate Layer	7.68 / 8.26	3032 / 3275	3238 / 3281
			Deep Layer	7.73 / 7.76	3283 / 3304	3309 / 3335
2003	open	17	Surface Mixed Layer	8.26 / 8.29	3016 / 3041	3243 / 3248
			Intermediate Layer	7.68 / 8.24	3056 / 3280	3245 / 3296
			Deep Layer			
2003	open	18	Surface Mixed Layer	8.25	3039 / 3044	3250 / 3252
			Intermediate Layer	7.68 / 8.21	3070 / 3275	3255 / 3289
			Deep Layer	7.73 / 7.75	3285 / 3366	3304 / 3393
2003	open	20	Surface Mixed Layer	8.24	3027	3233

Table 3. 1. (continued) Minimum and maximum values of pH, TA and TCO₂ (2003 R/V Knorr Cruise Data)

Cruise	Location	Station	Water Layer	pH Min / Max	TCO₂ (μmol kg⁻¹) Min / Max	TA (μmol kg⁻¹) Min / Max
			Intermediate Layer	7.68 / 8.26	3019 / 3268	3230 / 3284
			Deep Layer	7.71 / 7.75	3241 / 3270	3259 / 3298

Table 3. 2. Minimum and maximum values of pH, TA and TCO₂ (2001 R/V Knorr Cruise Data)

Cruise	Location	Station	Water Layer	pH Min / Max	TCO₂(μmol kg⁻¹) Min / Max	TA (μmol kg⁻¹) Min / Max
2001	coastal	3 (Leg1)	Surface Mixed Layer	8.32 / 8.35	2923 / 2928	3234 / 3259
			Intermediate Layer	7.67 / 8.33	2976 / 3246	3228 / 3259
			Deep Layer	7.74	3207	3232
2001	open	5 (Leg1)	Surface Mixed Layer	8.41 / 8.42	2809 / 2819	3172 / 3189
			Intermediate Layer	7.72 / 8.32	2940 / 3258	3204 / 3277
			Deep Layer	7.73 / 7.78	3258 / 3334	3277 / 3368
2001	open	6.1 (Leg1)	Surface Mixed Layer	8.34	2877 / 2879	3198 / 3201
			Intermediate Layer	7.67 / 8.37	2890 / 3276	3207 / 3303
			Deep Layer	7.74 / 7.77	3262 / 3336	3291 / 3375
2001	open	6.2 (Leg1)	Surface Mixed Layer	8.33	2906 / 2907	3232
			Intermediate Layer	7.67 / 8.38	2906 / 3251	3235 / 3281
			Deep Layer	7.75 / 7.81	3257 / 3332	3281 / 3364
2001	open	7 (Leg1)	Surface Mixed Layer	8.46 / 8.47	2825 / 2849	3252 / 3282
			Intermediate Layer	7.69 / 8.31	3013 / 3265	3237 / 3285
			Deep Layer	7.75 / 7.76	3272 / 3330	3297 / 3363
2001	coastal	9 (Leg1)	Surface Mixed Layer	8.50	2829 / 2832	3277 / 3280

Table 3. 2. (continued) Minimum and maximum values of pH, TA and TCO₂ (2001 R/V Knorr Cruise Data)

Cruise	Location	Station	Water Layer	pH Min / Max	TCO₂($\mu\text{mol kg}^{-1}$) Min / Max	TA ($\mu\text{mol kg}^{-1}$) Min / Max
			Intermediate Layer	7.71 / 8.25	3048 / 3287	3255 / 3292
			Deep Layer	7.74 / 7.77	3282 / 3308	3311 / 3342
2001	coastal	10.1 (Leg1)	Surface Mixed Layer	8.50 / 8.51	2842 / 2843	3310 / 3317
			Intermediate Layer	7.76 / 8.27	3045 / 3254	3234 / 3292
			Deep Layer	7.77 / 7.80	3241 / 3291	3286 / 3343
2001	coastal	10.2 (Leg1)	Surface Mixed Layer	8.35	2866 / 2870	3219 / 3227
			Intermediate Layer	7.74 / 8.37	2868 / 3254	3227 / 3278
			Deep Layer	7.77 / 7.79	3266 / 3281	3301 / 3321
2001	open	2 (Leg 2)	Surface Mixed Layer	8.34	2905 / 2909	3254 / 3258
			Intermediate Layer	7.67 / 8.35	2907 / 3256	3242 / 3278
			Deep Layer	7.74 / 7.77	3264 / 3312	3295 / 3353
2001	coastal	3 (Leg 2)	Surface Mixed Layer	8.46 / 8.47	2804 / 2807	3233 / 3239
			Intermediate Layer	7.67 / 8.34	2987 / 3266	3232 / 3285
			Deep Layer	7.73 / 7.75	3268 / 3296	3292 / 3330
2001	open	12 (Leg 2)	Surface Mixed Layer	8.32 / 8.33	2925 / 2932	3222 / 3232
			Intermediate Layer	7.67 / 8.33	2938 / 3273	3229 / 3296
			Deep Layer	7.74	3270 / 3277	3299 / 3308
2001	open	13 (Leg 2)	Surface Mixed Layer	8.33 / 8.34	2902 / 2906	3242 / 3248
			Intermediate Layer	7.69 / 8.36	2899 / 3257	3237 / 3282
			Deep Layer	7.74 / 7.76	3259 / 3327	3291 / 3364

3.2.3. Relationship between physical parameters and TA, TCO₂

Generally, salinity and TA are well correlated in the oceans. TA is mainly controlled by salinity in the oceans then controlled by biogeochemical processes (Wolf-Gladrow et al., 2007). In the surface waters of the ocean, salinity has an impact which is more than 80% on TA variability and next to salinity freshwater input and evaporation influence also the variations of TA (Millero et al., 1998) In the absence of TA data, by using SSS (Sea Surface Salinity) and SST, TA data can be derived (Lee et al., 2006) and also estimation of TA from SSS and SST could be combined with fCO₂ to derive TCO₂ values thus the parameters of seawater carbonate system become available to evaluate the carbon buffer capacity of the ocean (Millero et al., 1998).

Figure 3.7, 3.8, 3.9 and 3.10, 3.11 3.12 represent the Salinity vs TA and Salinity vs. TCO₂ graphs for 2001 and 2003 cruises respectively. Correlation coefficients (r) and coefficients of determination (r^2) were calculated for different water layers and/or similar-homogeneous water masses, for example for surface mixed layer, intermediate layer and the deep layer.

Stations which were classified as coastal and open stations or stations having similar hydrophysical characteristics were represented by the same colors in the surface water and deep layer graphs while for the intermediate graphs each station was represented individually (by different colors) because of the variations in the parameters.

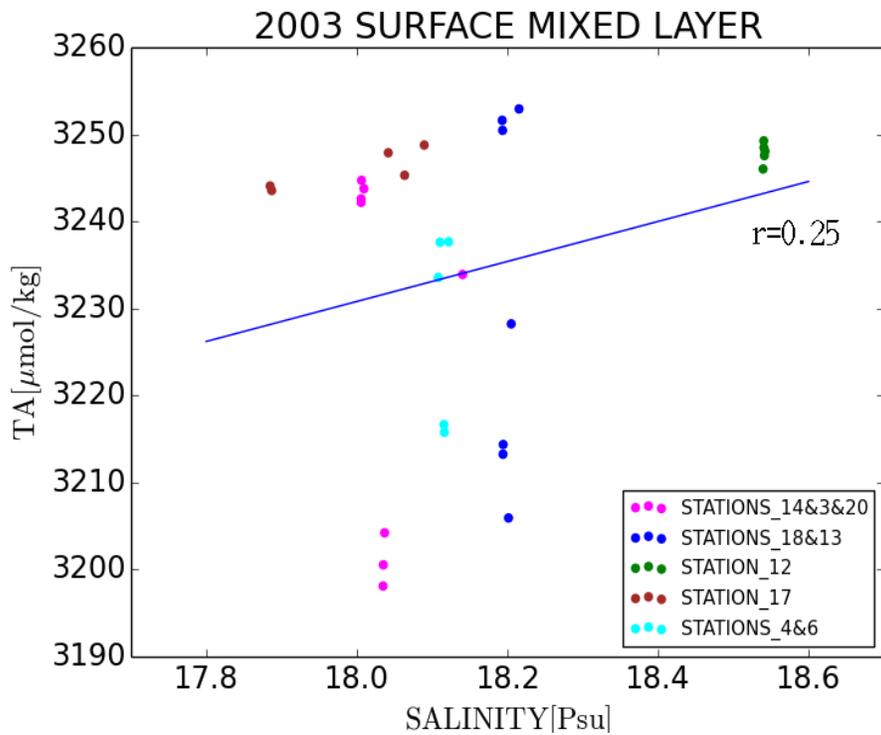
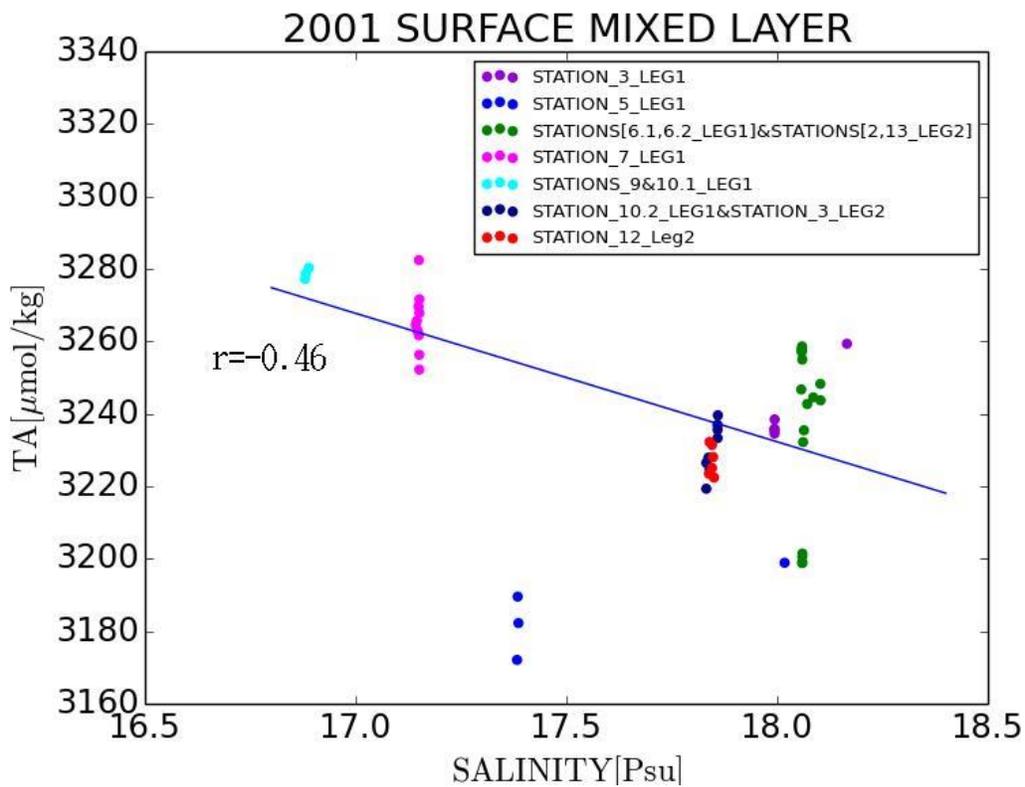


Figure 3.7. Salinity vs TA for 2001 and 2003 Surface Mixed Layer data

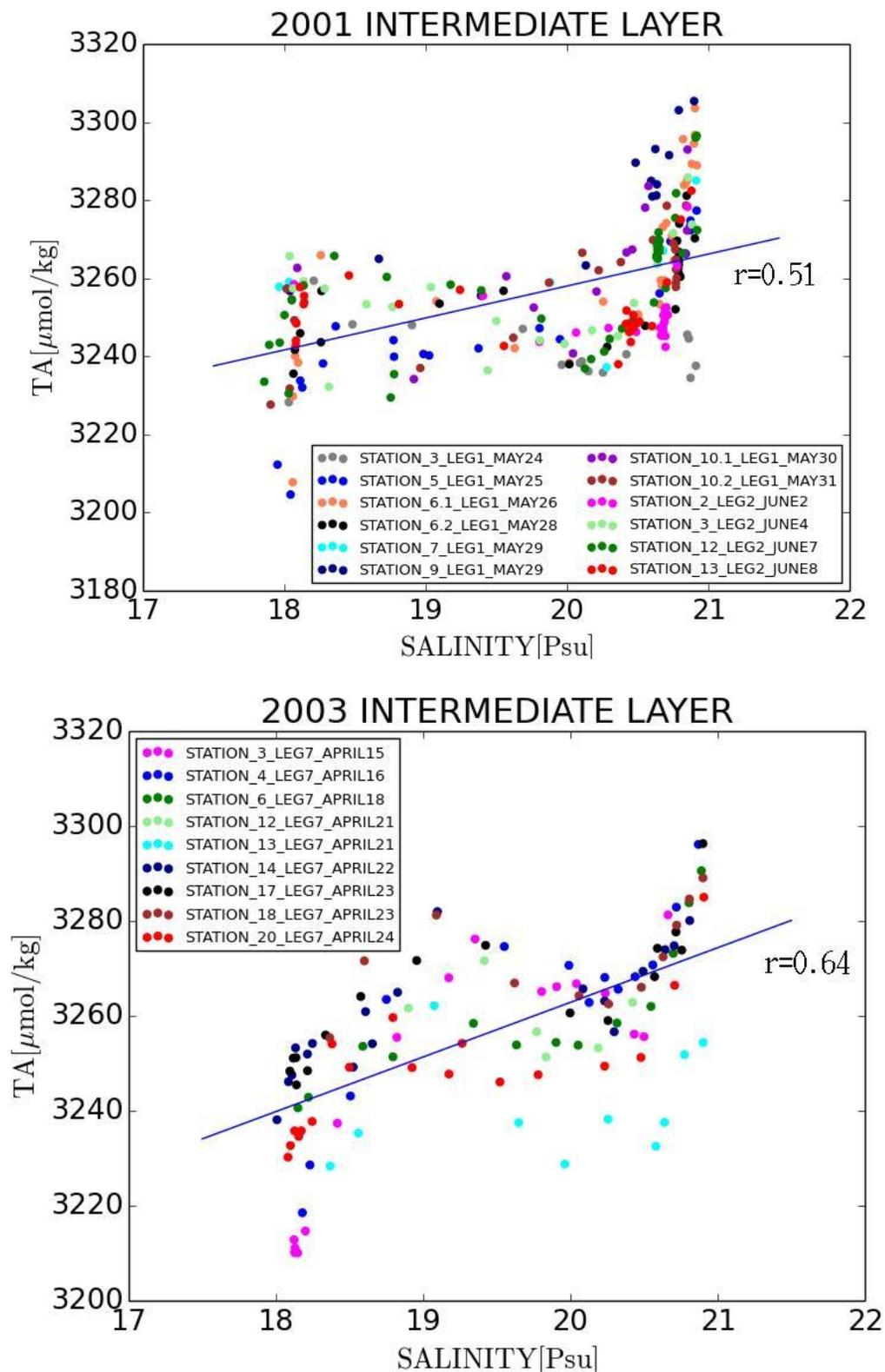


Figure 3.8. Salinity vs TA for 2001 and 2003 Intermediate Layer data

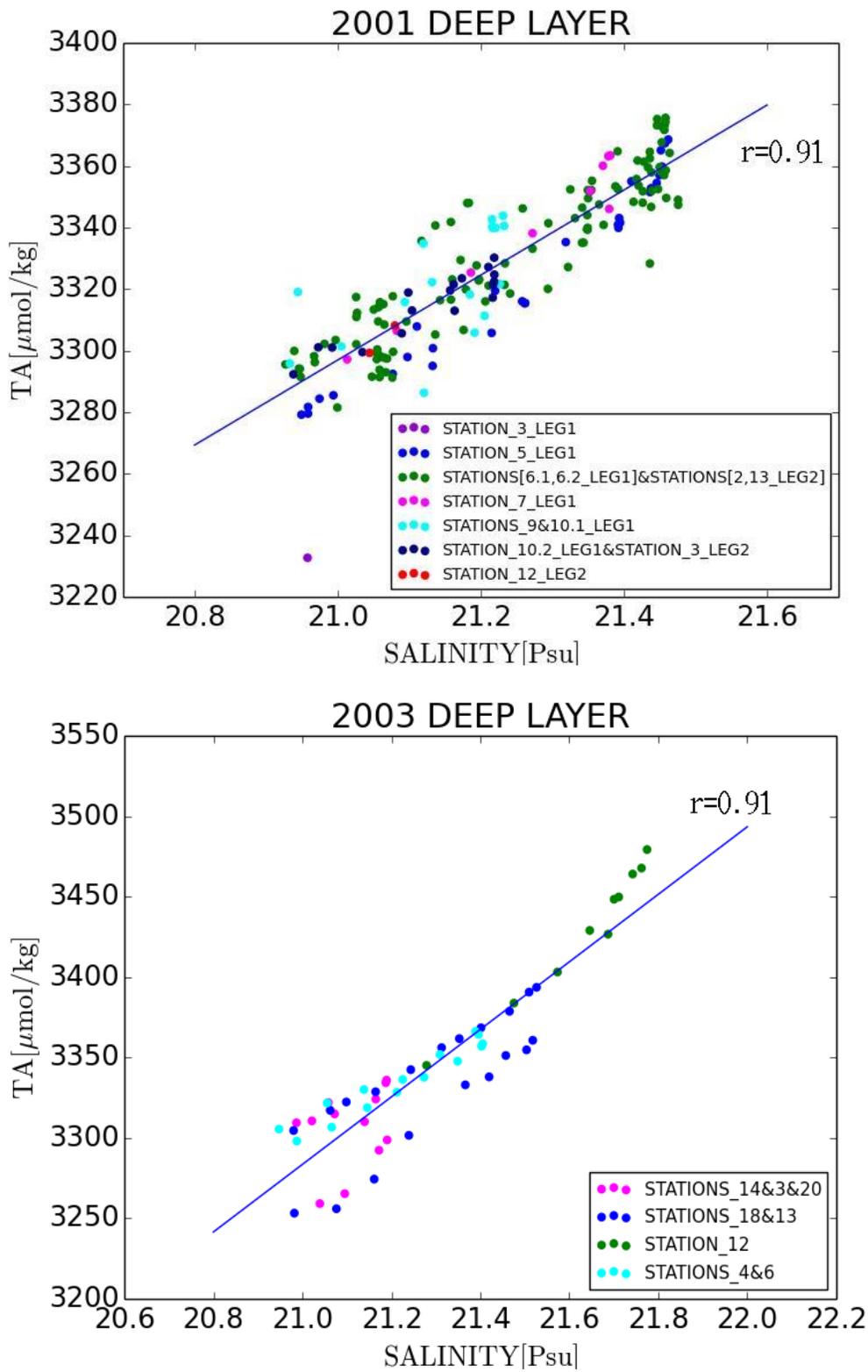


Figure 3.9. Salinity vs TA for 2001 and 2003 Deep Layer data

Table 3.3. r and r² values of Salinity vs TA

Water layer	R/V Knorr 2001 Cruise	R/V Knorr 2003 Cruise
Surface	r=-0.46 r ² =0.21	r=0.25 r ² =0.62
Intermediate	r=0.51 r ² =0.26	r=0.64 r ² =0.41
Deep	r=0.91 r ² =0.83	r=0.91 r ² =0.83

The highest correlation between salinity and TA was observed in the deep layer for both 2001 and 2003 data where the r is >0.9 (Table 3.3). In the correlation calculation for deep layer of 2001 data, the station 3 (Leg1) data was excluded however data point was represented in the figure. The station 17 in 2003 had no data in the deep layer (since the sigma value is lower than 16.2) therefore it was not represented in the deep layer figures.

It is seen from Table 3.4 that r (correlation coefficient) values in the surface waters of the Black Sea are lower than oceanic values and Mediterranean Sea, riverine input with high TA and low salinity could be one of the reasons of low r values in the surface layer of the Black Sea.

Table 3.4. Comparison of r (Salinity- TA) with oceanic values (Source: Fry et al., 2015) and Mediterranean Sea (Source: Schneider et al., 2007)

Atlantic Ocean (2015)	Indian Ocean (2015)	Pacific Ocean (2015)	Mediterranean Sea (2007)	Black Sea (2001 &2003)
r_surface=0.94	r_surface=0.87	r_surface=0.92	r_surface=0.99	r_surf.(2001)=0.46 r_surf.(2003)=0.25
			r_deep =0.82	r_deep(2001)=0.91 r_deep(2003)=0.91

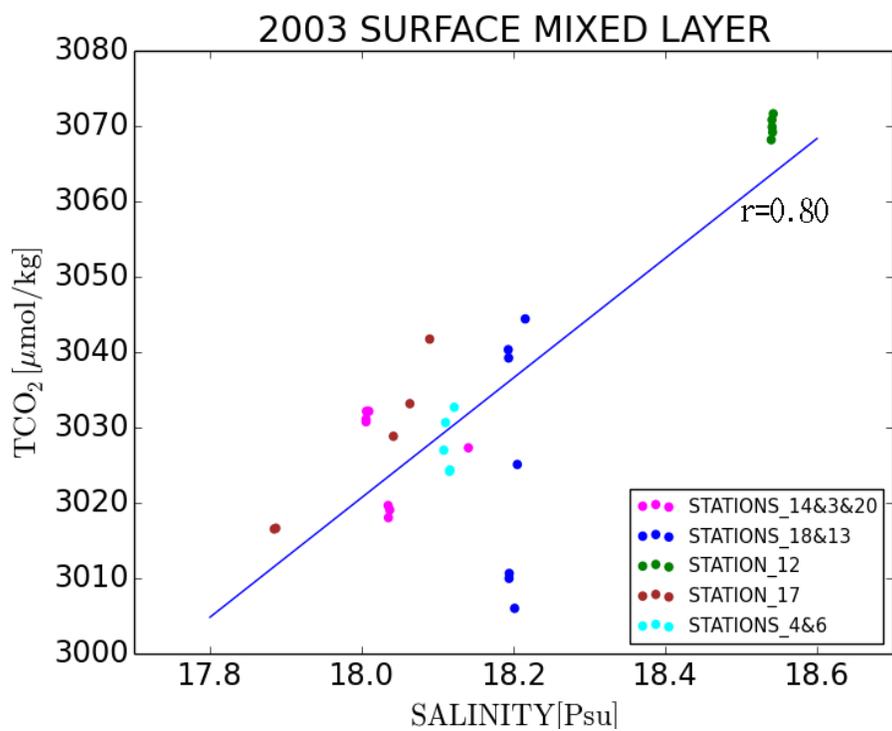
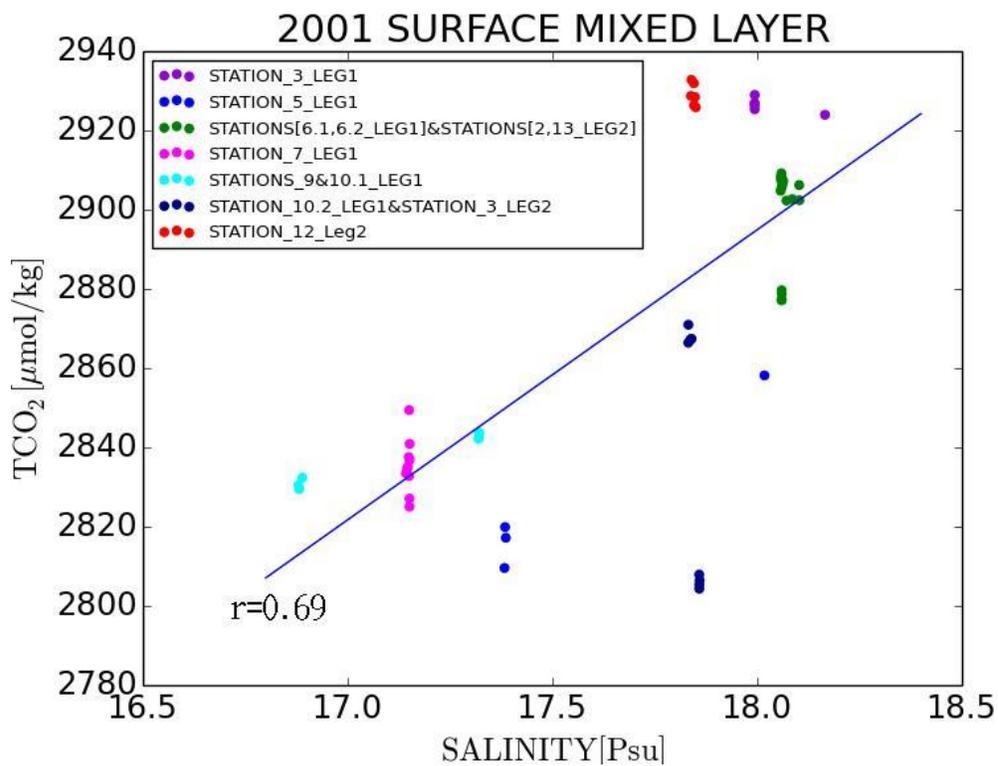


Figure 3.10. Salinity vs TCO_2 for 2001 and 2003 Surface Mixed Layer data

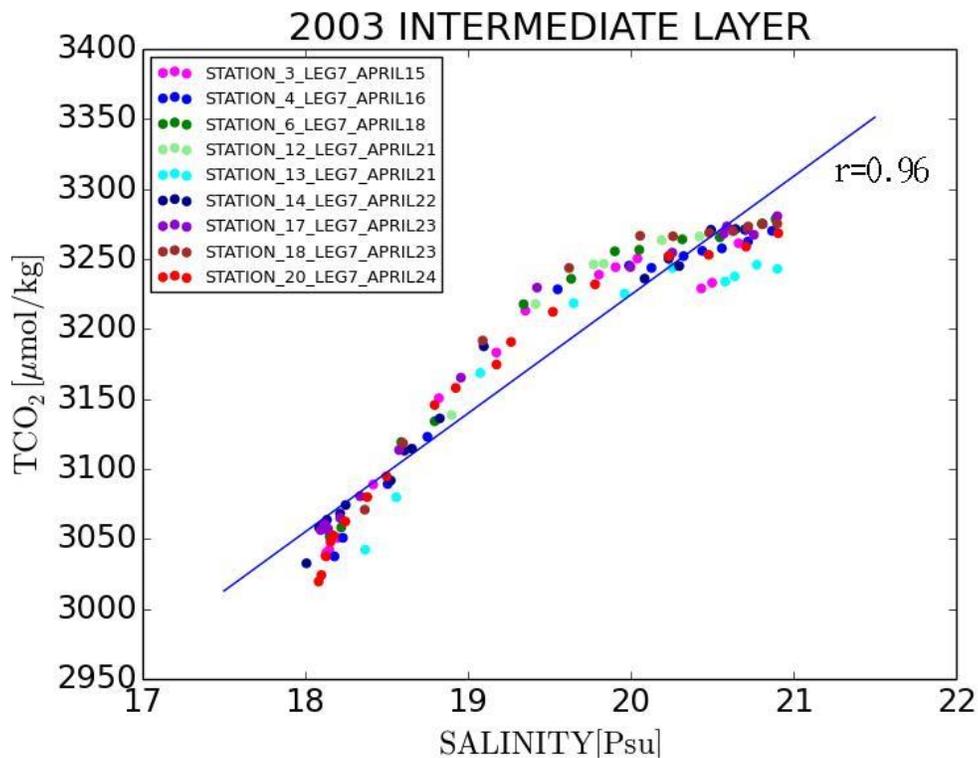
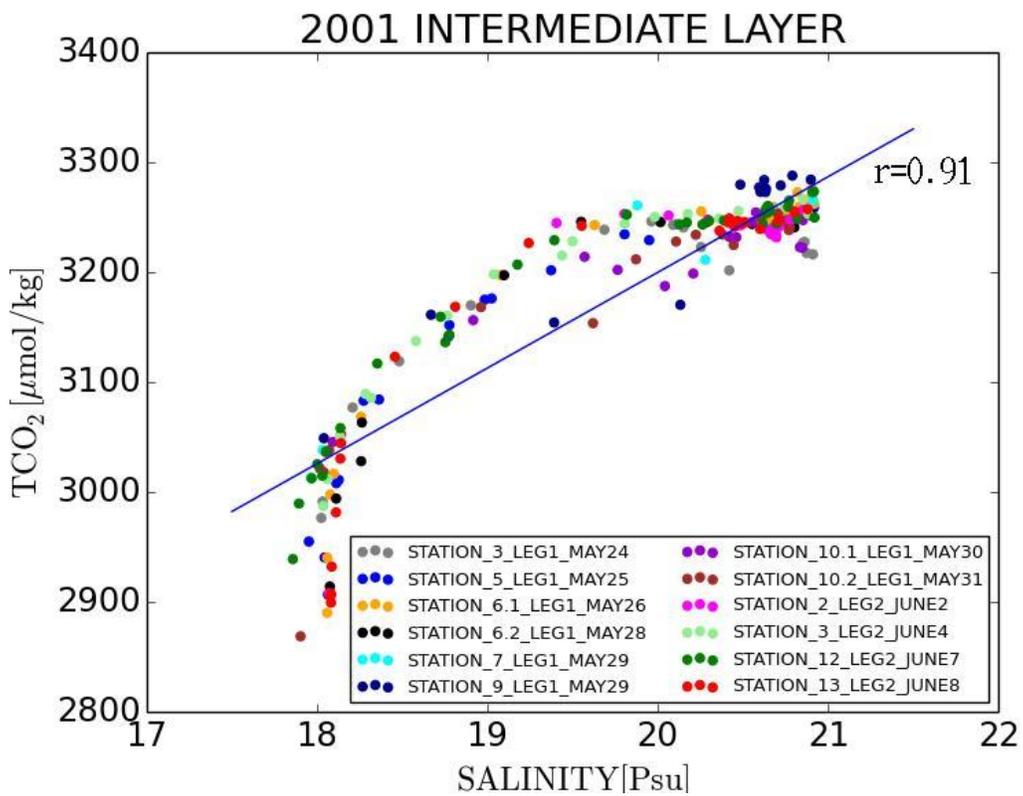


Figure 3.11. Salinity vs TCO₂ for 2001 and 2003 Intermediate Layer data

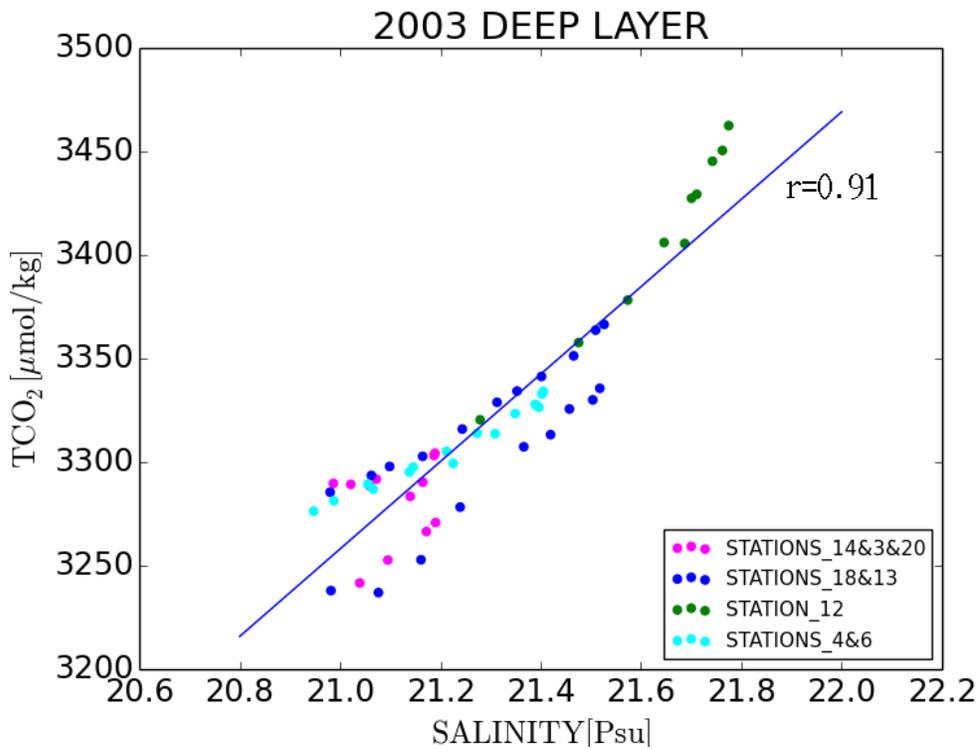
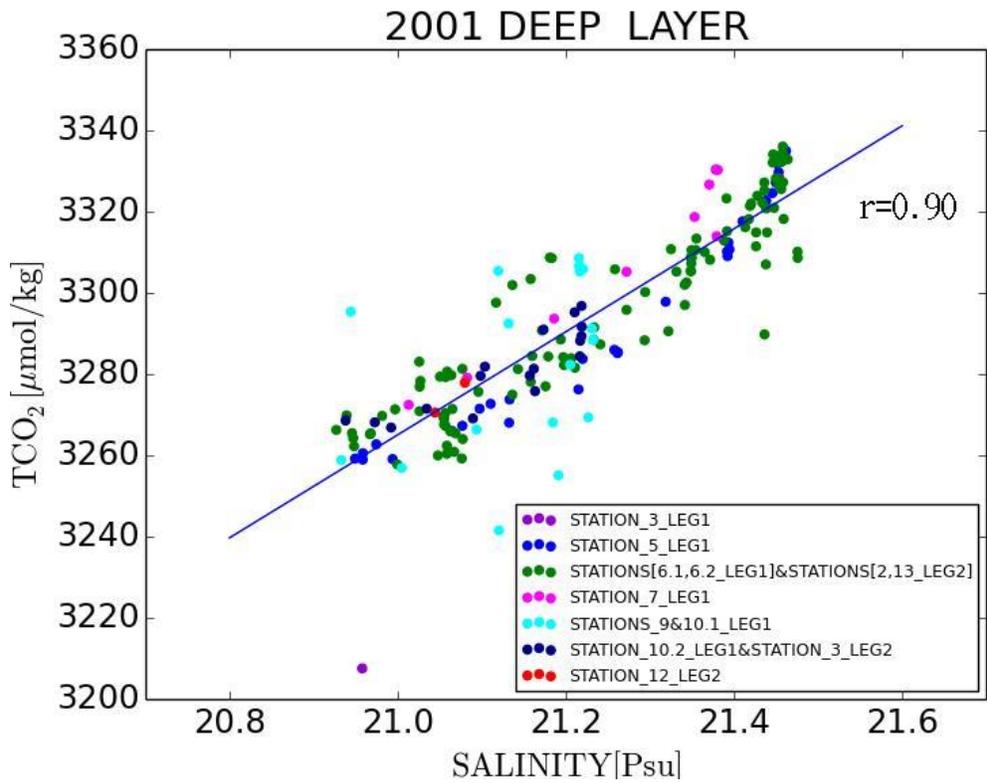


Figure 3.12. Salinity vs TCO₂ for 2001 and 2003 Deep Layer data

Table 3.5. r and r² values of Salinity vs TCO₂

Water layer	R/V Knorr 2001 Cruise	R/V Knorr 2003 Cruise
Surface	r=0.69 r ² =0.47	r=0.80 r ² =0.64
Intermediate	r=0.91 r ² =0.83	r=0.96 r ² =0.92
Deep	r=0.90 r ² =0.81	r=0.91 r ² =0.83

Regarding Salinity vs TCO₂ figures, the values above the regression line represent the production of TCO₂ and the values below the regression line represent the consumption of TCO₂ through biological activities. The highest correlation between salinity and TCO₂ was found in intermediate layer for both 2001 and 2003 data (Table 3.5).

3.2.4. Derived Carbonate Chemistry Parameters: Omega and Revelle Factor

In a closed system, the precipitation of 1 mole CaCO₃ always results in a reduction of 1 mole TCO₂ and 2 moles in TA and dissolution of CaCO₃ has a reverse effect on TA and TCO₂ and also in open system such as ocean mixed layer, an increase in CO₂ leads to outgassing and further decrease in TCO₂ (Wolf-Gladrow et al., 2007). Therefore saturation state of the ocean with respect to CaCO₃ represents a significant control on seawater carbonate system.

In the context of R/V Knorr 2001 and R/V Knorr 2003 seawater carbonate system data, the saturation coefficient omega (Ω_{ar} , Ω_{ca}) was calculated for every layer to see the saturation levels of the Black Sea with respect to calcium carbonate and also Revelle Factor was calculated to see the carbon sink capacity of the Black Sea. In Table 3.6 and 3.7 the minimum and maximum values of omega aragonite, omega calcite and Revelle Factor were listed for 2003 and 2001 data respectively.

Table 3. 6. Minimum and maximum values of Ω_{ar} , Ω_{ca} and Revelle Factor (2003 R/V Knorr Cruise Data)

Cruise	Location	Station	Water Layer	Ω_{ar} (Min/Max)	Ω_{ca} (Min/Max)	Revelle Fact. (Min/Max)
2003	open	Station 3	Surface Mixed Layer	2.52 / 2.60	4.26 / 4.40	16.44 / 16.71
			Intermediate Layer	0.99 / 2.47	1.64 / 4.17	16.92 / 22.65
			Deep Layer	1.14	1.89	22.25 / 22.28
2003	open	Station 4	Surface Mixed Layer	2.67 / 2.68	4.52 / 4.53	16.17 / 16.21
			Intermediate Layer	0.99 / 2.54	1.65 / 4.29	16.66 / 22.59
			Deep Layer	1.11 / 1.19	1.84 / 1.96	22.15 / 22.34
2003	open	Station 6	Surface Mixed Layer	2.82 / 2.85	4.77 / 4.82	15.65 / 15.73
			Intermediate Layer	0.88 / 2.63	1.47 / 4.44	16.40 / 22.72
			Deep Layer	1.03 / 1.09	1.70 / 1.80	22.30 / 22.40
2003	open	Station 12	Surface Mixed Layer	2.48 / 2.52	4.19 / 4.26	16.82 / 16.92
			Intermediate Layer	0.86 / 1.91	1.44 / 3.23	19.41 / 22.71
			Deep Layer	1.08 / 1.12	1.78 / 1.86	22.26 / 22.30
2003	open	Station 13	Surface Mixed Layer	2.76 / 2.82	4.66 / 4.76	15.70 / 15.84
			Intermediate Layer	0.88 / 2.59	1.47 / 4.37	16.47 / 22.72
			Deep Layer	1.01 / 1.10	1.67 / 1.81	22.27 / 22.37
2003	open	Station 14	Surface Mixed Layer	2.90 / 2.92	4.91 / 4.94	15.47 / 15.51
			Intermediate Layer	0.90 / 2.82	1.50 / 4.78	15.73 / 22.59
			Deep Layer	1.04 / 1.13	1.73 / 1.87	22.28 / 22.41
2003	open	Station 17	Surface Mixed Layer	2.84 / 3.10	4.80 / 5.25	14.93 / 15.70
			Intermediate Layer	0.91 / 2.68	1.51 / 4.54	16.20 / 22.65
			Deep Layer			
2003	open	Station 18	Surface Mixed Layer	2.87 / 2.92	4.84 / 4.93	15.51 / 15.64
			Intermediate Layer	0.90 / 2.58	1.50 / 4.36	16.61
			Deep Layer	1.05 / 1.12	1.74 / 1.85	22.27 / 22.39
2003	open	Station 20	Surface Mixed Layer	2.87	4.84	15.63
			Intermediate Layer	0.89 / 2.89	1.48 / 4.89	15.50 / 22.70
			Deep Layer	0.98 / 1.09	1.63 / 1.81	22.30 / 22.38

Table 3. 7. Minimum and maximum values of Ω_{ar} , Ω_{ca} and Revelle Factor (2001 R/V Knorr Cruise Data)

Cruise	Location	Station	Water Layer	Ω_{ar} (Min/Max)	Ω_{ca} (Min/Max)	Revelle Fact. (Min/Max)
2001	coastal	Station 3 (Leg 1)	Surface Mixed Layer	4.24 / 4.58	7.08 / 7.63	11.95 / 12.47
			Intermediate Layer	0.85 / 3.80	1.42 / 6.38	13.27 / 22.69
			Deep Layer	1.04	1.72	22.32
2001	open	Station 5 (Leg 1)	Surface Mixed Layer	4.93 / 5.02	8.25 / 8.41	11.20 / 11.28
			Intermediate Layer	0.98 / 3.55	1.63 / 5.98	13.62 / 22.63
			Deep Layer	1.04 / 1.18	1.72 / 1.95	22.15 / 22.40
2001	open	Station 6.1 (Leg 1)	Surface Mixed Layer	4.38 / 4.39	7.31 / 7.33	12.09 / 12.12
			Intermediate Layer	0.86 / 4.27	1.43 / 7.16	12.25 / 22.57
			Deep Layer	1.06 / 1.16	1.76 / 1.92	22.02 / 22.32
2001	open	Station 6.2 (Leg 1)	Surface Mixed Layer	4.47 / 4.51	7.45 / 7.51	12.04 / 12.08
			Intermediate Layer	0.87 / 4.49	1.45 / 7.48	12.04 / 22.76
			Deep Layer	1.07 / 1.27	1.78 / 2.10	21.92 / 22.36
2001	open	Station 7 (Leg 1)	Surface Mixed Layer	5.87 / 5.95	9.81 / 9.95	10.42 / 10.49
			Intermediate Layer	0.90 / 3.31	1.51 / 5.59	14.38 / 22.57
			Deep Layer	1.08 / 1.15	1.79 / 1.90	22.22 / 22.36
2001	coastal	Station 9 (Leg 1)	Surface Mixed Layer	6.14 / 6.17	10.29/10.34	10.23 / 10.26
			Intermediate Layer	0.96 / 2.86	1.60 / 4.83	15.67 / 22.54
			Deep Layer	1.07 / 1.15	1.78 / 1.91	22.24 / 22.41
2001	coastal	Station 10.1 (Leg 1)	Surface Mixed Layer	6.42 / 6.54	10.70 / 10.91	9.98 / 10.06
			Intermediate Layer	1.08 / 2.95	1.79 / 4.99	15.35 / 22.35
			Deep Layer	1.12 / 1.23	1.86 / 2.04	21.83 / 22.17
2001	coastal	Station 10.2 (Leg 1)	Surface Mixed Layer	4.89 / 5.0	8.12 / 8.30	11.38 / 11.50
			Intermediate Layer	1.03 / 4.92	1.71 / 8.20	11.43 / 22.52
			Deep Layer	1.13 / 1.18	1.88 / 1.96	22.15 / 22.29
2001	open	Station 2 (Leg 2)	Surface Mixed Layer	4.83	8.01 / 8.02	11.65
			Intermediate Layer	0.85 / 4.82	1.43 / 8.01	11.64 / 22.79
			Deep Layer	1.07 / 1.17	1.77 / 1.93	22.13 / 22.34

Table 3.7. (continued) Minimum and maximum values of Ω_{ar} , Ω_{ca} and Revelle Factor (2001 R/V Knorr Cruise Data)

Cruise	Location	Station	Water Layer	Ω_{ar} (Min/Max)	Ω_{ca} (Min/Max)	Revelle Fact. (Min/Max)
2001	open	Station 3 (Leg 2)	Surface Mixed Layer	5.84 / 5.90	9.72 / 9.82	10.33 / 10.38
			Intermediate Layer	0.86 / 3.75	1.44 / 6.30	13.38 / 22.76
			Deep Layer	1.03 / 1.11	1.71 / 1.83	22.26 / 22.37
2001	open	Station 12 (Leg 2)	Surface Mixed Layer	4.03 / 4.09	6.75 / 6.85	11.78 / 12.70
			Intermediate Layer	0.86 / 3.99	1.44 / 6.70	12.83 / 22.67
			Deep Layer	1.06 / 1.07	1.75 / 1.77	22.20 / 22.21
2001	open	Station 13 (Leg 2)	Surface Mixed Layer	4.69 / 4.71	7.81 / 7.83	11.77 / 11.78
			Intermediate Layer	0.91 / 4.68	1.51 / 7.81	11.76 / 22.71
			Deep Layer	1.06 / 1.14	1.76 / 1.88	22.05 / 22.24

Results of the study published by Tyrrell et al., in 2008 indicated that The Black Sea and the Baltic Sea are comparable since they are both brackish and the Black Sea is supersaturated for all year long with respect to aragonite and calcite (Table 3.8) and this situation is mainly attributed to the presence of the strong coccolithophore *Emiliana huxleyi* blooms (Çokacar et al., 2004).

Table 3.8. Comparison of Revelle factor & Omega with other Sea's (Source: Tyrrell et al., 2008)

Gotland Sea Surface water mean value May (2001)	Black Sea surface water mean value (2001 & 2003)
$\Omega_{ca} = 2.86$ $\Omega_{ar} = 1.57$	$\Omega_{ca} (2001) = 8.51$ $\Omega_{ar} (2001) = 5.10$
	$\Omega_{ca} (2003) = 4.70$ $\Omega_{ar} (2003) = 2.78$

The lowest Ω_{ca} and Ω_{ar} values were found in intermediate layers for both 2001 and 2003 data (Table 3.7 and Table 3.6). The highest Revelle factor values were found in the deep layers of the Black Sea. The highest values of Ω_{ca} and Ω_{ar} , which indicate the saturation of seawater since $\Omega > 1$, and lowest values of Revelle factor were found in the surface water of the Black Sea when both 2001 and 2003 data were analyzed (Table 3.7 and Table 3.6).

Higher Revelle factor values are related to lower carbon uptake capacities (Sabine et al., 2004). When 2001 surface water data was examined individually the lowest Revelle factor was found at station 10.1 and highest Revelle factor was at station 6.1. And for 2003 surface water data, the highest Revelle factor was at station 12 and the lowest Revelle factor was at station 17. Increased values of Revelle factor at surface waters of

the Black Sea for 2003 data indicate that the carbon sink capacity was diminished compared to 2001 data.

The highest Ω_{ar} and Ω_{ca} values for 2001 data were found in the station 10.1 and the lowest values of Ω_{ar} and Ω_{ca} were found in station 12 for surface water data. For 2003 surface water data, the highest Ω_{ar} and Ω_{ca} values were found in station 17 and lowest values of Ω_{ar} and Ω_{ca} were found in station 12 (Table 3.7, 3.6).

It was demonstrated in Table 3.7 and 3.6 that under saturation of seawater with respect to calcium carbonate was seen in the intermediate and in deep layer where Ω values were lower than 1.

When omega values of 2003 surface water data were compared to 2001 data, it was seen that 2003 omega values of surface water were lower than 2001 data (Table 3.8) and this situation was consistent with low pH values, and high TCO_2 values in the surface water of the Black Sea. The elevated levels of TCO_2 in surface water also resulted in high Revelle factor values for 2003 data which presented low carbon uptake capacity.

Results of the study published by Bates et al. in 2012 indicated that as a result of elevated levels of anthropogenic CO_2 in the atmosphere, the Revelle factor in surface waters of North Atlantic increased and signs of ocean acidification pH and Ω values decreased by ~ 0.05 (0.0017 yr^{-1}) and $\sim 7\text{-}8\%$ respectively according to the data record covering the period 1983–2011. When 2001 and 2003 surface water mean Revelle factor values are compared it is seen that 2003 data is 4.52 units higher than 2001 data (Table 3.9).

Table 3.9. Comparison of Revelle factor of the Black Sea 2001 and 2003 data mean value

Revelle Factor (range 8-15)	2001 surface water mean value	2003 surface water mean value
		11.38

3.2.5. Air-Sea CO₂ Fluxes for the Black Sea

The air-sea CO₂ flux represents the variations of both the concentration difference of CO₂ across the air-water interface and wind speed (Krasakopoulou et al., 2009). One of the controls of air-sea CO₂ flux, the concentration difference of CO₂ was firstly investigated in the present study.

Atmospheric pCO₂ (almost same values for all stations and extracted from NOAA Greenhouse Gas Marine Boundary Layer (MBL) Reference data bank) values were listed along with pCO₂ in the surface mixed layer, then $\Delta p\text{CO}_2$, which is the difference between partial pressure of CO₂ in seawater and the partial pressure of CO₂ in the atmosphere, and they were all listed in Table 3.10.

Table 3.10. Partial pressure of CO₂ in seawater, in atmosphere and their difference

Cruise	Location	Station	pCO ₂ (seawater) (µatm)	pCO ₂ (atmos) (µatm)	ΔpCO ₂ (µatm)
2001	coastal	Station 3 (Leg1)	327.4	375.1	-47.7
2001	open	Station 5 (Leg1)	247.9	375.1	-127.2
2001	open	Station 6.1 (Leg1)	301.4	375.2	-73.8
2001	open	Station 6.2 (Leg1)	314.1	375.2	-61.1
2001	open	Station 7 (Leg1)	219.6	375.1	-155.5
2001	coastal	Station 9 (Leg1)	205.6	375.1	-169.5
2001	coastal	Station 10.1 (Leg1)	202.1	375.1	-173.0
2001	coastal	Station 10.2 (Leg1)	300.9	375.1	-74.2
2001	open	Station 2 (Leg 2)	308.4	371.4	-63.0
2001	open	Station 3 (Leg 2)	218.1	371.5	-153.4
2001	open	Station 12 (Leg 2)	318.3	371.5	-53.2
2001	open	Station 13 (Leg 2)	308.0	371.4	-63.4
2003	open	Station 3	421.4	380.4	41.0
2003	open	Station 4	410.9	380.4	30.5
2003	open	Station 6	383.3	380.4	2.9
2003	open	Station 12	437.3	380.5	56.8
2003	open	Station 13	393.6	380.4	13.2
2003	open	Station 14	375.2	380.4	-5.2
2003	open	Station 17	350.2	380.4	-30.2
2003	open	Station 18	387.5	380.4	7.1
2003	open	Station 20	397.4	380.4	17.0

pCO₂ values of surface water are mainly influenced by the physical chemical processes, biological processes, transport processes and CO₂ flux between atmosphere and seawater and all these processes are generally influenced by sea surface temperature (SST) (Park et al., 2010).

Results of the study published by Lueger et al. in 2008 indicated that temperature together with mixed layer depth are very significant parameters to define the regional variability of the CO₂ flux between atmosphere and seawater. In this context, the correlation between SST and pCO₂ in seawater was investigated and Figure 3.13 represented the relation between SST and pCO₂ values in surface water.

In general an increase in sea surface temperature diminishes solubility of CO₂ thus results in decrease in pCO₂ values of surface water and vice versa (Cossarini et al., 2015). This inverse relation between SST and pCO₂ was observed in Figure 3.13. There is a negative correlation ($r < 0$) between SST and pCO₂ in seawater for both 2001 and 2003 data. The lower values of SST are related to higher values of pCO₂ in seawater and vice versa.

The low r values calculated for SST and pCO₂ indicate that pCO₂ is controlled by other parameters such as river input with high alkalinity and low salinity, the existence of coccolithophores, biological processes. A similar study conducted in Atlantic Ocean by Benson et al. in 2014 indicated that pCO₂ might not be affected only by SST variations but also biological and physical processes and this situation resulted in low r values ($r = -0.56$) for these two parameters.

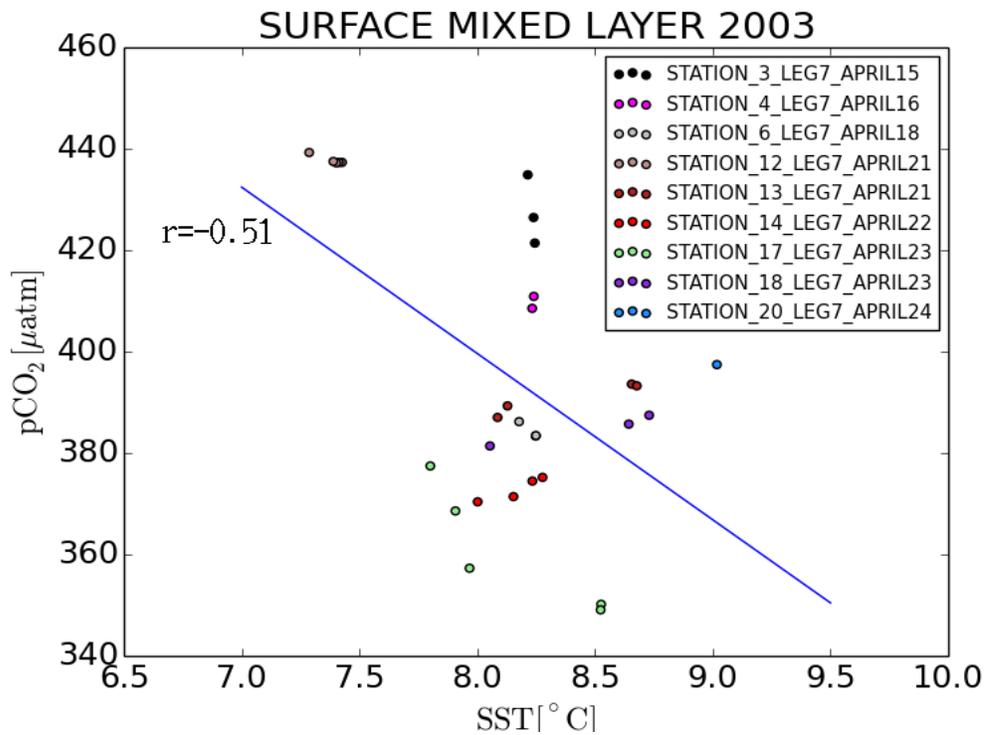
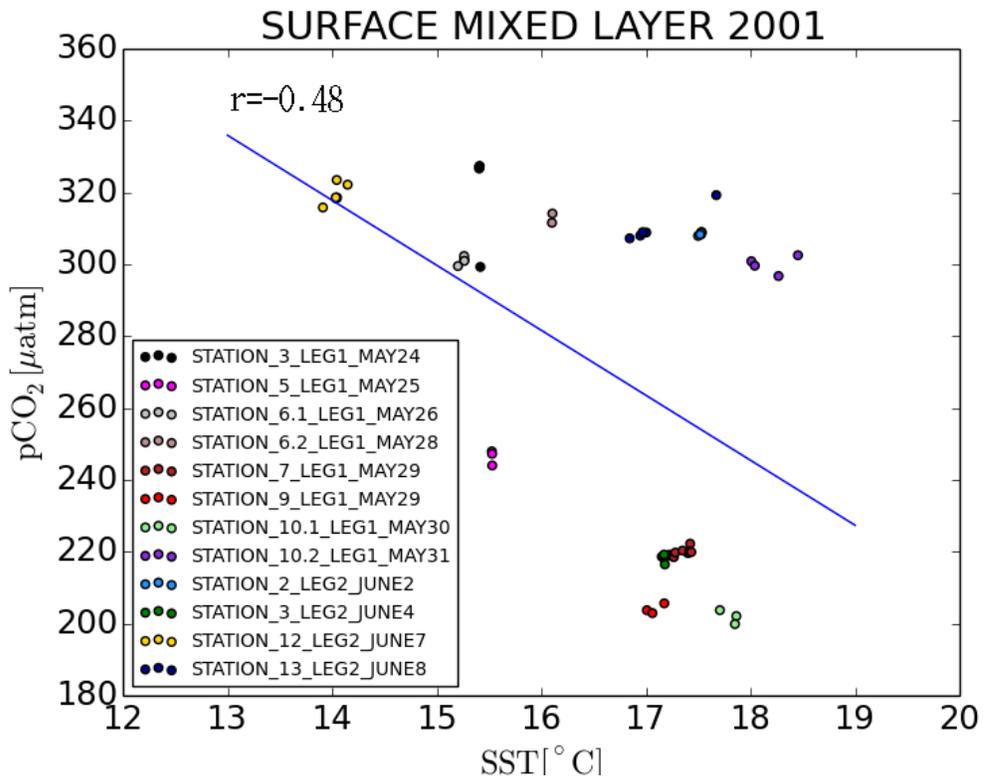


Figure 3.13. SST vs pCO₂ in seawater for 2001 and 2003 data (r represents the correlation coefficient)

It was demonstrated in Table 3.10 that the most negative value of $\Delta p\text{CO}_2$ of 2001 cruise data was found at Station 10.1 (Leg 1) which implied significantly low concentration of CO_2 in surface water with respect to atmospheric CO_2 concentration and the most positive value of $\Delta p\text{CO}_2$ of 2001 cruise data was found in station 3 (Leg 1).

The mean $p\text{CO}_2$ values of surface water of Black Sea was 271(μatm) and 395 (μatm) for 2003 data. The $p\text{CO}_2$ values of surface water of the entire 2001 data was lower than the atmospheric $p\text{CO}_2$ values indicating the undersaturation of surface waters with respect to the atmosphere (Table 3.10). The undersaturation of the surface water resulted in negative $\Delta p\text{CO}_2$ values. Hence surface waters of the Black Sea represented a sink in general for atmospheric CO_2 during 2001 cruise.

When 2003 data were analyzed the highest difference between atmospheric CO_2 and seawater CO_2 was found in Station 12 (Table 3.10). However in this case the partial pressure of CO_2 in surface water was considerably high when compared to partial pressure of CO_2 in atmosphere implying the character of being source. The most negative value of $\Delta p\text{CO}_2$ was in station 17 (Table 3.10).

During 2003 cruise both negative and positive $\Delta p\text{CO}_2$ values were seen (Table 3.10) which indicated that surface water of the Black Sea was both undersaturated and saturated with respect to atmosphere. In this context, surface waters of the Black Sea represented both a source and a sink for atmospheric CO_2 .

When both 2001 and 2003 data were taken into account it was seen that generally lower pH values coincided with lower salinity and higher $p\text{CO}_2$ values in seawater (Table 3.1, Figure 3.2 and Table 3.10). The minimum values of Revelle factor were found where the most negative $\Delta p\text{CO}_2$ values were found confirming that the lower Revelle factors indicated higher carbon sink capacity and also in the context of saturation, the higher omega values were related to most negative $\Delta p\text{CO}_2$ values (Table 3.6, Table 3.7 and Table 3.10). Since the solubility of CO_2 depends on alkalinity

(Cossarini et al, 2015), $\Delta p\text{CO}_2$ values are also influenced by TA values (Table 3.10). In Table 3.11 CO_2 fluxes calculated by three different approaches (Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Ho et al., 2006) were listed along with cruise name, related station, leg, date, latitude and longitude and 10 m wind speed data.

The flux calculation program used in the present study includes the three different wind speed parameterizations and these models were set through different set of experiments. Therefore they estimate different gas transfer velocities which result in very high difference at high wind speeds. This difference results in variations in the flux values. However the same wind speed values were used for all three different wind speed dependent models (Figure 3.14). Since wind speed is one of the main controls of the CO_2 flux, a change in wind speed affects flux values (Table 3.11).

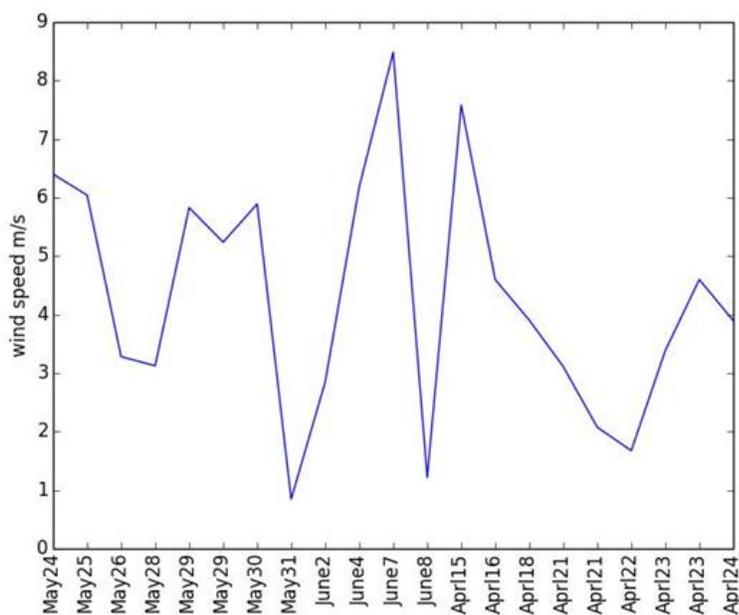


Figure 3.14. Wind speed data retrieved from ECMWF ERA Interim Model for the selected stations of 2001 and 2003.

Table 3.11. Calculated CO₂ fluxes between seawater surface and atmosphere

R/V Knorr Cruise	Station	Leg	Date	Latitude (degrees)	Longitude (degrees)	Wind (m/s)	FluxW92 (mmol m ⁻² d ⁻¹)	FluxMcG99 (mmol m ⁻² d ⁻¹)	FluxHo06 (mmol m ⁻² d ⁻¹)
2001	3	1	24 th of May	41.50	29.25	6.4	-5.51	-3.20	-4.48
2001	5	1	25 th of May	41.97	29.94	6.0408	-13.00	-7.12	-10.56
2001	6.1	1	26 th of May	42.50	30.76	3.2811	-2.25	-0.67	-1.83
2001	6.2	1	28 th of May	42.50	30.76	3.1261	-1.68	-0.48	-1.37
2001	7	1	29 th of May	41.88	30.50	5.8281	-14.80	-7.83	-12.03
2001	9	1	29 th of May	41.48	30.50	5.2375	-13.04	-6.19	-10.60
2001	10.1	1	30 th of May	41.45	30.26	5.8914	-16.76	-8.96	-13.63
2001	10.2	1	31 st of May	41.50	30.25	0.8454	-0.15	-0.01	-0.12
2001	2	2	2 nd of June	42.50	30.77	2.8475	-1.43	-0.37	-1.16
2001	3	2	4 th of June	44.12	30.91	6.1793	-16.25	-9.11	-13.21
2001	12	2	7 th of June	44.28	32.25	8.4846	-10.81	-8.32	-8.79
2001	13	2	8 th of June	42.50	30.77	1.2169	-0.26	-0.03	-0.21
2003	3	7	15 th of April	41.58	29.16	7.5805	6.62	4.55	5.38
2003	4	7	16 th of May	41.83	29.34	4.5968	1.79	0.74	1.45
2003	6	7	18 th of May	41.70	29.83	3.9059	0.06	0.02	0.05
2003	12	7	21 st of May	42.50	31.00	3.1114	1.56	0.44	1.27
2003	13	7	21 st of May	41.83	30.69	2.075	0.15	0.03	0.12
2003	14	7	22 nd of May	41.48	30.54	1.6742	-0.06	-0.01	-0.05
2003	17	7	23 rd of May	41.34	30.83	3.3853	-1.07	-0.33	-0.87
2003	18	7	23 rd of May	41.83	30.91	4.5986	0.34	0.14	0.28
2003	20	7	24 th of May	41.44	29.58	3.896	0.70	0.25	0.57

It was presented in Table 3.11 that all windspeed dependent models agreed on the sign of the fluxes. When 2001 flux data were taken into account, all of the fluxes were negative and into the sea.

The air-sea CO₂ fluxes were close to neutral where the flux values were around 0. When 2003 flux data were considered, some of the fluxes were positive and in this case CO₂ fluxes were towards the atmosphere.

The strongest sink was diagnosed at station 10.1 in 2001 as a result of highly negative $\Delta p\text{CO}_2$ and strong wind. Among the stations in 2001 cruise, the highest TA, pH Ω_{ar} and Ω_{ca} and lowest Revelle values in the surface water were observed in station 10.1. On the other hand, the weakest sink was diagnosed at station 10.2 due to weak wind speed. In 2003, the strongest uptake of CO₂ was found at station 17 where the highest pH, Ω_{ar} and Ω_{ca} and lowest Revelle values and also second highest TA values were found. The weakest uptake of CO₂ was found at station 14 and the remainder of the stations represented outgassing of CO₂.

Models estimate that the oceans capture most CO₂ released to the atmosphere over several centuries as CO₂ is dissolved at the ocean surface waters and afterward mixed with deep layer. Hence, the storage amount of CO₂ in the ocean on longer time scale (e. g. millennium) depends on oceanic balance with the atmosphere (IPCC, 2005).

The Black Sea has an area of 436.400 km² and if one considers the maximum rate of flux and estimates the CO₂ uptake rate;

- Molar mass of CO₂ = 44.0095 g/mol
- 16 mmol m⁻²d⁻¹ = 0.7 g m⁻²d⁻¹ (Maximum flux in 2001; Table 3.11)
- 0.7 g m⁻²d⁻¹ * 436.400 10⁶ m² * 365 d = 0.1 x 10³ t yr⁻¹

This very rough quantity represents only the CO₂ flux by the solubility pump. The carbon sink capacity of the Black Sea is considered to be driven mainly by biological pump since the primary production is relatively high in the Black Sea [Open waters:

112-587 $\text{mgCm}^{-2}\text{d}^{-1}$ and NW Shelf and Coastal Waters: 405-2140 $\text{mgCm}^{-2}\text{d}^{-1}$ estimated for the 1960-2001 period (Yılmaz et al., 2006)]. Studies on annual budget for N cycling in the Black Sea by Mc Carthy et al. (2007), estimates a particle export rate from the surface layer to the deep anoxic waters equivalent to 8 % of the total N production while an annual mean f-ratio of 0.38 by the conventional formulation was calculated. However, the balanced N budget permits a direct comparison of allochthonous sources of N to total N production in this unusual aquatic ecosystem, resulting in an f-ratio of 0.17 which is the ultimate removal process of biologically produced Org-C.

A similar study was conducted for the Aegean Sea and the absorption capacity was estimated to be 6.2 – 11.8 $\text{mmol/m}^2\text{d}^{-1}$ (Krasakopoulou et al., 2006) which indicates a lower capacity than the estimated capacity of the Black Sea with 2001 data. And also the global carbon uptake capacity was investigated by Takahashi et al in 2009 and it was calculated as 2.0 PgC y^{-1} .

CHAPTER 4

4. CONCLUSIONS

In this thesis, an empirical approach to estimate the carbon sink capacity of the Black Sea was made through investigating seawater carbonate system of the Black Sea and its' the interaction with the atmosphere. The physical features and the components of the seawater carbonate system (TA, TCO₂, pH and pCO₂) were discussed for surface, intermediate and deep layer considering their relation with other physical parameters (temperature, salinity). For the present study only carbon dioxide fluxes and inorganic carbon were investigated. Other components of carbon cycle (Org-C, DOC, export particle flux) were not included.

These datasets together with the wind speed, mean sea level pressure and sea surface temperature are utilized to use a model allowing evaluating CO₂ fluxes at the Black Sea-atmosphere interface. The estimation of the CO₂ absorption in the surface waters of the Black Sea was provided in the present study for the first time but our empirical estimation could be enhanced through increasing the quality of the data and spatial widening of the observations for long term periods. Therefore it is essential to observe carbonate system along with atmospheric CO₂ and other necessary physical parameters (both in the atmosphere and in the sea) covering wide the whole Black Sea systematically and repeatedly for a precise estimation of carbon budgets, annual air sea CO₂ exchanges and to quantify the role of the Black Sea as a sink basin. The continuous observations also indicate the variations in the carbon cycle on larger time scales.

CHAPTER 5

5. FUTURE WORK

To obtain more accurate results for the Black Sea, the spatial coverage has to be extended and has to cover the entire Black Sea basin. Time series of seawater carbonate system parameters and meteorological parameters have to be included to see the variations in the atmosphere-seawater interaction. Biological pump is an important process for the carbon cycle in seawater hence its impact on the CO₂ uptake has to be taken into account. A comprehensive model which influences the whole ecosystem to represent atmosphere-seawater interaction should be set for the Black Sea.

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