ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

DETERMINATION OF PAH POLLUTION AND SOME OCEANOGRAPHICS CHARACTERISTIC THROUGH THE İSTANBUL STRAIT (BOSPHORUS)

M.Sc. Thesis by

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Department : Ocean Engineering

Programme: Ocean Engineering

JANUARY 2008

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JANUARY 2008

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

İSTANBUL BOĞAZI BOYUNCA PAH KİRLENMESİNİN BOYUTLARININ VE OŞİNOGRAFİK KARAKTERİNİN BELİRLENMESİ

YÜKSEK LİSANS TEZİ

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CONTENTS

TABLE LIST

FIGURE LIST

İSTANBUL BOĞAZI BOYUNCA PAH KİRLENMESİNİN BOYUTLARININ VE OŞİNOGRAFİK KARAKTERİNİN BELİRLENMESİ

ÖZET

İstanbul ve kıyısal çevresi (İstanbul Boğazı) atıksu deşarjları, nüfüs artışı ve yoğun gemi trafiğinden güçlü bir şekilde etkilenmektedir. İstanbul Boğazı'nın oşinografik özellikleri yoğun bir şekilde çalışılmış olmakla beraber Boğaz ekosistemi ve Boğaz'daki önemli kirleticiler hakkında detaylı bir çalışma yapılmamıştır. Bu çalışmada, yüzey sedimanı, midye (*Mytilus galloprovincialis,* Lamarck, 1819) ve deniz suyu örnekleri Boğaz boyunca 24 istasyondan toplanmıştır. Sediman ve midye örnekleri 25 ayrı Poli Aromatik Hidrokarbon için analiz edilmiştir. Analizler yüksek çözünürlükte gaz kromotografisi/yüksek çözünürlükte kütle sepektrometrisi (HRGC/HRMS) kullanarak yapılmıştır. Sedimanlara sediman toksisite testi ve midyelere biyogösterge teknikleri (Lizozomal stabilite ve Filtrasyon hızı) uygulanmıştır. Yüzey deniz sularında sıcaklık ve tuzluluk ölçülmüş, besin elementleri ($N\text{-}NO_3$, $PO_4\text{-}P$, Si) ve klorofil a analizleri mevsimsel olarak yapılmıştır. Besin elementleri ve klorofil-a analizleri UV-visible spektrofotometre ile gerçekleştirilmiştir. Sonuçlar yüzey sedimanında T-PAH (Σ16 EPA PAH; Environmental Protection Agengy; Çevre Koruma Örgütü) konsantrasyonunun 1,1 ng/g ile 3152 ng/g kuru ağırlık arasında değiştiğini göstermektedir. Midye örneklerinde ise T-PAH konsantrasyonu 42,9 ng/g ile 601 ng/g ıslak ağırlık arasında değişmektedir. PAH'ların kaynaklarını (petrol veya yanma kökenli) belirlemek üzere LMW/HMW oranı (düşük moleküler ağırlıktaki PAH'lar/yüksek moleküler ağırlıktaki PAH'lar), Phe/Ant (Phenanthrene / Anthracene) oranı ve Flu/Pyr (Fluoranthene / Pyrene) oranı kullanılmıştır. Elde edilen sonuçlar Boğaz'dan toplanan örneklerin büyük çoğunluğunun yanma kökenli PAH'lar ile kirlendiğini göstemiştir. Sediman toksisitesi ve biyogösterge tekniklerinin sonuçları İstanbul Boğazı'ndan bazı bölgelerin sedimanlarının önemli toksik özellik gösterdiğini ve midyelerin sağlık durumlarının ise bozulmuş olduğunu göstermiştir.

DETERMINATION OF PAH POLLUTION AND SOME OCEANOGRAPHIC CHARACTERISTICS THROUGH THE İSTANBUL STRAIT (BOSPHORUS)

SUMMARY

Istanbul and its coastal environment (Istanbul Strait) have been strongly affected by the wastewater discharges, high population and heavy ship traffic. Although, the oceanographic characteristic of the Istanbul strait are well studied before, the Strait ecosystem and priority pollutants in the Strait have not been studied in detail previously. In this study surface sediment, mussel (*Mytilus galloprovincialis,* Lamarck, 1819) and seawater samples were collected from 24 stations along the Istanbul strait. Sediment and mussel samples were analyzed for individual (25 compounds) Polycyclic Aromatic Hydrocarbons (PAHs). Analyses have been performed by High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Toxicity tests were applied to sediments and biomarker techniques (Neutral Red retention-Lysosomal stability and Filtration rate of mussels) were applied to the mussels. In the surface waters, temperature and salinity were measured and nutrients ($N\text{-}NO_3$, $P\text{-}ortoPO_4$, Si), chlorophyll-a were analyzed seasonally. Nutrients and chlorophyll-a analysis were performed by using UV-visible spectrophotometer. The results show that T-PAH (Σ16 EPA PAHs; Environmental Protection Agency) concentrations of surface sediments are ranging from 1.1 ng/g dry wt to 3152 ng/g dry wt. for the mussel samples, T-PAH concentrations ranged from 42.9 ng/g to 601 ng/g wet weight. PAHs are investigated to determine their source of origins (pyrolytic or petrogenic origin) by using the LMW/HMW ratio (sum of the low molecular weight PAHs / the sum of higher molecular weight PAHs), Phe/Ant (Phenanthrene / Anthracene) ratio and Flu/Pyr (Fluoranthene / Pyrene) ratio. The results indicate for the majority of the samples from Istanbul Strait that the origin of PAHs pollution is pyrolytic. Sediment Toxicity test and biomarker techniques results show that some of the sediments show toxic properties and there is degradation in the health status of mussels.

1 INTRODUCTION

1.1 Aim of The Study

Turkey has an important strategic position. This position doesn't only imply a geological connection between Europe and Asia, but also historical and cultural link between two continents. The city of Istanbul takes a significant role in this connection. Within more than 3000 years history, Istanbul has been the most crowded (15% of the total population) and industrialized city in Turkey (TCIB, 2007). Because of the increasing rate of industry and population, Istanbul has faced with many pollution problems.

Although the oceanographic characteristics (salinity, temperature, nutrients, currents etc.) of Istanbul Strait have been studied extensively (Özsoy et al.; Oğuz and Sur, 1989; Oğuz et al., 1990; Güler et al, 2006), the levels of individual priority pollutants which constitutes a major concern in aquatic ecosystems were not well documented. And to prevent the pollution problem, the source and the levels of the pollution are needed to be stated. In this thesis, sediment, mussel and water samples were collected from 24 stations along the Strait. Sediment and mussel (*Mytilus galloprovincialis,* Lamarck, 1819) samples were analyzed for Polycyclic Aromatic Hydrocarbons (PAHs). Source of PAHs (petrogenic or pyrolytic) were found by using some molecular ratios as tools. The effect of pollution in the ecosystem was evaluated by application of several biomonitoring techniques; Toxicity tests were applied to sediments and biomarker techniques were applied to the mussels. In the surface waters, temperature and salinity were measured and nutrients [(NO_3+NO_2) – N], [$(o\text{-}PO_4)$-P, Si] and chlorophyll-a were analyzed. This thesis will provide a data base for further research including a better management strategy and risk assessment studies in the target area.

1.2 Istanbul Strait

Istanbul strait (Bosphorus) and Çanakkale Strait (Dardanelles) form The Turkish Straits System (TSS) together with the Marmara Sea. The system provides a connection between The Mediterranean Sea and The Black Sea (Figure 1.1). The length of Istanbul Strait is approximately 31km and its width varies from 0.7 km to 3.5 km. The average width of Istanbul Strait is 1.3 km. Water depths vary around a mean of 33 m with a maximum depth of 110 m (Güler et al., 2006; Yazıcı and Otay, 2006).

Figure 1.1: Position of Istanbul Strait**.** (NASA, google earth, 2007)

1.2.1 Oceanographic Characteristics of Istanbul Strait

Researches in the Strait dating as early as 16th century (Marsigli, 1681) has shown that two separate layers were found in the Strait. The upper-layer current is flowing towards to the Sea of Marmara and the lower-layer current is towards the Black Sea (Figure 1.2).

Salinity and level differences between Marmara and Black Sea are the main reasons of the two layers current flow. There is a 20-40 cm level difference between Marmara and Black Sea. Due to the fresh water inputs by rivers and lower evaporation rate compared to Marmara Sea, the level of the Black Sea is higher than the level of the Marmara Sea. Weather conditions also affect the current system.

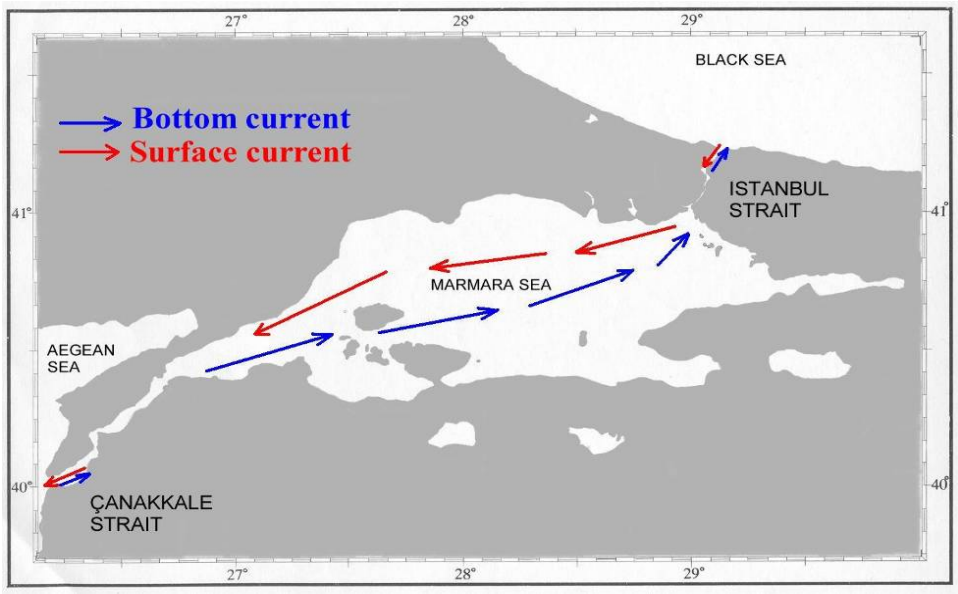


Figure 1.2: Two layer current flow between Aegean Sea and Black Sea (TÜDAV, 2007).

The salinity of the first 10 m is changing from 17 to 24 ppt and temperature is from 6°C to 20°C depending on the seasons. The depth between 10-30 m is the intersection layer (halocline and thermocline). The lower layer after 30 m depth has a 33-38 ppt salinity and 14°C (stable) (Oğuz et. al., 1990; Özsoy et al., 2001; Çoşkun, 1992)(Figure 1.3).

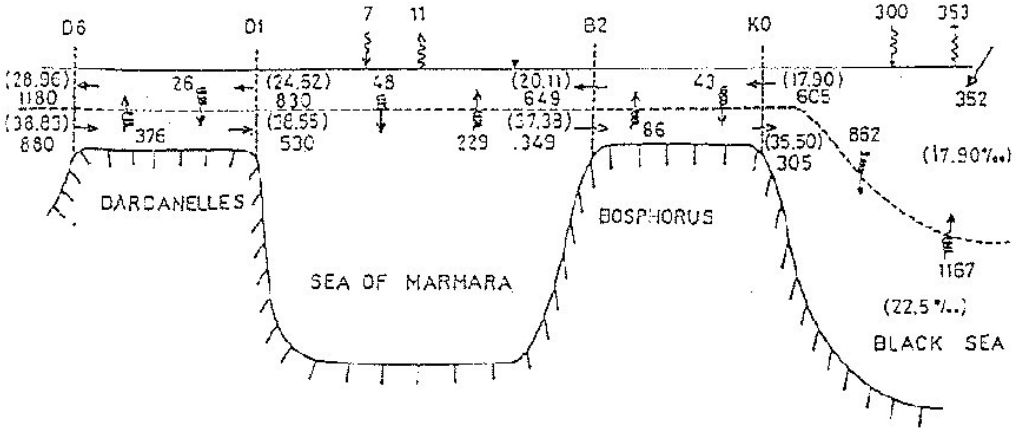


Figure 1.3: Salinity and volumetric water flow (km^3/y) in the system containing Turkish Strait and Black Sea. Long-time salinity measurement mean averages at the connections and water capacity in Black Sea are predicated on the calculation of flows (Ünlüata et al, 1990; Beşiktepe et al., 1994).

The average speed of the surface and lower layer currents are 4 and 1-2 knots per hour respectively. By the effects of weather condition such as wind speed and

direction, the surface current speed may exceed 7 knots per hour (Sariöz and Narlı, 2003). Additionally, there are a number of eddies and reverse currents caused by several sharp turns along the Strait. These sharp turns may be as much as 80 degrees. (Figure 1.4).

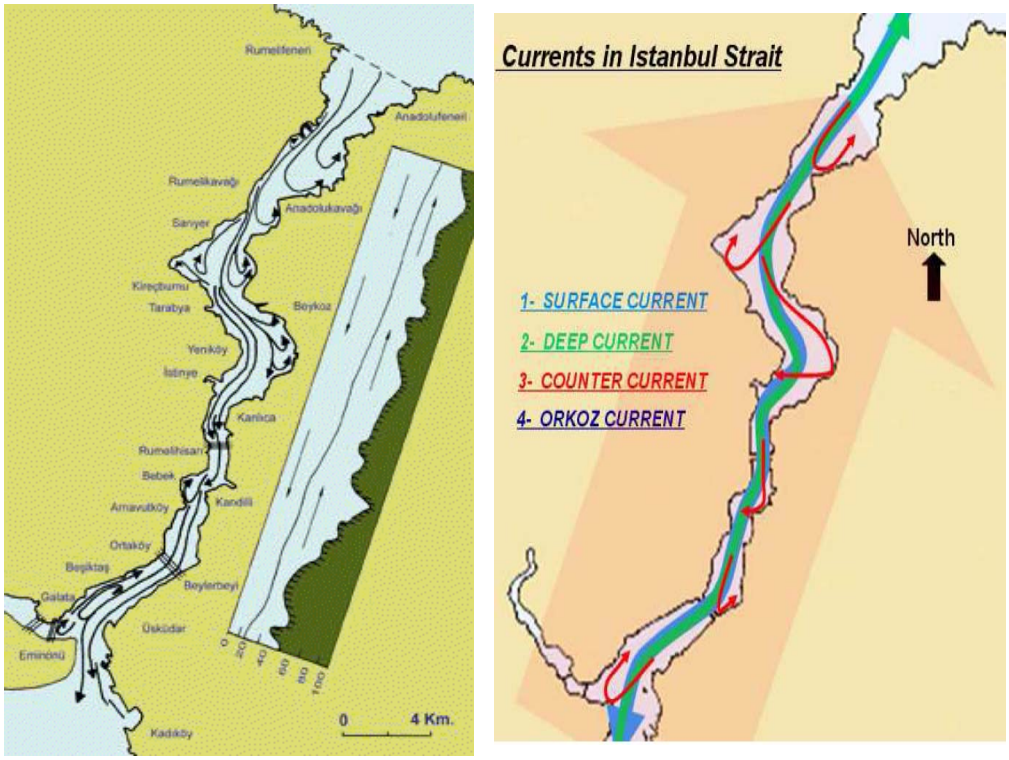


Figure 1.4: Istanbul strait water currents (TUDAV, 2007).

1.2.2 The Pollution Sources of Istanbul Strait

Pollutant can be described as a chemical which causes actual environmental harm or damage. Many different chemicals are regarded as pollutants, ranging from simple inorganic ions to complex organic molecules. Generally the level of the pollutants is an important factor. Also pollutants may be harmful for one organism while the other organism may not be affected from the same pollutant (Walker et al., 2001). Pollutants may enter ecosystems through: unintended release in the course of human activities (e.g. fires and ship accidents); disposal of wastes (e.g. sewage, industrial effluents); deliberate application of pesticides etc. Once they enter the environment they may transport by air, water and biologically (e.g. fish, birds and bioaccumulation process).

The pollution problem of Istanbul Strait basically results from the high population of the city Istanbul, Black Sea inflow and ship traffic. Istanbul is the most populated (15 % of the total population) and industrialized (50 % of the total industry) city in Turkey. The city is also a world heritage with 3000 years of history, as well as a city of industry and business. Istanbul now hosts more than 12 million inhabitants. Average population increase in Istanbul is about 500.000 inhabitants per year (TCİB, 2007). That constantly growing population of Istanbul causes increasing pollution, especially, by wastewater discharges to the Strait. Black Sea inflow is another pollution source for the Strait. Also Istanbul Strait is a gateway for Azeri, Kazakh and Russian oil transport. Those produce a huge amount of ship traffic.

1.2.2.1 The Wastewater Discharges on the Strait

The discharges of Istanbul city have been given into the lower layer of Marmara Sea and carried into the Black Sea in the last 5-7 years. The wastewaters have been discharged directly into the surface waters until the sewage outfalls installed by "The Istanbul Water and Sewage Authority" (ISKI). ISKI wastewater discharges along the Strait cost line shown on Figure 1.5. There are also several uncontrolled discharges along the Strait coast line.

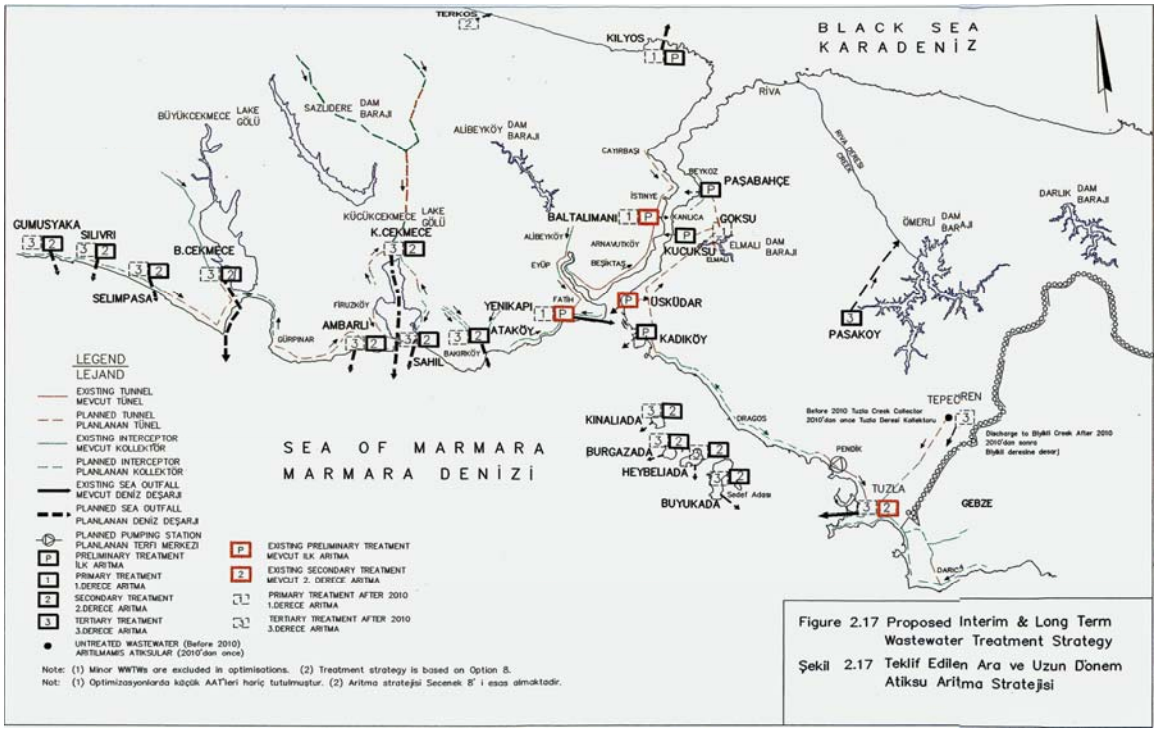


Figure 1.5: ISKI wastewater discharges along the Strait cost line (ISKI, 1999)**.**

1.2.2.2 Black Sea

Being the biggest anoxic sea of the world, the structure of the Black Sea is also important for this study. Below 200 m, the dissolved oxygen concentration drops to zero and in 2000 m, the hydrogen sulphide concentration reaches to 10.2 mg/L (Çoşkun, 1992). Because of this unique structure, it tends to be used like a waste container by the countries which have a connection to the Black Sea. Danube River carries most of the pollutants to the Black sea (Figure 1.6).

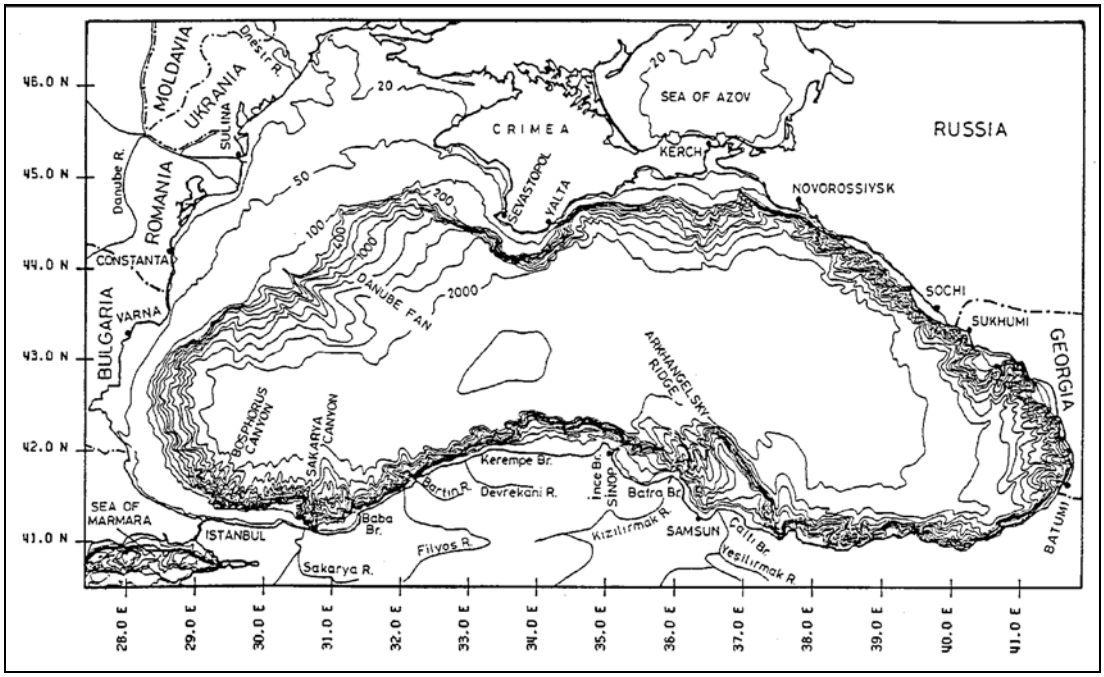


Figure 1.6: Bathymetry and location of the Black Sea (Yılmaz et al., 1998).

Previous studies clearly demonstrate the physical oceanography of the Black Sea upper layer to be dominated by the quasipermanent cyclonic gyres in the eastern and western halves of the basin. The two gyres are separated from a series of anticyclonic eddies in the coastal zone by the cyclonically undulating Rim current. The influence of the freshwater input, mainly from the Danube, Dnepr and Dnester rivers at the northwestern shelf, can be traced down to the Bosphorus region (Figure 1.7) (Yılmaz et al., 1998).

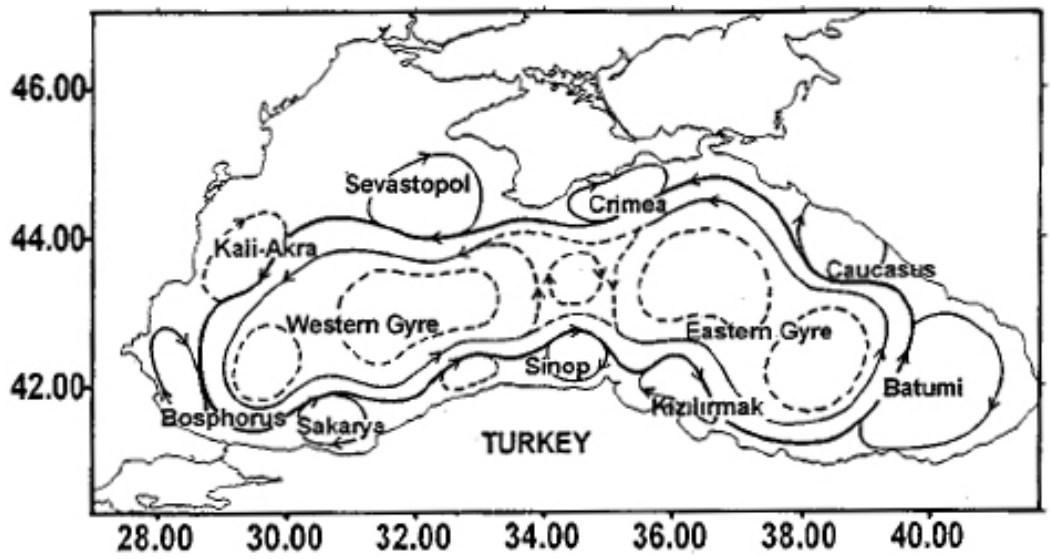


Figure 1.7: Schematic representation of the main features of the upper layer circulation of the Black Sea (Oğuz et al., 1993).

1.2.2.3 Ship Traffic

Istanbul Strait is one of the busiest waterways on the Earth. Each year 50000 ships pass trough the Strait. When the local traffic is taken into account, almost another 2000 cross a day. (Akten et al., 2002; Koldemir et al, 2005) These and countless fishing boats, cruise boats and leisure craft, contribute to make the Strait as one of the most crowded waterways in the world (Sariöz and Narlı, 2003).

The Montreux Convention allowed Turkey to regulate the passage of warships, through the Straits, but required the free passage of merchant traffic. Section I, Article 2 of the Montreux Convention states: "In times of peace merchant vessels shall enjoy complete freedom of transit and navigation in the Straits, by day or by night, under any flag and with any kind of cargo, without any formalities. . . .". (Brito, 2000). This makes it easier for ships to pass the Strait and each year, the amount of ship crossing the Strait has been increasing. Around 10 % of the navigating vessels contain dangerous liquid cargo, especially oil. Carrying oil by a tanker (using the Strait) costs less then 20 cents per barrel while the pipeline costs $1- $2 per barrel (Brito, 2000). And more than 80-100 MTPA (million tons per annum) of Azeri, Kazakh and Russian oil were transported through the Strait (Plant, 2000).

As the number of ships through the Straits grows, the risk of accidents increases (Figure 1.8 and Table 1.1), and the traffic will likely increase as the six countries surrounding the Black Sea develop economically. This increased congestion has led to a growing number of accidents (TCBBYEGM, 2007). Increased shipping traffic endangers the health of Strait ecosystem and 12 million residents of Istanbul that live on both sides of the Strait.

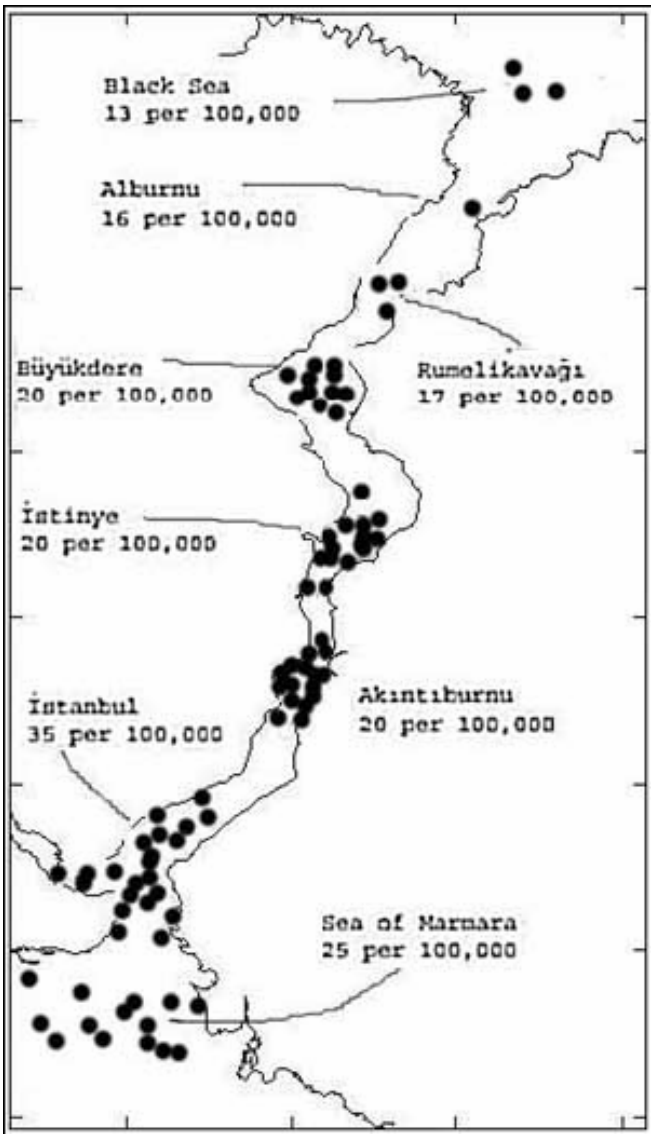


Figure 1.8: Historical ship accident data (Kornhauser and Clark, 1995).

Table 1.1: The ship accidents in the Istanbul Strait (TCBBYEGM, 2007)

Years	Total ship number	Total accidents
1995	46954	4
1996	49952	7
1997	50942	10
1998	49304	11
1999	47906	11
2000	48079	9
2001	42637	20

The major ship accidents and effects in the marine ecosystem are shown in Table 1.2. With the high volume of oil being shipped through the Bosphorus, oil tanker accidents can release large quantities of oil into the marine environment. In March 1994, when the Greek Cypriot tanker *Nassia* collided with another ship, 20 000 tons of oil spilled into the Straits. In this accident, sea lettuce and velvet horns were affected by oil dispersion and resulted in a mass mortality of these two species. In December 1999, the Volgoneft-248, a 25-year old Russian tanker, ran aground and split into two, in close proximity to the southwest shores of Istanbul. Fuel oil on board spilled into the Marmara Sea, covered the coast of Marmara with fuel-oil and affected about 5 square miles of the sea. The oil also entered a wetland lagoon and the freshwater reservoir of the city of Istanbul. The ecological damage from this accident was a 90 % mortality of marine life. Among the losses were the algae species comprising velvet horns, sea lettuce, starfish and spiny starfish, mussel, oyster, razor shell, limpets, green shrimp and pink prawn; and the fish species of rock gobby, common sole, grey mullet and gurnard (Öztürk et al., 2001).

Due to various environmental problems mainly related with oil spills, 52 marine species in the Straits are severely threatened (Öztürk et al., 2001). Accidents of shipping in the Straits are examined under four categories: collision, grounding, fire and stranding. Each of them has a direct effect on the marine ecosystem. Groundings are particularly dangerous for the benthic organisms such as mussel beds and vulnerable seagrass meadows in local coastal areas.

Table 1.2: The major ship accidents and effects in marine ecosystem.(Öztürk et al., 2001)

	INDEPENDENTA	**NASSIA**	**VOLGANEFT**
Year	1979	1994	1999
Area	Marmara Sea and Istanbul Strait	Black Sea and Istanbul Strait	Marmara Sea
Cause	Bad weather	Bad weather	Bad weather and poor condition of the ship
Amount (oil)	94 000 tons	20 000 tons	1279 tons
Distance	>60 mil	40 mil	3 mils
Benthic community	96% mortality	4 crustacean sp, 6 molluscs sp. 9 algae species were not recovered	90 % mortality
Birds mortality	17000	>1500	<3000 seagulls, ducks etc.
Marine mammals mortality		Bottlenose dolphins Harbour porpoises	
Other information	Spawning grounds for fish were polluted Sea bottom of 5.5 km in diameter was covered with thick tar of the concentration of 46g/m^2	Spawning grounds for fish were polluted Most bays and beaches were covered with oil and pitch 5 years later, some are still so.	The ship broke in two The recreational area was affected

1.2.2.4 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. Naphthalene is one of the best known PAH which consists of two benzene rings. They are relatively low solubility in water and highly lipophilic (tend to dissolve in fats, oils, lipids, and non-polar solvents such as hexane or toluene). The lower molecular weight PAHs have significant acute toxicity to aquatic organisms, whereas the high molecular weight PAHs, 4 to 7 ring, do not. However, several members of the high molecular weight PAHs have been known to be carcinogenic/mutagenic. They affect a variety of biological processes and can be potent cell mutagens and carcinogens (Pelkonen and Nebert, 1982). The best known and studied carcinogenic PAH is benzo[a]pyrene (BaP). Table 1.3 shows the carcinogenic potencies of various PAHs relative to BaP. Once the PAHs have settled in the sediment, filter feeders and benthic organisms may be affected with the

potential bioaccumulation of those compounds in their tissues. PAHs can be also harmful for human as a result of their carcinogenic and mutagenic properties (Okay and Karacık 2007; WHO, 1998; Jacob, 1996).

Table 1.3: Carcinogenic potencies of various PAHs relative to benzo[a]pyrene = 1, 00 [$CP_{rel.\ B[a]P}$] (Jacob,1996)

	$CP_{rel.\ B[a]P}$
Benzo[a]pyrene	1,00
Dibenzo[a,l]pyrene	>>2,00
Dibenz[a,h]anthracene	1,91
Anthanthrene	0,19
Cyclopenta[cd]pyrene	0,15
Benzo[b]fluoranthene	0,11
Indeno[1,2,3-cd]pyrene	0,08
Benzo[k]fluoranthene	0,03
Benzo[j]fluoranthene	0,03
Chrysene	0,03
Benzo[b]naphtho[2,1-d]thiophene	0,02
Benz[a]anthracene	0,01
Fluoranthene	0,00

Polycyclic aromatic hydrocarbons (PAHs) are usually introduced into the environment as a result of anthropogenic activities which have increased dramatically in the last 20-25 years. PAHs are produced generally as a result of pyrolytic processes, especially the incomplete combustion of organic materials during industrial and other human activities, such as processing of coal and crude oil, combustion of natural gas, including for heating, combustion of refuse, vehicle traffic, cooking and tobacco smoking, as well as in natural processes such as carbonization, forest fire. PAHs also have a petrogenic origin and naturally are found in crude oil. In marine ecosystems, petrol refinery and oil spills can be other PAHs source.

Commercially PAHs are used to make dyes, plastics and pesticides. Some are even used in medicines. And some of PAHs are manufactured for research purposes.

Physical and chemical characteristics of PAHs vary also with molecular weight. The properties of some PAHs analyzed in this study are given in Table 1.4.

There are several studies carried out about PAHs in different parts of the world. Total PAH (sum of 18 PAH) concentration of Mediterranean Sea sediments was found as 0.3 – 8400 ng/g dry wt (Baumard et al., 1998). From Danube coastline of Black Sea, the T-PAH (Σ17 PAHs) concentration was between 31 – 608 ng/g dry wt (Readman et al., 2002). The levels were found for Izmit Bay, as 120 – 11400 ng/g dry wt (Σ 14 PAHs) (Tolun et al., 2006), for Gemlik Bay as 51 – 13482 ng/g dry wt (Σ 14 PAHs) (Ünlü and Alpar, 2006). The Black Sea entrance of the Strait has a T-PAH (Σ 17 PAHs) concentration in sediments changing from 14 to 531 ng/g dry wt (Readman et al., 2002).

Table 1.4: Properties of PAHs (Gangolli S., 2005).

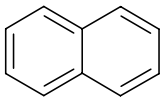
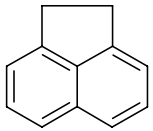
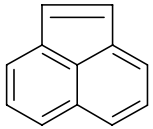
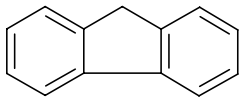
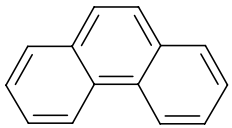
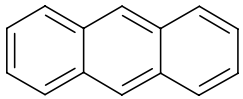
Compound	Molecular structure	MW	Solubility (μg/L) at 25 °C	Carcinogenicity	Log K_{ow}*	Occurrence and Uses
Naphtalene (NA)		128.2	12500 to 34000	Non-carcinogenic	3.37	Used in manufacture of dyes, synthetic resins, celluloid, lamp-black, smokeless powder, hydronaphthalenes. Moth repellent and insecticide. Topical antiseptic, anthelmintic. Most abundant single constituent of coal tar/dry coal tar contains about 1% naphthalene.
Acenaphthene (AC)		154.2	2920 to 6140	Non-carcinogenic	3.92	A product of coal combustion emissions, found in coal tar and diesel fuel. It is used as a dye intermediate, in manufacturing plastics, and as an insecticide and fungicide. Volatile component of cassava and nectarines
Acenaphthylene (ACL)		152.2	3420	Non-carcinogenic	4.00	In cigarette smoke and in soot generated by the combustion of aromatic hydrocarbon fuels containing pyridine
Fluorene (FL)		166.2	2000	Non-carcinogenic insufficient evidence	4.18	Present with other PAHs in cigarette smoke, flue gases and engine exhausts, and in tars from fossil fuels.
Phenanthrene (PHE)		178.2	1260	Non-carcinogenic	4.57	Uses: Dyestuffs, explosives, synthesis of drugs and biochemical research. Present in crude oil and gasoline. Has been detected in surface water, tap water and wastewater.
Anthracene (AN)		178.2	59	Non-carcinogenic	4.54	Intermediate for anthraquinone dyestuffs. Urban air, incomplete combustion. Obtained from coal tar.

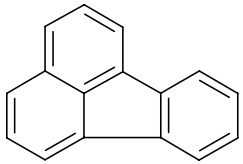
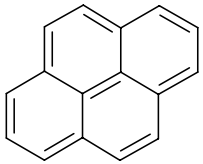
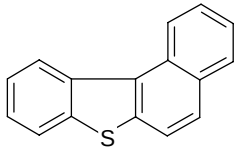
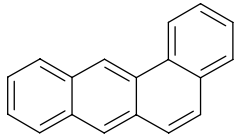
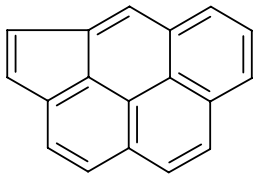
Table 1.4 (continue)						
Fluoranthene (FA)		202.3	260	Non-carcinogenic Inadequate indications	5.22	Present with other PAHs in cigarette smoke, flue gases and engine exhaust and in tars from fossil fuels. Residues have been isolated from soils, water and sediments
Pyrene (PY)		202.1	135	Non-carcinogenic	5.18	In fossil fuels. Occurs ubiquitously in products of incomplete combustion, including tobacco smoke and fossil fuel emissions
Benzo(b)naphtha (1,2-d)thiophene		234.3				Combustion product from fossil fuels, particularly from diesel engines. Found in metal working oils and machine oils
Benz(a)anthracene (BaA)		228.3	11.0	Carcinogenic	5.91	In gasoline, bitumen, crude oil, oil and waxes
Cyclopenta(cd)pyrene (CPP)		226.3		Not classificable Limited indications		

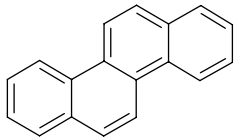
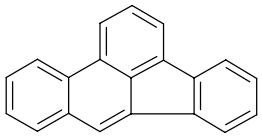
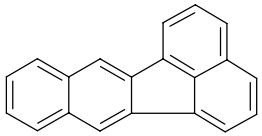
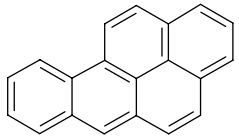
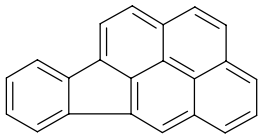
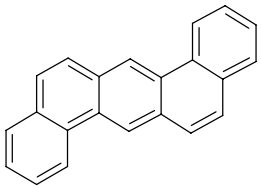
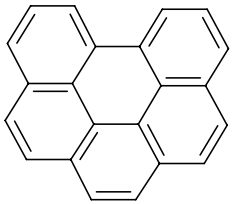
Table 1.4 (continue)						
Chrysene (Chr)		228.3	2	Weakly carcinogenic	5.86	Coal tar. Crude petroleum. From cigarette smoke at 1.5-13.3 ng m-3 in community air Also found during distillation or pyrolysis of fats or oils.
Benzo(b)fluoranthene (BbFA)		252.3	1.5	Carcinogenic	5.80	In crude oil
Benzo(k)fluoranthene (BkFA)		252.3	0.8	Carcinogenic	6.00	Present in man-made pollution sources including gasoline exhausts and sewage sludge. Occurs as a pollutant in tap water and groundwater
Benzo(a)pyrene (BaP)		252.3	4	Strongly carcinogenic	6.04	Occurs in cigarette smoke and from the combustion of fuels.
Indeno(1,2,3-cd)pyrene (IP)		276.3	62	Carcinogenic	6.58	In fresh motor oil 0.03 mg kg^{-1}, used motor oil after 10,000 km 46.7-83.2 mg kg^{-1} and petrol 0.04-0.18 mg kg^{-1}. In exhaust gases of petrol-engine cars 11-87 mg m^{-3}. In coke oven emissions 101.5 mg g $sample^{-1}$. Cigarette smoke 0.4 mg 100 $cigarettes^{-1}$.
Dibenz(a,h)anthracene (DBahA)		278.3	0.5 at 27°C	Carcinogenic	6.75	Contaminant in wood preservative sludge. Coal tar. Emissions from automobile exhaust gas and cigarettes. Pollutant in water. Formed as pyrolysis product of the tobacco constituent stigmasterol. Contaminant detected in a range of foodstuffs, including meat, vegetables, vegetable oils and cereals

Table 1.4 (continue)						
Benzo(g,h,i)perylene (BghiP)		276.4	0.29	Non-carcinogenic	6.50	Present in coal tar. Gasoline engine exhausts. Contaminant in tap water, groundwater and sediment. Occurs in domestic effluent.

* Log K_{ow} : The octanol-water partition coefficient is the ratio of the concentration of a chemical in octanol and in water.

1.2.2.5 Nutrients

In marine environment, nutrients are mainly chemical elements like nitrate (N), phosphate (P), silicate (Si), carbon dioxide and water consumed by micro algae and macro algae (primary producers). Despite the levels of water and carbon dioxide are abundance in marine ecosystems, the level of phosphate and nitrate may be limited.

Generally, P is limiting element for freshwater environments and N is limiting for marine waters. Limiting nutrients control the population size and distributions of marine plants.

Ratio between C (carbon), P and N in phytoplankton is called Redfield ratio (Redfield, 1934). The stoichiometric ratio is C: N: P = 106:16:1. If nitrogen is limiting, then input of N to the aquatic ecosystem results in plant population to increase. Carbon is found excess amounts in the marine environment, so it can not be a limiting nutrient, thus the ratio between N and P (16:1) plays an important role to determine the limiting nutrient.

Silicate is another important nutrient for phytoplankton. Diatoms use silicate to build up their cell walls.

Source of nutrients may occur via both natural process in marine environment (remineralization) and human related process like land clearing, production and applications of fertilizers, discharge of human waste, animal production, and combustion of fossil fuels etc. (Cloern, 2001).

Excess nutrient inputs stimulate primary production (algae growth) and cause eutrophication. Eutrophication is mainly a coastal phenomenon. Some results of eutrophication are:

- Increased biomass of phytoplankton
- Changes in ecosystem composition and biomass
- Decreases in water visibility
- Colour and smell of water change

- Dissolved oxygen -(DO) depletion
- Fish kills caused by DO depletion and by toxic algal blooms

Istanbul Strait is under the effect of Marmara and Black Seas. High nutrient inputs into the Black Sea and Marmara Sea cause eutrophication in both seas. Istanbul Water and Sewerage Administration (ISKI) discharge locations for wastewaters along the Strait cost line are shown in Figure 1.5. Also there are several other local discharges and rivers along the coast line. ISKI reports (1999) show that there are 106 streams; 32 of these streams are in Istanbul region and directly connected to the Strait.

From Black Sea to Marmara Sea, each day 20,000 m^3/sn water is carried by the upper layer currents and contains:

500 t nitrates (N),

30 t phosphates (P),

200 t silicates (Si) (ISKI, 1999)

Table 1.5 indicates the average nutrient concentrations and N/P values in the Strait.

Table 1.5: Average nutrient results [phosphate (PO_4 - P), total oxidized nitrogen [TNO_x=(NO_3 +NO_2)N)] and nitrogen/phosphate ratios (based on units of weight) from Yılmaz et al (1998).

Bosphorus								
Mar–Apr	1995	Sept–Oct	1995	April	1996	June–July	1996	
PO_4P	**TNO_x**	**PO_4P**	**TNO_x**	**PO_4P**	**TNO_x**	**PO_4P**	**TNO_x**	
1.24	5.88	2.48	14.98	7.44	7.84	3.72	7.7	µg/L
N/P		**N/P**		**N/P**		**N/P**		
4.74		6.04		1.05		2.06		

Chlorophyll a (Ch-a) is a good indicator for algal biomass. It is the most common algal pigment and 1% to 2 % (dry weight) of phytoplankton contain Ch-a. It can be traced by remote sensing (satellite images) or direct water analysis by spectrophotometric methods.

Figure 1.9 (Sancak et al., 2005) shows Ch-a distribution along the Mediterranean and Black Sea. It can be easily seen that Marmara and Black Seas are more eutrophic than Mediterranean Sea.

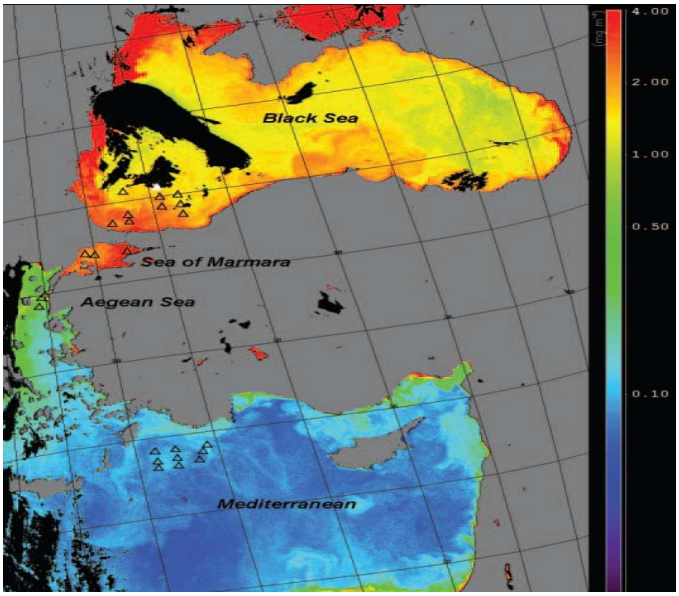


Figure 1.9: SeaWiFS measured chlorophyll-a distribution showing different trophic states. (Sancak et. al, 2005).

Some parameters related with eutrophication in three water systems surrounding Turkey are given in Table 1.6. (Yılmaz, 2005).

Table 1.6: Comparison of the regional Seas of Turkey (Yılmaz, 2005).

Parameter	Black Sea	Marmara Sea	North-Eastern Mediterranean
Sechhi Disk depth (m)	9.3 ± 1.6	6.5 ± 0.7	20.9 ± 3.5
Euphotic zone (m) (%1 light depth)	29.6 ± 4.9	16.3 ± 3.9	76.8 ± 10.5
Max Ch-a (µg/L)	0.74 ± 0.37	2.2 ± 1.1	0.14 ± 0.11
Surface Ch-a (µg/L)	0.30 ± 0.22	1.39 ± 1.32	0.03 ± 0.02
Integrated Ch-a (µg/L) (in euphotic zone)	14.2 ± 5.8	26.8 ± 19.7	3.2 ± 1.4
Primary production mg C/m^2day	487 ± 184	1521 ± 465	194 ± 143

1.2.3 Bio-monitoring

Some pollutants such as Persistent Organic Pollutants (POPs) and PAHs are chemical substances that may persist in the environment, bioaccumulate through the food web, and pose a risk of causing adverse effects to human health and the environment.

Monitoring is a repetitive observation for defined purposes of one or more chemical or biological elements according to a prearranged schedule over time and space, using comparable and standardized methods (according to the definition of the United Nations Environmental Program (UNEP)). Biomonitoring methods are performed in order the see the quality of ecosystems. Biomonitoring is the use of living organisms to evaluate the changes in environmental quality (Oost et al., 2003). Biomonitoring can be classified as:

- Bioaccumulation monitoring (BAM): measurement of contaminant levels in biota (bioaccumulation);
- Biological effect monitoring (BEM) : determining the effects in the organisms (bioassays and biomarkers);

Bioaccumulation of chemicals in biota may be used to monitor quality of ecosystems and gives significant information about toxicity level. Concentrations of chemicals in molluscs are related to the levels of chemicals in the water that they inhabit and in the food that they filter from the water. When chemical concentrations increase or decrease in the water and in food sources, the concentrations increase or decrease in molluscs. It is possible to monitor chemical concentrations in water and in suspended particles, but for many technical reasons, it is simpler to measure concentrations in molluscs. In this study, concentrations of PAHs in mussel tissue were measured to determine the bioaccumulation intensity.

Bioaccumulation of organic substances depends on K_{ow} values. The octanol-water partition coefficient (K_{ow}) is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. Octanol is an organic solvent that is used as a surrogate for natural organic matter. This parameter is used in many environmental studies to help determine the fate of chemicals in the

environment. An example would be using the coefficient to predict the extent a contaminant will bioaccumulate in fish. The octanol-water partition coefficient has been correlated to water solubility; therefore, the water solubility of a substance can be used to estimate its octanol-water partition coefficient (USGS, 2007).

Bioassays: Survival, growth and reproduction of individuals are chosen as endpoints of the classic laboratory ecotoxicity tests. In the framework of this thesis, sediment toxicity bioassay is applied. Sediments serve as both sink and source of organic and inorganic materials. Most anthropogenic organics tend to be associated to the suspended particles and organic materials, and concentrate in the sediments. Sediment contamination may be detrimental for benthic communities and loss of a biological community from an ecosystem may affect indirectly or directly other components of the system. Sediments frequently contain higher concentrations of pollutants than are found in the water column. Sediment bioassays that measure the toxic effects of contaminated sediments on the test organisms have been recently developed and a large variety of bioassays is becoming available. They provide information on the toxicity of contaminated sediments that can be neither derived from chemical analysis nor from ecological surveys. Testing procedures have included numerous techniques such as static tests, flow-through tests and elutriate tests (Tolun et al., 2001). Static sediment toxicity test was used in this study. Water soluble extraction of sediment was used and algal growth was determined to find out the sediment toxicity.

Biomarkers are the responses of the organisms to the environmental stress. Numerous and varied biological responses have been suggested as potential techniques for determining the biological effect of chemicals. Especially molluscs are widely used because of their capability of bio accumulate the chemicals. In the mid 1970s it was recognized that the geographical extend and degree of marine contamination and the associated biological impact was largely unknown and undocumented. In the USA a mussel watch monitoring programme was established to assess the spatial and temporal trends in chemical contamination in coastal areas. Then similar local and regional “Mussel Watch” programmes were established in many countries in the world. The primary reasons for that were to protect human health and to protect valuable living natural sources.

In the framework of this thesis, two biomarker techniques are applied to the mussels (*Mytilus galloprovincialis,* Lamarck, 1819); Filtration rate and lysosomal stability. Filtration rate is a part of "Scope for Growth" (SfG) used for biomonitoring purposes; Scope for Growth involves determination of filtration rate, respiration rate and food absorption efficiency. The advantages of SfG are when measured under standardized conditions (with food availability, temperature, salinity and dissolved oxygen held constant), the SFG reflects the underlying toxic effects of pollutants accumulated in the body tissues (Windows, 2001). The most sensitive of those parameters, the simplest to measure and the most quantatively important was indicated as filtration rate (Widdows, 1985). The lysosomal membrane stability has been indicated to be a sensitive biomarker (Moore et al., 1990; Moore and Willows, 1998). The retention time of this dye is used as a determinant of effect. Previous studies have demonstrated the use of this technique to identify pollution problems related to various kinds of pollutants as well as polycyclic aromatic hydrocarbons (Okay et al., 2000).

2 MATERIAL METHODS

2.1 Sampling and Storage

Sea water, sediment and mussel (*Mytilus galloprovincialis,* Lamarck, 1819) samples were collected from the coastal parts of the Istanbul strait. Samples were shared into glass vials and plastic containers in the laboratory depending on the type of analysis. Seawaters were taken by using 5 L plastic containers for nutrient and Ch-a analysis. Seawater samples were filtered through GFC filter paper (GF6, 47 mm diameter, Schleicher and Schuell, Dassel, Germany) by applying vacuum and filter papers were stored at -20^{o}C for Ch-a analysis. The seawater samples for nitrate and phosphate analysis were stored at -20^{o}C and for silicate analysis at + 4^{o}C until analysis (max. 1 week).

Seawater samples were collected seasonally (4 times). Sampling schedule is given in Table 2.1.

Table 2.1: Sampling schedule.

Sampling Schedule	
1st Sampling	April 2006
2nd Sampling	June 2006
3rd Sampling	September 2006
4th Sampling (Mussel, Sediment and Seawater)	January-February 2007

Mussel and sediment sampling were performed during the period of January-February 2007. PAHs analyses were applied to sediment and mussel samples. Mussel

and sediment samples were also used for the application of biomarker techniques and toxicity tests respectively. Sampling was performed in two day intervals.

Surface sediments (0-10cm) were collected in one liter of glass bottles by SCUBA and/or free diving methods. Sampling depth range was 1m - 5 m. Samples were immediately transferred to the laboratory in foam boxes filled with ice. A total amount of 1000-1500 g. of sediment was collected from each station. Sediment samples were sub divided into the glass vials in the laboratory for humidity determination, toxicity testing and PAHs analysis. Vials were stored at -20^{o}C until analysis.

Mussels (4-5cm) were also collected from sediment sampling locations. Mussels for biomarker applications were wrapped into wet tissues to transfer to the laboratory. Then, they were placed into aquariums containing filtered seawater and microalgae at 7 - 8^{o}C depending on *situ* temperature in a temperature controlled room for 24 h. (for acclimization) (Okay et al, 2005).

Mussels for PAH analysis were dissected in the laboratory, transferred into vials and frozen at -20^{o}C until the analysis.

2.1.1 Cleaning

All laboratory and sampling equipments were carefully cleaned depending on the type of the analysis. For PAH analysis, sampling vials, glass and dissecting material were cleaned by mild detergent with tap water, dilute HCl, hot tap water, distilled water and then rinsed with HPLC grade hexane. The glassware used for nutrient analysis and toxicity testing were cleaned by hot tap water, hot dilute HCl and distilled water. The materials used for biomarker studies were cleaned by detergent, hot tap water and distilled water.

2.2 Description of Sampling Stations

The samples were collected from 24 coastal stations of Istanbul Strait situated at the both sides of the Strait from Black Sea to the Marmara Sea (Figure 2.1 and Table 2.3). Two of those stations are situated at relatively clean sites of Marmara Sea

(Büyükada Island) to be as reference sites. Eleven samples were taken from each part of the Strait.

Sampling stations of 1 and 12 are situated at the entrance of the Black Sea part and those areas are relatively less populated and have some agricultural activities. There are 4 main freshwater inputs into the Strait. Those are Büyükdere, İstinye and Baltalimanı, Küçüksu - Göksu rivers close to the stations of 4, 6 7 and 18 respectively. There are two hospitals close to the Stations 6 and 7. Station 9 is a touristic site occupied with restaurants, cafes etc. Depending on the season, the coastal waters at that station are exposed to the runoff water carrying some domestic wastes from the watershed area. (19 and 18 have similar muddy surface characteristics). Station 23 is a sandy beach on Büyükada Island. Station 4, 5, 17 and 20 have been affected by strong water current and located on sharp turn points of the Strait.

Table 2.2: Mussel and sediment sampling stations.

Sampling Sites No	Sampling Sites Name	Mussel	Sediment
1	**Rumeli feneri ilerisi**	-	+
2	**Garipçe köyü**	+	+
3	**Rumeli Kavağı**	+	+
4	**Büyükdere**	+	+
5	**Tarabya**	+	+
6	**İstinye**	+	+
7	**Balta Limanı**	+	+
8	**Bebek**	+	+
9	**Ortaköy**	+	+
10	**Beşiktaş**	+	+
11	**Ahırkapı ilerisi**	-	-
12	**Anadolu Feneri**	-	+
13	**Poyraz**	+	+
14	**Anadolu Kavağı**	+	-
15	**Yalıköy- Beykoz**	+	-
16	**Çubuklu**	+	-
17	**Kavacık**	+	-
18	**Kandilli**	+	+
19	**Kuzguncuk**	+	+
20	**Üsküdar**	+	+
21	**Moda iskelesi**	+	+
22	**Büyük ada iskele**	+	-
23	**Büyük ada plaj**	+	+
24	**Midyeciler**	+	-
	Total=	**21**	**17**

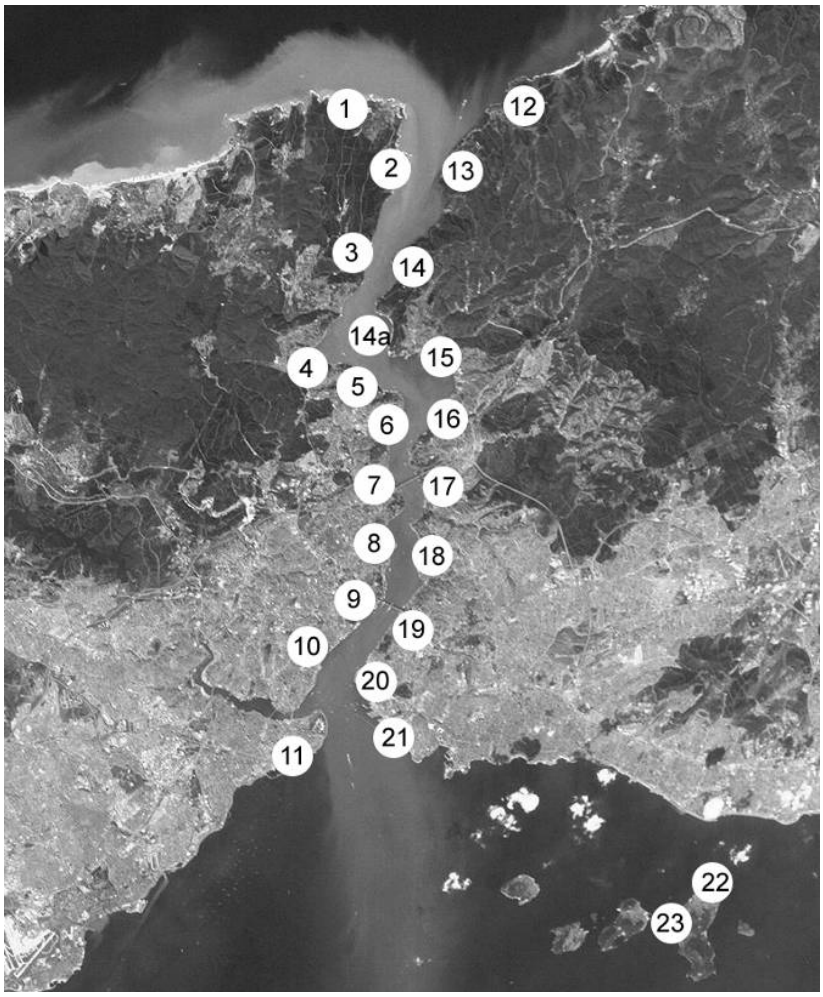


Figure 2.1: Sampling locations (NASA Earth Observatory-April 16, 2004).

Because of the weather conditions and coastal structure only water samples could be taken from station 11.

In total, mussel samples were collected from 21 and sediment samples were collected from 17 stations (Table 2.2).

Sampling station 14a was added as a sampling point during the study. Commercial mussel catchers (collector) collect mussels from that site. Mussels which were collected from this site are consumed extensively in Istanbul markets and restaurants thus, the concentration of PAHs in these mussels is important to determine the potential human health effects.

Table 2.3: Sampling locations and coordinates.

Sampling Sites	Local Name	Coordinate
1	**Rumeli feneri ilerisi**	41º 14.455 N - 029º 05.855 E
2	**Garipçe köyü**	41º 12.818 N - 029º 06.594 E
3	**Rumeli Kavağı**	41º 11.022 N - 029º 04.574 E
4	**Büyükdere**	41º 09.207 N - 029º 02.324 E
5	**Tarabya**	41º 08.232 N - 029º 03.444 E
6	**İstinye**	41º 06.633 N - 029º 03.515 E
7	**Balta Limanı**	41º 05.963 N - 029º 03.256 E
8	**Bebek**	41º 04.803 N - 029º 03.084 E
9	**Ortaköy**	41º 02.829 N - 029º 01.639 E
10	**Beşiktaş**	41º 02.429 N - 029º 00.343 E
11	**Ahırkapı**	41º 00.256 N - 028º 58.981 E
12	**Anadolu Feneri**	41º 12.907 N - 029º 09.109 E
13	**Poyraz**	41º 12.334 N - 029º 07.596 E
14	**Anadolu Kavağı**	41º 10.191 N - 029º 05.190 E
15	**Yalıköy- Beykoz**	41º 08.149 N - 029º 05.288 E
16	**Çubuklu**	41º 06.808 N - 029º 05.189 E
17	**Kavacık**	41º 05.221 N - 029º 03.974 E
18	**Kandilli**	41º 04.451 N - 029º 03.541 E
19	**Kuzguncuk**	41º 02.380 N - 029º 02.144 E
20	**Üsküdar**	41º 01.285 N - 029º 00.411 E
21	**Moda iskelesi**	40º 58.786 N - 029º 01.488 E
22	**Büyük ada iskele**	40º 52.481 N - 029º 08.144 E
23	**Büyük ada plaj**	40º 51.550 N - 029º 06.769 E
14a(24)	**Midyeciler**	

2.3 Measurements and Chemical Analysis

2.3.1 Nutrient Analysis

Nitrite and nitrate nitrogen [(NO_3+NO_2) – N)], orthophosphate phosphate [(o-PO_4)-P] and silicate (Si) were analyzed according to Standard Methods (APHA, 1989). Calculations were achieved according to the calibration curves prepared by the standard solutions (4-5 standards). Standard addition method is used during the analysis of nutrients.

2.3.1.1 Nitrite and nitrate nitrogen [(NO_3+NO_2) – N]

The samples were analysed by spectrophotometer (Chebios Optimum-One UV–Vis spectrophotometer) according to the cadmium reduction method was used. The cadmium reduction method is a colorimetric method that involves contact of the nitrate in the sample with cadmium particles, which cause nitrates to be converted into nitrites. The nitrites then react with sulfonylamide and N-1 naphthylethylenediamine in acidic conditions to form a pink colour whose intensity is proportional to the original amount of nitrate. The pink colour was then measured by spectrophotometer and the absorbance value is converted to the equivalent concentration of nitrate by using a standard curve.

2.3.1.2 Orthophosphate phosphate [(o-PO_4)-P]

Orthophosphate amount in the sea water samples were analyzed according to the ascorbic acid method by using a spectrophotometer (Chebios Optimum-One UV–vis spectrophotometer). A liquid containing ascorbic acid and ammonium molybdate react with orthophosphate in the sample to form a blue compound. The intensity of the blue colour is directly proportional to the amount of orthophosphate in the water.

2.3.1.3 Silicate (Si)

Dissolved silicate in the samples was analyzed according to the molybdosilicate method by using a spectrophotometer (Chebios Optimum-One UV–Vis spectrophotometer). The principal of the analysis method of soluble reactive silica is based upon the formation of yellow silicomolybdic acid from the reaction of ammonium molybdate and silica at low pH.

2.3.2 Chlorophyll a Method

Chlorophyll a (Ch-a) was determined spectrophotometrically (Wisconsin State Lab of Hygiene, 1991).

Samples were concentrated by filtering (GF6, 47 mm diameter, Schleicher and Schuell, Dassel, Germany) and the filters papers were deep-frozen (-20^{o}C) until analysis. The filter papers are placed in vials and 10 mL of aqueous acetone solution (mix 90 parts reagent grade acetone with 10 parts distilled water) was added. The solution was mixed vigorously and placed in the fridge at 4^{o}C in a dark box and allowed to be extracted for overnight. Then, the extract was centrifuged at 6000 rpm for 20 min and the absorbance was measured at wavelengths of 750, 663, 645 and 630 nm.

Calculations were done according to the following equation:

$$\text{Chlorophyll a } (\mu\text{g/L}) = \frac{\left[11.64\,(\text{Abs663}) - 2.16\,(\text{Abs645}) + 0.10\,(\text{Abs630})\right]E(F)}{V(L)} \quad \textbf{(2.1)}$$

Where:

F = Dilution Factor

E = The volume of acetone used for the extraction (mL)

V = The volume of water filtered (L)

L = The cell path length (cm)

2.3.3 Temperature, Salinity

The salinity of seawater samples were measured by pH/Cond. Meter (WTW inoLab pH/Cond Level 1). *In situ* temperature was measured during sampling by a thermometer and/or a diving watch.

2.3.4 Water Content of Sediment

Ten grams of sample was weighed and transferred into the tare aluminium weigh pans. Samples were dried at 105°C for 24 hours. Sediment samples were removed and cool in desiccators until a constant weight was achieved. The differences give the water content of sediment (ASTM, 1996).

For calculations:

$$\% \text{ Water Content} = [(M1-M2) / m] \times 100 \quad \textbf{(2.2)}$$

Where:

M1= Wet sample weight

M2= Dry sample weight

m = Wet sample weight

2.3.5 PAHs Analysis of Sediment Samples

For total, 25 PAHs were analyzed in this study (Table 2.4). Sixteen of them are in the list of US EPA (United States Environmental Protection Agency) priority pollutants and other 9 PAHs are carcinogenic and environmentally important pollutants (Jacop, 1996). In year 2001 US EPA add also those 9 PAHs to the existing polycyclic aromatic compounds (PAC) category in the list of toxic chemicals subject to the reporting requirements. (EPA, 2001)

Table 2.4: Analyzed PAHs

US EPA 16 PAHs	
Naphthalene	Cyclopenta(c,d)pyrene
Acenaphthylene	5-Methylchrysene
Acenaphthene	Dibenzo(a,l)pyrene
Fluorene	Dibenzo(a,e)pyrene
Phenanthrene	Dibenzo(a,i)pyrene
Anthracene	Dibenzo(a,h)pyrene
Fluoranthene	Benzo(c)fluorene
Pyrene	Benzo(b)naphtho(2,1-d)thiophene
Benzo(a)anthracene	Anthanthrene
Chrysene	
(Benzo(b)fluoranthene, Benzo(j)fluoranthene)	
Benzo(k)fluoranthene	
Benzo(a)pyrene	
Indeno(1,2,3-c,d)pyrene	
Benzo(g,h,i)perylene	
Dibenzo(a,h)anthracene	

2.3.5.1 Sample preparations

Samples were stored at -20^{o}C in freezer until homogenization.

2.3.5.2 Homogenization

Sediment samples (20 g) were homogenized and mixed with hydromatrix. The mixtures were transferred into 33 mL of extraction cells. First, the filter was placed into extraction cell and 2 g of sea sand (heated at 650^{o}C), filter, sample mixtures, filter and the standards were placed and cells were closed (Figure 2.2).

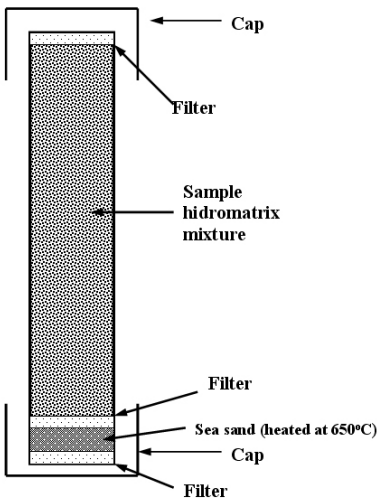


Figure 2.2: Extraction cell.

2.3.5.3 Extractions

Extraction cells were placed into accelerated solvent extractor (Dionex ASE 200 Accelerated Solvent Extraction System). Samples were extracted with 75:25 Acetone: Hexane mixture under 120 bar pressure at 120^{o}C.

Extracted samples were collected in 60 mL of vials. Funnels were filled with water free-sodium sulphates to remove water in the samples. The sample vials were rinsed 3 times with a small quantity of toluene and were transferred into the flasks.

The sample volumes were reduced to approximately 2 mL on a rotary evaporator (Buchi R205 rotary evaporator system with vertical water condenser B-490 water bath) at 60^{o}C, 140rpm and a pressure from 700mbar to 500mbar)

2.3.5.4 Clean-up

Clean-up procedure was achieved in two steps;

1st Step Clean-up with silica gel and alumina B

Preparation of the column: 10 g of silica gel were weighed and transferred into the chromatography column by a glass funnel. In the same way 5 g of alumina B with 3% distilled water was weighed and transferred into the column. At the end, 2g of water-free sodium sulphate was added.

In order to avoid contaminations, the column was rinsed with 60 mL of n-hexane: dichloromethane mixture (1:1). The rinsed solvent was discarded.

The extracted samples were transferred into the column with a Pasteur pipette. Sample flask was rinsed 3 times with small quantity of n-hexane: dichloromethane mixture (1:1). Then the dropping funnel was filled with 100 mL of n-hexane: dichloromethane mixture (1:1). The solvent was slowly dropped into the column. The sample (dropping rate 2 drops/second) was collected in a round flask.

The volumes of the collected samples were reduced to approx. 1mL at a rotary evaporator (Buchi 011 Style Rotovap) at 50^{o}C, 85 rpm and a pressure from 400 mbar to 260 mbar (Norm DIN EN ISO/IEC 17025).

2nd Step Clean-up with C18 column

After the first clean-up step, the samples were carefully reduced to dryness (approx. ½ drop) by light stream of nitrogen and 0.2 mL of acetonitrile was added.

Preparation of the C18 column: PTFE (Polytetrafluoroethylene) frit was inserted into a 8mL of glass cartridge. Cartridge was filled with 1g of C18 material (C18 is an octadecyl modified silica gel). Then another PTFE frit was inserted.

C18 column was connected to vacuum (900 mbar) and was rinsed with 5 mL of acetonitrile to prevent background contaminations. The rinsed solvents were discarded.

The samples (0.2 mL) were added to the column by a Pasteur pipette. The sample flask was rinsed with 0.4 mL of acetonitrile and rinsed solvent was added to the column. Another 0.4 mL of acetonitrile was used to rinse the sample flask and 3 mL of acetonitrile was added to the column. For collecting the samples, 8 mL of glass vials were used.

The volume of sample in the vials from C18 column was reduced under light stream of nitrogen at the sample concentrator (Trockentemperier- System TCS, Labor Technik Barkey). At the end of evaporation, the solvent was changed (toluene). Then the sample was immediately transferred into the micro volume sampling vials.

The volume of the samples was reduced by nitrogen in the sample concentrator until 20 µl sample left. Micro volume sampling vials were stored -28^{o}C until HPGC/HPMS analysis.

2.3.5.5 HRGC/HRMS Analysis

High resolution gas chromatography/high resolution massspectrometry (HRGC/HRMS) was used for PAHs' analysis. Operating conditions for HRGC/HRMS were given Table 2.5.

Table 2.5: Operating conditions for HRGC/HRMS.

GC:	Type: Agilent 6890
	Column: Rtx-Dioxin2, 60 m, 0.25 mm ID, 0.25 µm film thickness (Restek)
	Temperature programme: 60°C, 1.5 min, 10°C/min, 160°C, 20°C/min, 260°C, 5°C/min, 315°C, 35 min for PAH;
	60°C, 1.5 min, 25°C/min, 140°C, 8°C/min, 300°C, 20 min for OCP
	Carrier gas: helium, constant flow: 1.5 ml/min
	Injector: Cold on column system KAS 4 (Gerstel)
	Temperature program injector: 90°C, 12°C/s, 280°C, 5 min
	Temperature transferline: 300°C
	Autosampler: CTC A200S
	Injection volume: 0.1 µl pulsed splitless for PAH, 1 µl pulsed splitless for OCP
MS:	Type: MAT 95S (Thermo)
	Ionisation mode: EI, 50 eV, 260°C
	Resolution: > 9000
	Detection: SIM mode

2.3.5.6 PAH Internal Standard Mix

The PAH Internal Standard Mix 26 (4000mg/l) were used. All substances in the Internal Standard Mix (10mg/l in Acetone) are directly spiked into the sample. The internal standard contains the following substances:

*AcenaphtheneD10,

*ChryseneD12,

*NaphthaleneD8, and

*PhenanthreneD10

*9, 10 AnthraquinoneD8 (99.3%-d8),

*DibenzofuranD8 (99.6%-d8),

*n-TetracosaneD50

**$^{13}C_6$ Phenol

*Dr. Ehrenstorfer, Augsburg, Germany.

**Campro Scientific, Veenendaal, The Netherlands.

Calibration and recovery standards

All substances which are used to prepare the calibration standards are provided by Dr. Ehrenstorfer. This includes PAH-Mix 9 (100mg/l +/-1%) containing:

- Acenaphthene, Acenaphthylene,
- Anthracene, Benzo(a)anthracene,
- Benzo(b)fluoranthene, Benzo(k)fluoranthene,
- Benzo(ghi)perylene, Benzo(a)pyrene,
- Chrysene, Dibenzo(ah)antracene,
- Fluoranthene, Indeno(1,2,3-cd)pyrene,
- Naphthalene, Phenanthrene,
- Pyrene; 9, 10 Anthraquinone (100mg/l +/-1%);
- Dibenzofuran (10.01mg/l)
- Pentachlortoluene (PCT) which is used as recovery standard.

Additional chemicals are Toluene (Promochem, Wesel, Germany), Acetic anhydride (Fluka, Buchs, Switzerland) and Potassium hydroxide (KOH) provided by Merck, Darmstadt, Germany.

2.3.6 Analysis of PAHs in Mussel Samples

PAHs analysis for mussel samples was accomplished similar to the sediment analysis of PAHs except homogenization step.

2.3.6.1 Homogenization of mussel samples

Frozen mussel tissue samples were transferred into a mortar. Liquid nitrogen was used to keep sample frozen. The samples were brayed in the mortar until they become a powder. Homogenized samples were transferred into the glass vials and were stored at -20^{o}C until the analysis.

2.4 Bioassay and Biomarker Studies

2.4.1 Filtration rate of mussels

The principal of filtration rate (FR) biomarker technique depends on the filtration of microalgae by individual mussels in static systems (Widdows, 1985). The mussels from the stations are placed the aquariums each containing filtered seawater (GFC) at certain temperature (adjusted depending on *in situ* temperature from which the mussels were sampled) for 24 h. After that, ten mussels were placed separately in beakers filled with 2 L of filtered seawater (GFC) stirred by using magnetic stirrers and 24 000 cells of *Phaeodactylum tricornutum* (Bohlin) per mL were added to each beaker. The sub-samples from the beakers are counted at every 15 minutes for a period of one hour by using a Beckman Z2 Coulter Counter. Filtration rate of each mussel are calculated individually and the results were evaluated by taking the averages to calculate the filtration rate value for each station. For calculation:

$$\text{Filtration Rate (F.R.) (1/hour)} = \frac{2\ \text{L}\ (\ln C_0 - \ln C_t) - A}{\text{Time (Hour)}} \qquad \textbf{(2.3)}$$

Where:

C_0 and C_t: Counted algae between two time intervals (t)

A: Correction Factor (From control)

2.4.2 Neutral Red Retention Assay- Lysosomal stability

The method of lysosomal membrane integrity (neutral red retention Assay) is the same as described by Lowe et al. (1995). A neutral red stock solution was prepared by dissolving 20 mg of dye in 1 mL of DMSO, and then 10 µL of the stock solution was diluted with 5 mL of mussel physiological saline to yield a working solution. A 50 µL aliquot of the cell suspension was dispensed onto a microscope slide and placed in a light-proof humidity chamber for 15 min at room temperature to allow the cells to attach. Excess solution was tipped off, 40 µL of neutral red working solution was added, and a coverslip was applied. After 15 min incubation, the microscope slides were removed and inspected under a microscope. After a further 15-min incubation, the preparations were examined again and examined systematically thereafter at 30 min intervals to determine the time course of uptake into and dye loss. The test for each replicate was terminated when dye loss was evident in 50 % of the small granular hemocytes and the time recorded. Examinations under microscope ceased after 180 min. The mean retention time was then calculated for 10 individual mussels.

2.4.3 Sediment Toxicity Test

A. Preparation of sediment elutriates for toxicity testing

Sediment elutriates were prepared as follows: 4 parts of filtered (granulated charcoal, GFC and 0.45 µm Milipore) seawater (20-22 ppt) was added to 1 part of fresh weight sediment. The sediment-water suspension was agitated vigorously on a magnetic stirrer for 45 minutes. The suspension was allowed to stand for about 10 minutes and the supernatant was filtered through 0.45 µm membrane filter. The filtered samples were used for toxicity testing (Tolun et al., 2001).

B. Algal toxicity test

The batch algal bioassays have been performed at constant temperature (20 ± 2° C) and light (3500-4000 lux) conditions by using indicator algal species of *Phaeodactylum tricornutum* (Bohlin). The principle of the test is based on the method of US EPA bottle test (Miller et al., 1978). The sediment elutriates are incubated together with algal species in 100 mL Erlenmeyer flasks by adding

modified f/2 medium (Guillard and Ryther, 1962). Filtered (granulated charcoal, GFC and 0.45 μm Milipore) clean seawater (20-22 ppt) was used as dilution water and for preparation of control samples. The starting algal concentration of 10000 cells/mL was added and the production was followed by counting the cells with Coulter Counter (Beckman Z2) for a period of four days. Two replicates were used both for control and for elutriate dilutions.

3. RESULTS AND DISCUSSION

3.1 Sediment Characteristics

Different costal structures and water currents of the Strait affect the sediment deposition and characteristics. In some part of the Strait the bottom structure is rocky, so the surface sediments could not be sampled from all stations. Seventeen sediment samples were collected. Details of information about sediment samples are given in Appendix A. Sediment humidity data is shown in Table 3.1.

Table 3.1: Sediment water content samples.

Sampling Sites No	Sampling Sites Name	Water %
1	Rumeli feneri ilerisi	23.0
2	Garipçe köyü	23.2
3	Rumeli Kavağı	23.0
4	Büyükdere	29.8
5	Tarabya	17.1
6	İstinye	21.5
7	Balta Limanı	26.2
8	Bebek	25.3
9	Ortaköy	22.5
10	Beşiktaş	19.7
12	Anadolu Feneri	22.0
13	Poyraz	27.5
18	Kandilli	39.5
19	Kuzguncuk	35.7
20	Üsküdar	20.0
21	Moda iskelesi	26.3
23	Büyük ada plaj	25.4

3.2 Salinity and Temperature

Surface seawater salinity was similar to the previous studies (Oğuz et al., 1990). Salinity level increases from Black Sea to the Marmara Sea along the Strait (Table 3.2). The lowest salinity was 14.8 ppt and highest was 23.2 ppt changing spatially and temporally. Temperature correction for salinity were performed according to the salinity tables (Fofonoff. and Millard, 1983; Salinity Calculator, 2007)

Figure 1.3 shows the long time period data of salinity and water flow on the Strait system. The surface water salinity level observed in this study is similar with the previous data measured by several scientists (Ünlüata et al, 1990; Beşiktepe et al., 1994). Because of the high fresh water input to the Black Sea, low salinity values (14.8) were observed at the Black Sea entrance of the Strait in April. The salinity values increase along the Strait and reach 20.6 – 23.2 ppt at the stations closer to the Marmara Sea.

Sea water temperature was measured between 7 to 9^{o}C in April. During June, water temperature was between 15 to 18^{o}C and during September, it was between 22 to 24^{o}C. In winter (period between January and February) the sea water temperature was found as 7-8^{o}C. These values are similar to the data given in the previous studies (Ünlüata et al, 1990; Beşiktepe et al., 1994).

Table 3.2: Salinity and Temperature changes along the Strait.

		April 2006		June 2006		September 2006		January-February 2007	
Site No	**Local Name**	**T^1**	**S^2 at 15°C (ppt)**	**T^1**	**S^2 at 15°C (ppt)**	**T^1**	**S^2 at 15°C (ppt)**	**T^1**	**S^2 at 15°C (ppt)**
1	**Rumeli feneri ilerisi**	7°C	14.8	15°C	15.1	22°C	16.9	8°C	17.3
2	**Garipçe köyü**	8°C	16.2	15°C	15.1	22°C	17.3	8°C	15.6
3	**Rumeli Kavağı**	8°C	16.1	16°C	15.2	22°C	17.3	7°C	17.1
4	**Büyükdere**	8°C	16.3	16°C	15.1	22°C	17.4	7°C	17.3
5	**Tarabya**	8°C	16.4	17°C	15.2	22°C	17.4	8°C	20
6	**İstinye**	8°C	16.5	17°C	15.2	22°C	17.5	8°C	21.6
7	**Balta Limanı**	8°C	16.3	17°C	15.4	22°C	17.5	8°C	17.4
8	**Bebek**	8°C	16.8	16°C	16.8	22°C	17.9	8°C	17.8
9	**Ortaköy**	9°C	18	16°C	18.1	22°C	19.4	8°C	22.6
10	**Beşiktaş**	8°C	18.2	17°C	18.2	22°C	19.6	8°C	22.9
11	**Ahırkapı ilerisi**	8°C	18.3	17°C	18.8	22°C	20.3	8°C	19.3
12	**Anadolu Feneri**	7°C	15.7	17°C	16	23°C	17.1	7°C	17.1
13	**Poyraz**	8°C	16.1	18°C	15.9	23°C	17.4	7°C	17.4
14	**Anadolu Kavağı**	8°C	16.2	18°C	16.2	23°C	17.4	7°C	17.5
15	**Yalıköy- Beykoz**	8°C	16.6	18°C	16.6	23°C	17.4	7°C	17.4
16	**Çubuklu**	8°C	16.5	18°C	16.5	23°C	17.5	7°C	17.5
17	**Kavacık**	8°C	16.6	18°C	16.8	23°C	17.5	8°C	17.4
18	**Kandilli**	8°C	16.3	17°C	16.7	23°C	17.6	8°C	17.5
19	**Kuzguncuk**	9°C	16.9	17°C	17.8	23°C	18	8°C	18.2
20	**Üsküdar**	9°C	17.1	16°C	17.8	23°C	18.4	8°C	18.1
21	**Moda iskelesi**	8°C	21.4	16°C	21.2	23°C	23.2	8°C	20.7
22	**Büyük ada iskele**	8°C	20.6	18°C	20.9	24°C	22.3	7°C	22.3
23	**Büyük ada plaj**	8°C	22.6	18°C	21	24°C	21.9	7°C	22.3

T^1: Seawater Temperature, **S^2**: Salinity

3.3 Nutrients

3.3.1 Nitrite and nitrate nitrogen [(NO_3+NO_2) – N]

Seasonal changes of nitrogen [(NO_3+NO_2) – N] concentrations are shown in Figure 3.1 A and B for the European and Asian coast line of the Strait respectively. Detailed data set is given in Appendix B.

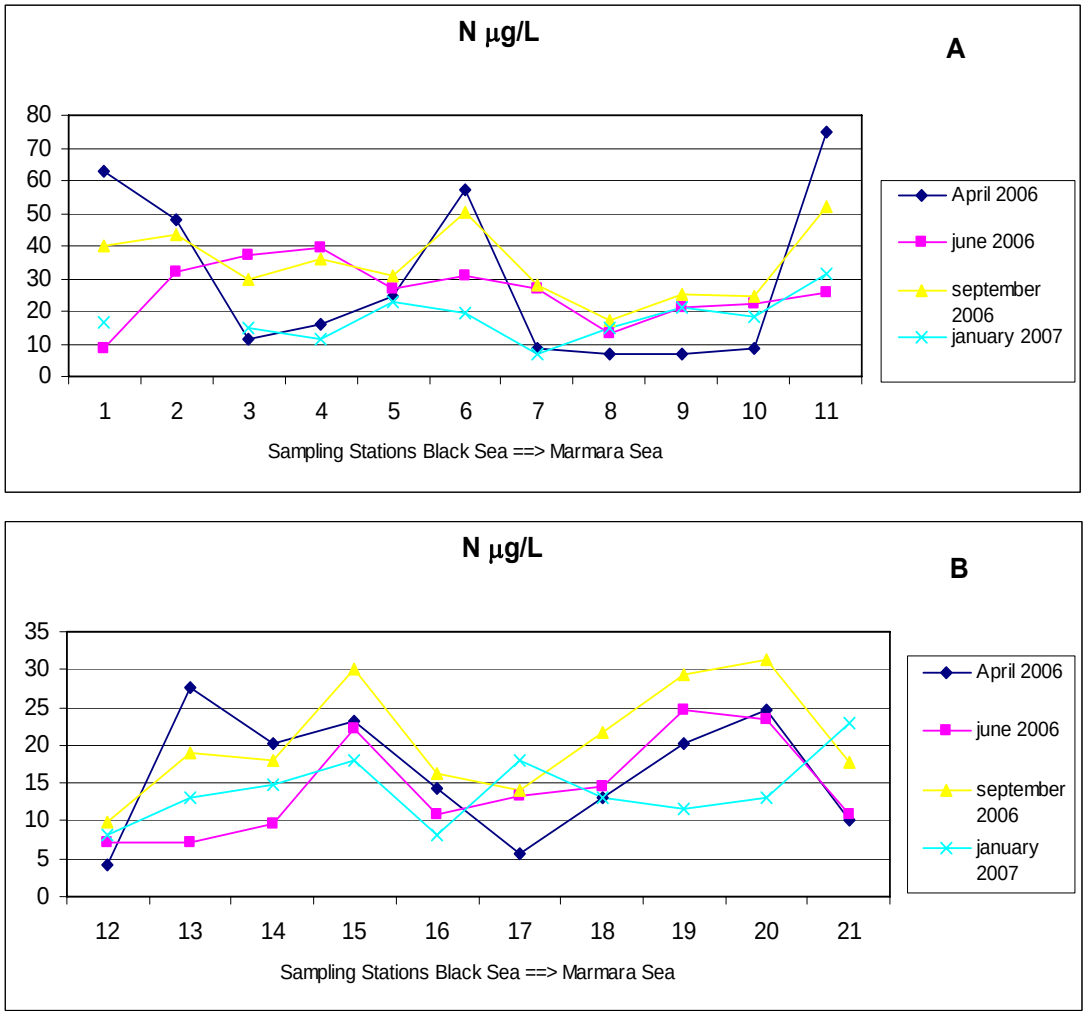


Figure 3.1: Concentration of nitrogen [(NO_3+NO_2) – N]. **A** is the European part of the Strait and **B** is the Asian part of the Strait.

Nitrogen [(NO_3+NO_2) – N] concentration varied between 1.1 µg/L and 74.7 µg/L and the average N concentration was 21.9 µg/L in April. Station 1 (62.9 µg/L), 2 (48.2 µg/L), 6 (57 µg/L) and 11 (74.7 µg/L) had higher N concentrations, while Station 7 (8.5 µg/L), 8 (7 µg/L), 9 (7 µg/L), 10 (8.5 µg/L), 12 (4.1 µg/L), 17 (5.6 µg/L) and 23 (1.1 µg/L) had lower (below 10 µg/L) N concentrations in April. In June, N

concentration range from 7.1 µg/L (Station 12 and 13) to 43.3 µg/L (Station 22) and the average N concentration was 21.1 µg/L. Station 2 (32.1 µg/L), 3 (37.1 µg/L), 4 (39.6 µg/L), 6 (30.8 µg/L) and 22 (43.3 µg/L) had high N concentrations in June. Station 1 (8.3 µg/L), 12 (7.1 µg/L), 13 (7.1 µg/L) 14 had low (below 10 µg/L) N concentration in June. N concentrations varied between 9.8 µg/L (Station 12) to 52.1 µg/L (Station 11) and the average was 28.1 µg/L in September. Station 2 (43.4 µg/L), 6 (50.3 µg/L), 11 (52.1 µg/L) and 22 (42.4 µg/L) had high N concentrations in September. Station 12 had the lowest (9.8 µg/L) N concentration in September. In January, N concentrations range from 6.5 µg/L (Station 7) to 370 µg/L (Station 2) and the average concentration was 30.9 µg/L. Station 2 (370 µg/L) had the highest N concentration in January. Station 5 (23 µg/L), Station 9 (21.3 µg/L), Station 11 (31.2 µg/L) and Station 23 (23 µg/L) had high N concentrations (over 20 µg/L) in January. Station 7 (6.5 µg/L), Station 12 (8.2 µg/L), Station 16 (8.2 µg/L) and Station 22 (9.8 µg/L) had low N concentrations (below 10 µg/L) in January.

General trend for all seasons in the European part of the Strait; Station 1 and 2 had relatively higher concentrations of N and the concentration of N decreases at Station 3, 4 and 5. N concentration at Station 6 gives a peak (in the middle part of the Strait), then, decrease again at Stations of 7, 8, 9 and 10. The concentration of N had the highest value at Station 11 which is the last station on European part of the Strait.

Asian part of the Strait had a different N concentration trend compared to the European part. Station 12 had lowest concentration of N. This may results from the main current system of the Black Sea which directly flows into the Strait. The satellite photo (Figure 3.2) also shows that the western part of the Strait is more affected by the Black Sea current system compared to the eastern part of the Strait. This may explain the differences in N concentrations between Station 1 and 12. Station 13, 14 and 15 had similar concentrations of N except in June. The concentration of N decreases in Stations of 16 and 17, and then increase again in the Stations of 18, 19 and 20.

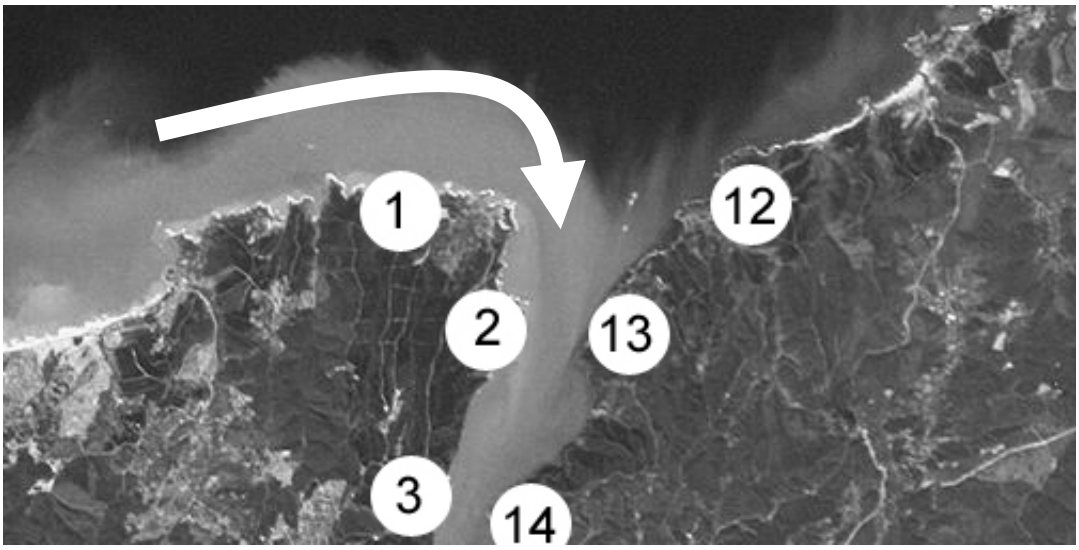


Figure 3.2: Black Sea entrance of the Strait (NASA Earth Observatory-April 16, 2004).

Additionally, high concentration of N at Station 1 during April and September could be the result of a water discharge by the creek near that station probably carrying the domestic wastewaters from the local settlements. While the other part of the Strait (Station 12) had a lower nitrogen concentration (<10 mg/L) in all seasons. Very high N concentration (January) in Station 2 may be a reason of local wastewater discharge at the sampling time.

3.3.2 Orthophosphate phosphate [(o-PO_4)-P]

Seasonal changes of phosphate [(o-PO_4)-P] concentration are shown in Figure 3.3 A and B at the European and Asian coast line of the Strait. Detailed data set is given in Appendix B.

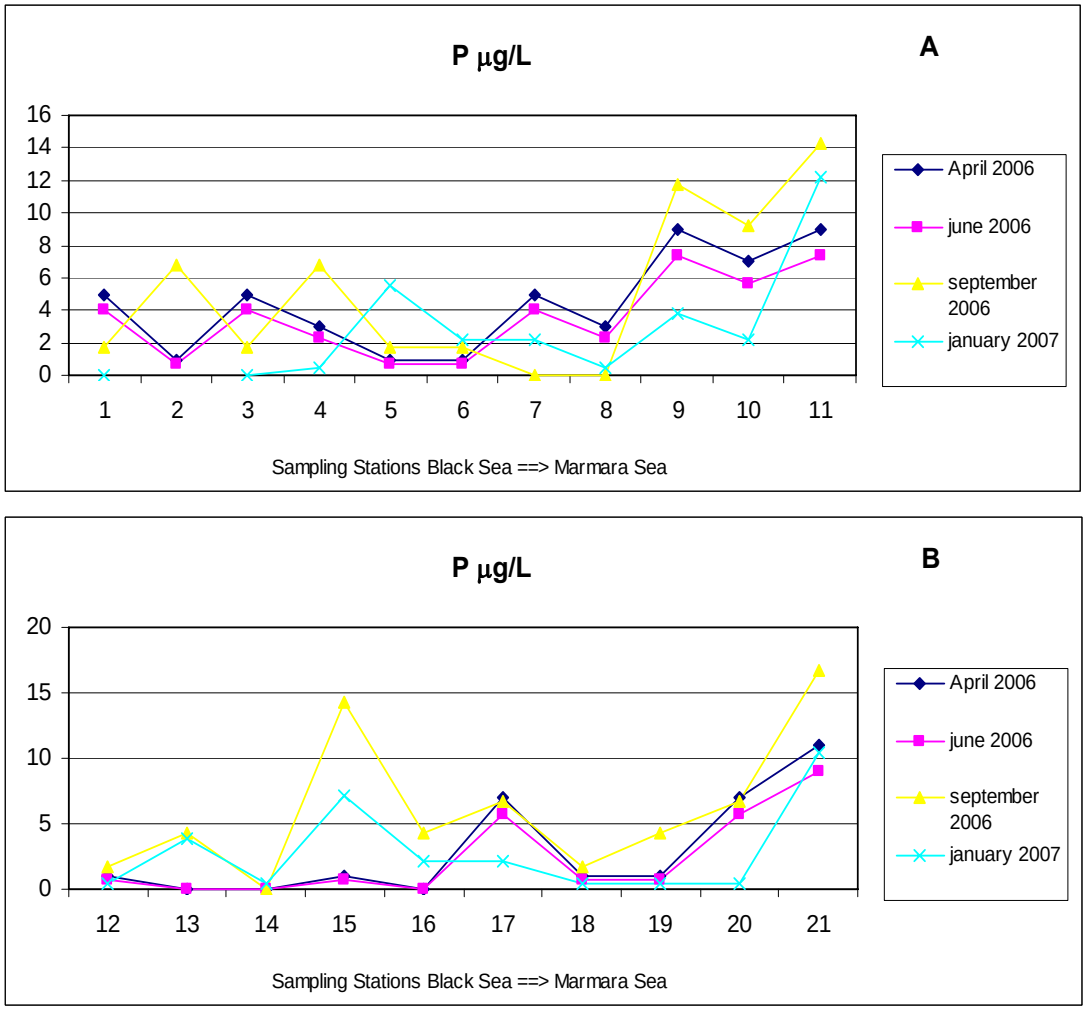


Figure 3.3: Concentration of phosphate. **A** is the European part of the Strait and **B** is the Asian part of the Strait.

The concentrations of phosphate [(o-PO_4)-P] varied between 0.9 µg/L to 11 µg/L and the average P concentration was 4.2 µg/L in April. Station 9 (9 µg/L), 10 (7 µg/L), 11 (9 µg/L), 17 (7 µg/L), 20 (7 µg/L) and 21 (11 µg/L) had higher P concentrations (over 7 µg/L) in April. The values measured at Stations of 13, 14 and 16 were below the detection limit in April. In June, concentrations of P range from 0.6 µg/L (Station 2, 5, 6, 12, 15, 18, and 19) to 9 µg/L (Station 21) and the average P concentration was 3.4 µg/L. Station 9 (7.3 µg/L), 11 (7.3 µg/L) and 21 (9 µg/L) had high concentrations of P (over 7 µg/L) in June. The values measured at Stations of 13, 14

and 16 were below the detection limit in June. Concentration of P varied between 1.7 µg/L (Station 1, 3, 5, 6, 12 and 18) and 16.7 µg/L (Station 21) with on average of 6.8 µg/L in September. Station 9 (11.7 µg/L), 10 (9.2 µg/L), 11 (14.2 µg/L), 15 (14.2 µg/L), 21 (16.7 µg/L), 22 (11.7 µg/L) and 23 (9.2 µg/L) had highes concentrations of P (over 7 µg/L) in September. The values measured at Stations of 7, 8 and 14 were below the detection limit in September. In January, concentrations of P range from 0.5 µg/L (Station 4, 8, 12, 14, 18, 19 and 20) to 43.8 µg/L (Station 2) and the average concentration was 5.1 µg/L. Station 2 (43.8 µg/L) had the highest P concentration in January. Station 11 (12.1 µg/L), Station 15 (7.1 µg/L) and Station 21 (10.5 µg/L) had higher concentrations of P (over 7 µg/L) in January. The values measured at Stations of 1 and 3 were below the detection limit in January.

Concentrations of P throughout the Strait were similar in April and June. As a general trend, the P concentrations increase from Black Sea towards to the Marmara Sea. P concentrations measured at Stations 21 and 11 had a high concentration of P for all seasons. Those Stations are placed on the Marmara Sea part of the Strait. High concentration of P measured at Station 2 (January) may be because of a local wastewater discharge at the sampling time.

3.3.3 Silicate (Si)

Seasonal changes of total silicate concentration are shown in Figure 3.4 A and B at the European and Asian coast line of the Strait. Detailed data set is given in Appendix B.

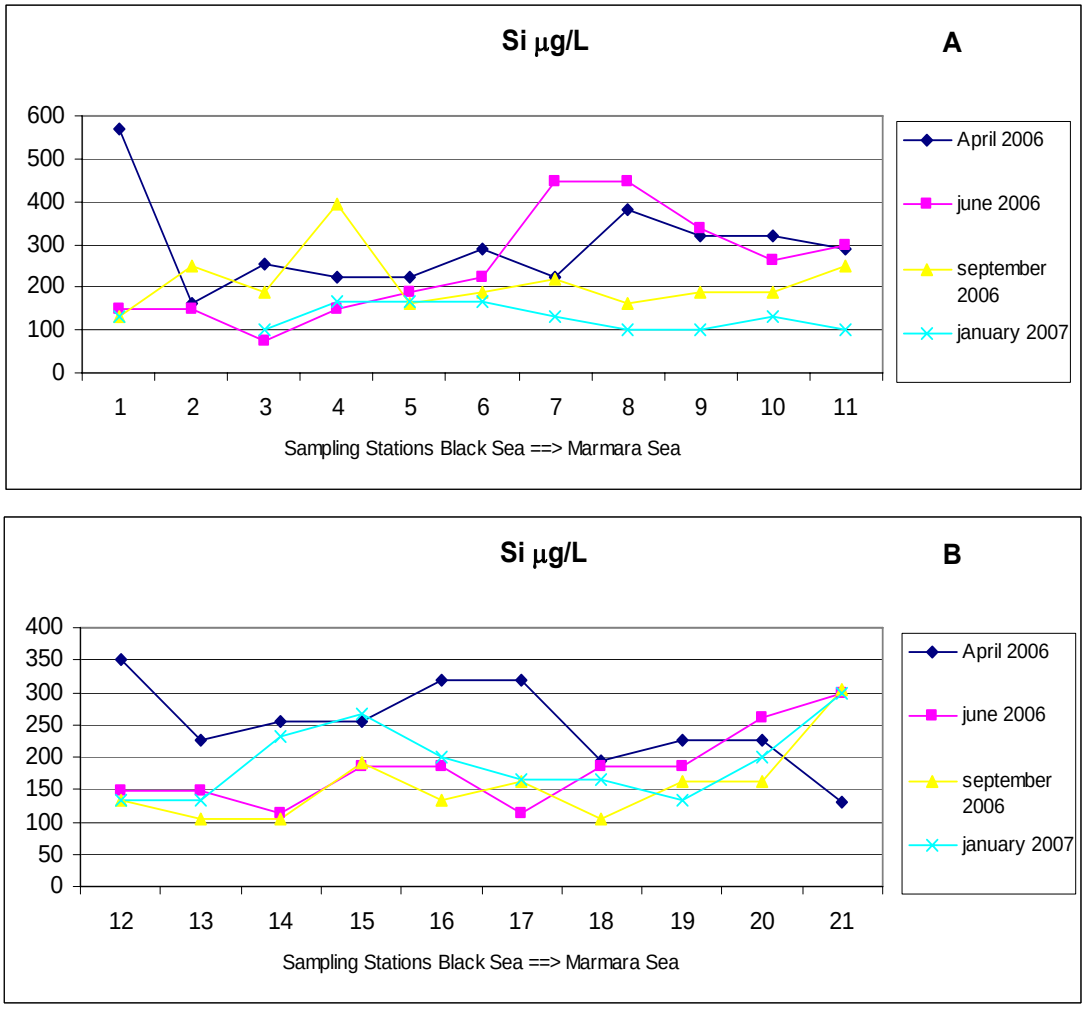


Figure 3.4: Concentration of silicate. **A** is the European part of the Strait and **B** is the Asian part of the Strait.

Concentrations of silicate varied between 131 µg/L and 569 µg/L and the average concentration of Si was 264 µg/L in April. Station 1 (569 µg/L), 8 (381 µg/L), 9 (319 µg/L), 12 (350 µg/L), 16 (319 µg/L) and 17 (319 µg/L) had high concentrations of Si in April. In June, the concentrations of Si range from 74.6 µg/L (Station 3) to 448 µg/L (Station 7 and 8) and the average concentration of Si was 223.9 µg/L. Station 7 (448 µg/L), 8 (448 µg/L), 9 (336 µg/L) and 23 (410 µg/L) had high concentrations of Si (over 300 µg/L) in June. The concentration of Si varied between 104 µg/L (Station

13, 14 and 18) to 392.5 µg/L (Station 4) and the average was 185.1 µg/L in September. Station 2 (248 µg/L), 4 (392.5 µg/L), 7 (219.1 µg/L), 11 (248 µg/L) and 21 (305.8 µg/L) had high concentrations of Si (over 200 µg/L) in September. In January, concentrations of Si range from 100 µg/L (Station 3, 8, 9 and 11) to 1566.7 µg/L (Station 2) and the average concentration was 226.1 µg/L. Station 2 (1566.7 µg/L) had the highest concentration of Si in January. Station 14 (233.3 µg/L), Station 15 (266.7 µg/L), Station 21 (300 µg/L) and Station 23 (233.3 µg/L) had high concentrations of Si (over 200 µg/L) in January.

When nutrient concentrations were compared with the previous studies (Yılmaz et al, 1998), nitrogen [(NO_3+NO_2) – N] concentration was found higher in this study, while the phosphate levels are similar. The differences could be the result of surface water sampling.

Table 3.3 shows the N/P ratios. The stoichiometric ratio is N: P = 16:1 based on weight units:

N_{16} = 14 X 16 = 224

P_1 = 31 X 1 = 31

Where:

14 = atomic weight of N

31 = atomic weight of P

The N: P ratio therefore makes up:

224 : 31 ~ 7 : 1

If the N : P ratio (based on units of weight) differs from 7, the estimation of N or P, being the growth limiting factor, depends on the concentration of the nutrients in the water body (Gargas et al, 1978).

- If N / P > 7, then P is limiting
- If N / P < 7, then N is limiting

In April, the N/P ratio in Stations of 1, 2, 5, 6, 11, 15, 18 and 19 were greater then 7 (Table 3.3) representing that P is limiting, while at Stations of 3, 4, 7, 8, 9, 10, 12,

17, 20, 21, 22, and 23, ratios were lower than 7 and the N is limiting for those stations. The concentration of P was below detection limit at Station 13, 14 and 16 so the N: P ratios could not be calculated for April. An estimation was made by using the detection limit value of P. Possible minimum N: P ratios were given for all seasons in Table 3.3. In June, P was limiting at the Station 2, 3, 4, 5, 6, 12, 15, 18, 19 and 22. N was limiting at the Station 1, 7, 8, 9, 10, 11, 17, 20, 21 and 23 in June. In September, P was limiting at the Station 1, 3, 5, 6 and 18. N was limiting at the Station 2, 4, 9, 10, 11, 12, 13, 15, 16, 17, 19, 20, 21, 22 and 23 in September. In January, P was limiting at the Station 2, 4, 6, 8, 12, 14, 17, 18, 19 and 20. N was limiting at the Station 5, 7, 9, 10, 11, 13, 15, 16, 21, 22 and 23 in January.

In general, Station 1, 2, 3, 5, 6, 14, 18 and 19 had high N:P ratios over the year representing a limitation of P, and for other sampling points N was a limiting nutrient.

Table 3.3: N / P ratios (based on weight units)**.** *: minimum possible ratio depends on the P detection limit. Bold values are greater than 7.

Sapmling Points	April 2006	june 2006	september 2006	January 2007
1	**12.6**	2.1	**22.8**	**32.9***
2	**51.4**	**48.2**	6.4	**8.4**
3	2.3	**9.3**	**17.0**	**29.6***
4	5.4	**17.0**	5.4	**23.0**
5	**26.3**	**40.7**	**17.8**	4.2
6	**60.8**	**46.3**	**28.8**	**9.1**
7	1.7	6.8	**16.1***	3.0
8	2.4	5.7	**9.9***	**29.6**
9	0.8	2.8	2.1	5.6
10	1.2	3.9	2.6	**8.3**
11	**8.3**	3.5	3.7	2.6
12	4.4	**10.7**	5.6	**16.4**
13	**29.4***	**10.7***	4.5	3.4
14	**21.6***	**14.4***	**10.3***	**29.6**
15	**24.7**	**33.2**	2.1	2.5
16	**15.3***	**16.3***	3.8	3.8
17	0.8	2.4	2.1	**8.3**
18	**13.8**	**21.9**	**12.4**	**26.3**
19	**21.6**	**36.9**	6.9	**23.0**
20	3.5	4.1	4.6	**26.3**
21	0.9	1.2	1.1	2.2
22	2.6	**10.8**	3.6	2.6
23	0.4	5.7	2.0	3.4

3.4 Chlorophyll a (Ch-a)

Figure 3.5 shows the concentration of Ch-a. April-June profiles indicated an increase in the Ch-a concentration in the surface layer. During the September-January period the concentration of Ch-a is relatively low compared to April-June period. The highest concentration on Station 11 in January may be the macroalgae pieces breaking off form the rocky surfaces as result of strong waves.

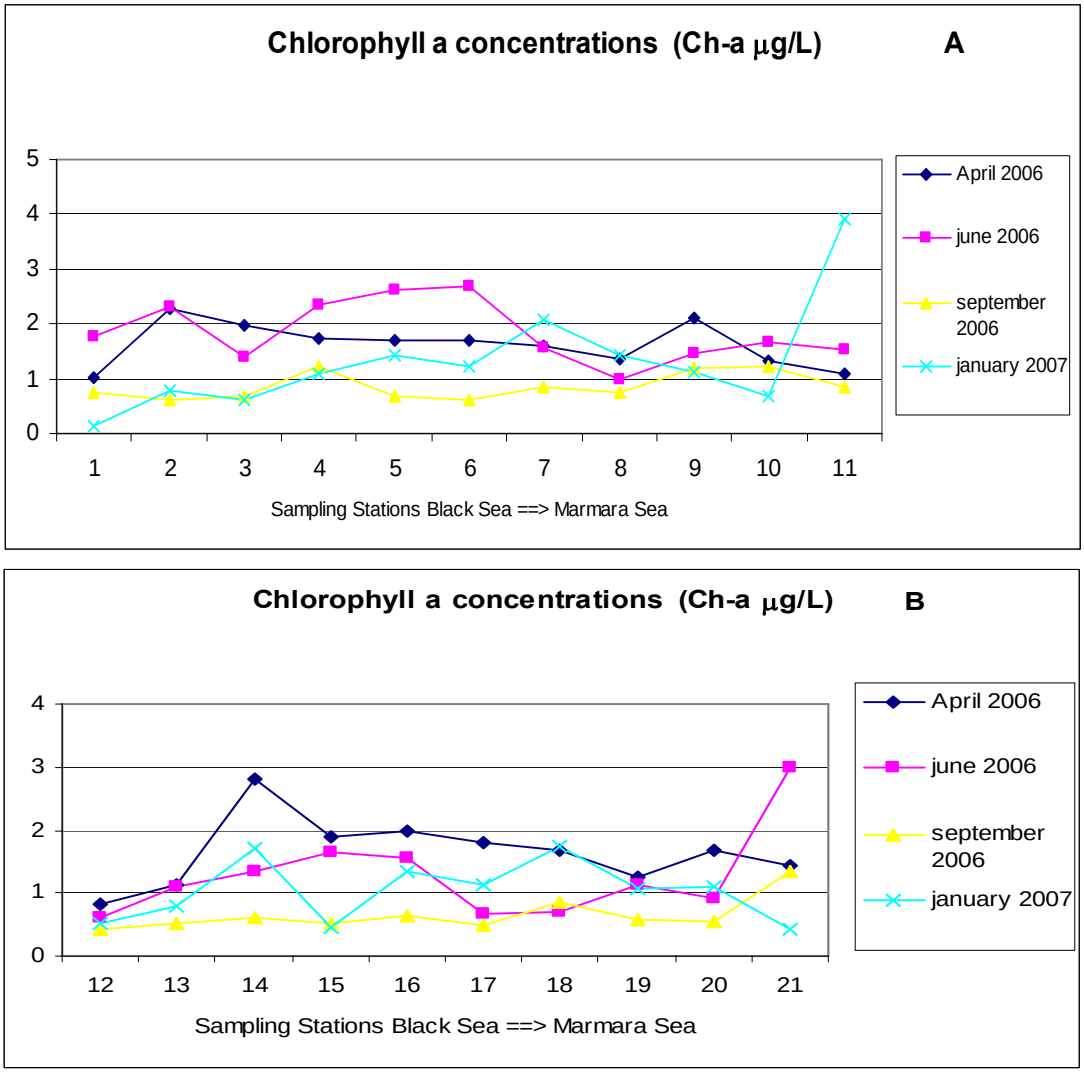


Figure 3.5: Concentration of Ch-a. **A** is the European part of the Strait and **B** is the Asian part of the Strait.

A previous study performed in 1995-96 indicates lower Ch-a concentrations of 0.27, 0.82 and 0.86 Ch-a μg/L in April, in June, in September respectively (Yılmaz et al, 1998). These results show that there is an increasing trend in Ch-a concentrations in the last 10 years period. As was indicated in the previous section, the increase in the nutrient concentrations affects the primary production and result in eutrophication.

Detailed Ch-a data set is given in Appendix B.

3.5 Results of PAHs

3.5.1 PAH Concentrations

The total PAH (T-PAH) concentrations (sum of the 16 EPA priority pollutants) in this study showed a wide range of concentrations. Concentrations of T-PAHs and individual PAHs in sediments are given in Figure 3.8 (and Table 3.8) and in Table 3.4 respectively. T-PAH concentrations of surface sediments are ranging from 1.1 ng/g dry wt to 3152 ng/g dry wt. Maximum sediment T-PAH level was found at station 6 (3152 ng/g dry wt) and the next highest concentration was measured at station 8 (1666 ng/g dry wt). The sediments sampled from the entrance of Black Sea (stations 1, 2 and 12, 13) have lower PAHs levels compared to the sediments taken from the other parts of the Strait. The results show that the T-PAH concentrations show an increasing trend from the Black Sea towards the Marmara Sea. Sediment T-PAH concentration was measured at station 1 as 2.1 ng/g dry wt, at station 2 as 9.6 ng/g dry wt, at station 12 as 1.1ng/g dry wt, and at station 13 as 8.75 ng/g dry wt.). Black Sea entrance parts of the Strait on both sites are urban areas and distant from extensive anthropogenic activities. This could be a reason of low level T-PAH at this part of the Strait.

According to a study carried out in the Black Sea region in 1995 (at the entrance of Istanbul Strait-Figure 3.6), Black Sea T-PAH (Σ17 PAHs) concentrations in sediments sampled from 80 m were found between 13.8 and 531 ng/g dry wt with an average value of 113 ng/g dry wt (Readman et al., 2002). In the same study, the T-PAH concentrations at stations 9 and 10 (Figure 3.6) were measured as 46.4 and 531 ng/g dry wt. Those values are much more higher compared to the values found in this study. In the same study, the Danube input concentration was given as 638 ng/g dry wt T-PAH (Σ17 PAHs).

In this study, Station 23 was chosen as to be a reference site, because it is an island situated in the Marmara Sea and supposed to be a relatively clean site, but the results show that, the sediment T-PAH content at station 23 is higher (144 ng/gr dry wt) than the Black sea stations (1,2 and 12,13).

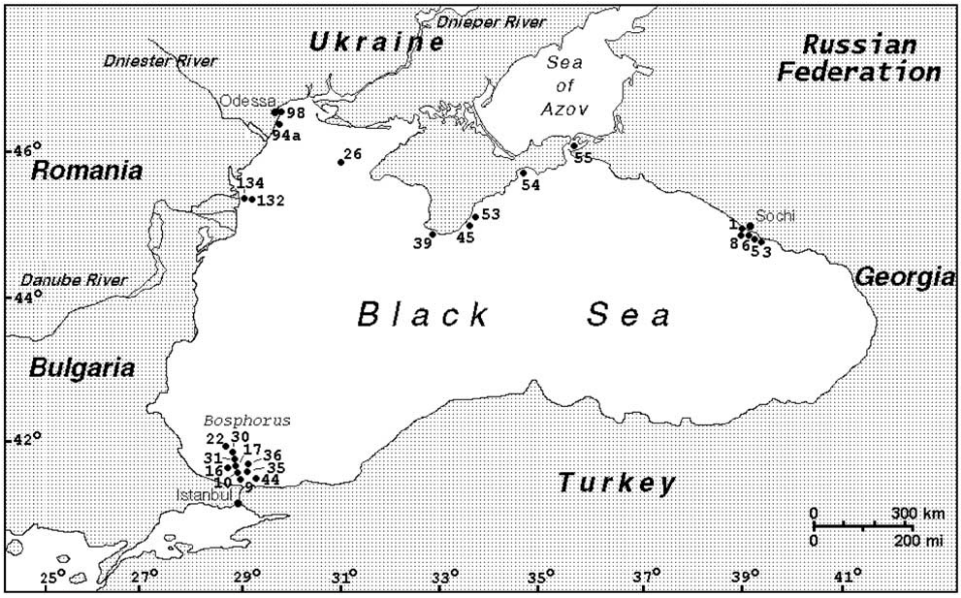


Figure 3.6: Sampling sites on the Black Sea (Readman et al., 2002).

Stations of 4, 6, 8 and 18 have relatively high T-PAH concentrations compared to all other stations. Generally, those stations receive water discharges from several sources. The coastal lines of those stations are highly populated. Additional to those, the reverse water currents may keep the pollution to stay in those sites. Station 4 (697 ng/g dry wt) is a cove, near a polluted river (Çayırbaşı) carrying the untreated wastewaters from two factories (Match and Tea) together with untreated domestic wastes. Shallow depth profile of Büyükdere cove (Station 4) and the reverse currents increase the accumulation of T-PAHs from this water inputs as well as carried by the waters of the Strait itself. Station 6 is also situated in a semi enclosed water body (3151 ng/g dry wt) and has been affected by the industrial contamination carried by İstinye River. The structure of the cove creates also reverse currents/eddies which may allow the pollutants to accumulate in. The Station heavily is used by leisure boats and most importantly, the area has been used as a shipyard for a long time period (70 years). The shipyard stopped its activities in 1991. Station 8 (1665 ng/g in dry wt) has the second highest T-PAH concentration. The structure of that station produces the reverse currents/eddies and the station is under the pressure of high population.

Table 3.4: Concentrations of individual PAHs in sediments (ng/g dry wt.)

Site No	*Nap*	*ACL*	*AC*	*FL*	*PHE*	*AN*	*FA*	*PY*	*BaA*	*CHR*	*BbFA, BjFA*	*BkFA*	*BaP*	*IP*	*BghiP*	*DBahA*	*CPP*	*5-MCH*	*BcFL*	*BbNdT*	*ATR*
1	0.30	0.00	0.00	0.10	0.40	0.00	0.30	0.40	0.10	0.10	0.10	0.00	0.10	0.10	0.10	0.00	0.10	0.00	0.00	0.00	0.00
2	1.00	0.20	0.00	0.20	0.80	0.20	0.90	0.90	0.70	0.70	1.30	0.50	1.00	0.50	0.60	0.20	0.30	0.10	0.10	0.10	0.10
3	1.00	0.30	0.00	0.00	0.30	0.10	1.20	0.90	0.20	0.60	1.10	0.30	0.60	0.40	0.40	0.10	0.10	0.00	0.10	0.10	0.00
4	5.20	1.00	8.60	9.70	88.3	20.6	138	122	51.6	43.1	69.9	20.8	63.1	21.7	26.3	5.90	8.10	1.70	15.2	3.20	7.90
5	1.00	0.10	0.10	0.20	1.10	0.30	1.30	1.70	0.00	0.00	1.40	0.40	0.90	0.60	1.00	0.10	0.00	0.20	0.20	0.10	0.10
6	19.3	9.90	23.1	25.3	322	81.9	539	615	245	211	400	98.0	291	112	129	29.9	36.2	7.50	57.9	15.8	40.9
7	15.7	1.60	1.70	3.80	28.4	6.00	50.5	46.9	19.3	16.8	33.4	9.10	23.1	12.2	14.4	3.00	4.90	1.50	4.20	1.60	3.80
8	51.8	3.80	10.7	18.8	233	74.1	306	285	133	96.2	168	42.3	126	48.8	52.0	13.9	17.9	6.20	52.6	8.10	20.2
9	51.1	1.50	2.30	3.50	31.8	7.60	53.0	46.3	20.5	17.7	40.7	10.6	23.7	10.9	11.4	2.90	4.30	1.10	3.40	1.70	2.40
10	17.3	3.40	1.70	3.10	11.1	9.80	34.9	38.6	16.3	14.2	27.2	7.80	23.6	11.7	13.1	2.60	4.80	0.90	6.60	1.30	4.50
12	0.10	0.00	0.00	0.00	0.10	0.00	0.20	0.10	0.10	0.10	0.10	0.00	0.10	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00
13	0.40	0.00	0.10	0.20	1.10	0.30	1.10	1.20	0.40	0.50	1.10	0.30	0.60	0.50	0.70	0.10	0.20	0.10	0.10	0.10	0.10
18	11.6	1.90	7.20	8.30	56.8	14.8	62.4	60.7	21.9	18.6	32.4	8.80	22.4	10.7	12.9	2.50	5.40	1.50	8.60	1.50	3.10
19	4.80	1.20	1.70	2.40	18.0	4.50	27.5	23.1	10.2	9.70	20.5	4.70	10.8	4.90	7.50	1.50	4.70	1.60	3.20	1.10	1.20
20	0.60	0.00	0.10	0.20	0.70	0.40	1.00	1.10	0.30	0.20	2.10	0.60	1.20	0.70	0.80	0.10	0.20	0.10	0.10	0.00	0.10
21	5.20	2.20	1.00	2.20	19.3	4.60	33.4	27.3	10.4	9.90	18.7	5.50	15.0	7.00	7.40	1.60	2.70	0.60	3.60	0.90	1.50
23	0.90	3.20	0.10	0.40	7.00	3.80	25.8	21.4	11.4	10.9	19.4	6.10	15.5	8.10	8.50	1.80	2.80	0.30	2.10	0.40	1.20

Naphthalene: *Nap*; Acenaphthylene: *ACL*; Acenaphthene: *AC*; Fluorene: *FL*; Phenanthrene: *PHE*; Anthracene: *AN*; Fluoranthene: *FA*; Pyrene: *PY*; Benzo(a)anthracene: *BaA*; Chrysene: *CHR*; Benzo(b)fluoranthene, Benzo(j)fluoranthene: *BbFA, BjFA*; Benzo(k)fluoranthene: *BkFA*; Benzo(a)pyrene: *BaP*; Indeno(1,2,3-c,d)pyrene: *IP*; Benzo(g,h,i)perylene: *BghiP*; Dibenzo(a,h)anthracene: *DBahA*; Cyclopenta(c,d)pyrene: *CPP*; 5-Methylchrysene: *5-MCH*; Dibenzo(a,l)pyrene: *DBalP*; Dibenzo(a,e)pyrene: *DBaeP*; Dibenzo(a,i)pyrene: *DBaiP*; Dibenzo(a,h)pyrene: *DBahP*; Benzo(c)fluorine: *BcFL*; Benzo(b)naphtho(2,1-d)thiophene: *BbNdT*; Anthanthrene: *ATR*.

This site is used as a marina for leisure boats which probably cause pollution by uncontrolled discharges. The temperature difference between Bebek (station 8) cove and the main Strait current show that the waters in the cove are not affected by the main current system and these two waters do not mix efficiently (Çoşkun,1992).

Station 18 (354ng/g in dry wt) is very close to Kandilli public ship transport port. Göksu and Küçüksu rivers carry industrial and domestic wastewaters and the pollutants in those discharges are carried to that station by the currents of the Strait (Figure 3.7).

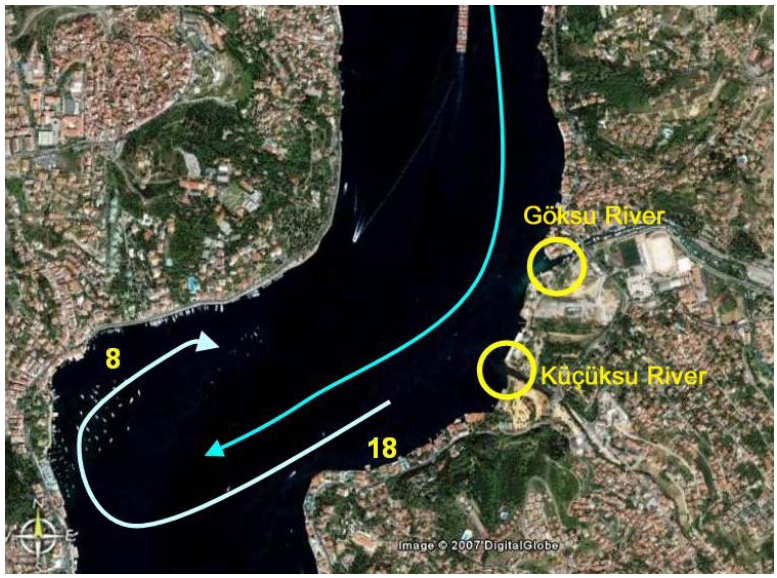


Figure 3.7: Position of Station 18 and 8 (earth.google.com)

Furthermore, the previous studies show that the concentrations of T-PAHs in the sediments of the Strait are comparable to the other seas. Table 3.5 shows worldwide concentrations of PAHs in sediments. The concentration of T-PAHs in the Strait sediments is lower than the Marmara Sea sediments measured in Izmit Bay (Tolun et al., 2006) 241 – 11437 ng/g in dry wt and in Gemlik Bay (Unlu and Alpar, 2006) 51-13482 ng/g in dry wt respectively. As is well known, both Izmit and Gemlik Bays have been heavily polluted by industrial and domestic inputs for several years.

Table 3.5: Worldwide concentrations of PAHs in sediments (ng/g dry wt.)

Area Survey	Year	Concentration	References
France, Mediterranean Sea	1996	36–6900 (Σ18 PAHs)	Baumard et al. (1998)
Spain, Mediterranean Sea	1996	1.2–8400 (Σ18 PAHs)	Baumard et al. (1998)
Majorca, Mediterranean Sea	1996	0.3–100 (Σ18 PAHs)	Baumard et al. (1998)
Baltic Sea	1993	9.5–1871 (Σ15 PAHs)	Witt (1995)
Western Coast, Australia	1991	1.0–3200 (Σ11 PAHs)	Burt and Ebell (1995)
Danube Coastline, Black Sea, Ukraine	1995	30.5–608 (Σ17 PAHs)	Readman et al. (2002)
Concentrations of PAHs in Turkey			
Izmit Bay, Marmara Sea, Turkey	1999	120-11400 (Σ14 PAHs)	Tolun et al.(2006)
Gemlik Bay, Marmara Sea, Turkey	2005	50.8–13482 (Σ14 PAHs)	Ünlü and Alpar (2006)
Bosphorus entrance, Black Sea, Turkey	1995	13.8-531 (Σ17 PAHs)	Readman et al. (2002)
Istanbul Strait, Turkey	2007	1.1-3152 (Σ16 PAHs)	This study

Mussels are filter-feeding bivalves that can retain particles larger than 4 μm (Hawkins and Bayne, 1992). They are exposed to both dissolved and particulate forms of pollutants present in the water. Concentrations of total and individual PAHs in mussels are given in Figure 3.8, (and Table 3.8) and in Table 3.6 respectively. T-PAH concentrations ranged from 601 ng/g to 42.9 ng/g wet weight. As for the sediment, most PAH polluted mussels were located around the discharge points. The mussels collected from Station 18 (601 ng/g in wet wt) have the highest and the mussels sampled from Station 14 (42.9ng/g in wet wt) have the lowest T-PAH concentrations.

Table 3.6: Concentrations of individual PAHs in mussel tissues (ng/g wet wt.)

Site No	2	3	4	5	6	7	8	9	10	13	14	14a	15	16	17	18	19	20	21	22	23
Nap	8.40	0.70	1.40	0.60	n.d.	0.70	0.40	0.50	2.30	1.10	0.50	3.50	0.60	1.10	1.20	11.1	0.80	0.8	1.2	n.d.	0.20
ACL	3.20	0.40	1.10	0.50	0.30	1.00	0.30	0.60	1.00	0.20	0.20	0.20	0.80	0.20	0.40	14.9	0.40	0.40	0.90	1.00	0.40
AC	7.10	0.20	2.20	0.20	0.20	9.80	1.20	0.60	0.80	0.20	0.10	2.60	0.90	0.50	0.40	35.0	0.90	3.10	0.50	0.30	0.10
FL	12.4	1.60	4.30	2.20	1.20	23.4	2.40	2.10	2.20	1.40	1.10	6.90	2.30	1.20	1.60	52.5	1.90	4.60	2.20	1.70	1.20
PHE	142	17.7	34.8	18.4	10.7	135	14.1	8.10	18.3	11.8	9.70	18.5	14.7	9.00	9.40	221	12.6	25.2	17.2	12.8	11.7
AN	19.9	1.90	11.4	1.30	0.70	20.5	5.10	1.70	2.60	1.40	0.80	3.10	4.20	2.10	3.90	37.4	1.10	2.50	2.10	1.70	0.90
FA	n.d.	11.8	n.d.	17.5	11.1	23.9	17.9	19.6	30.1	11.1	6.80	13.1	32.4	16.7	14.8	38.7	16.4	13.8	25.1	22.0	14.6
PY	n.d.	12.0	n.d.	15.1	14.1	39.2	29.0	13.8	33.8	8.10	4.90	7.40	43.8	16.0	15.7	75.1	13.2	12.3	22.8	10.9	6.40
BaA	n.d.	3.20	8.90	4.80	4.30	6.30	7.90	6.50	16.3	3.50	1.90	1.80	21.9	9.50	5.20	17.2	5.70	0.00	18.8	6.70	3.80
CHR	n.d.	6.40	19.4	10.8	9.60	15.3	16.1	12.6	21.0	8.40	6.30	6.70	37.2	17.2	12.0	32.4	12.1	0.00	26.8	12.8	8.50
BbFA, BjFA	71.0	5.10	21.1	11.3	11.8	12.7	12.8	11.3	25.0	7.00	6.20	5.90	39.9	22.7	11.1	37.0	13.6	11.7	24.5	15.6	5.90
BkFA	19.2	1.20	4.90	2.60	2.60	2.80	3.40	3.00	6.80	1.50	1.60	1.30	9.30	5.20	2.80	8.40	3.10	2.90	6.10	4.00	1.70
BaP	32.2	0.90	4.70	2.00	2.30	3.20	3.60	3.40	12.2	0.90	0.80	0.50	11.2	5.70	3.00	9.20	3.10	4.40	7.60	3.60	1.30
IP	10.9	0.60	2.60	1.20	1.80	1.70	2.20	2.00	5.20	0.70	0.90	0.60	7.10	4.10	1.60	4.20	1.40	2.10	3.20	2.00	0.80
BghiP	12.8	0.90	4.10	1.90	2.70	3.30	4.00	2.90	6.70	0.80	0.90	0.60	9.60	4.40	2.30	6.30	2.20	3.30	4.40	2.60	1.00
DBahA	2.60	0.10	0.50	0.30	0.30	0.50	0.50	0.50	1.30	0.10	0.20	0.10	1.40	0.80	0.30	1.00	0.40	0.50	0.80	0.40	0.20
CPP	n.d.	2.80	10.9	5.50	4.00	9.20	8.80	6.30	8.60	4.20	2.90	4.60	15.2	7.10	5.80	21.2	7.20	n.d.	9.60	6.40	3.60
5-MCH	n.d.	0.40	3.60	1.10	0.90	4.40	3.70	1.40	3.20	0.60	0.50	0.40	4.40	1.50	1.40	6.00	1.50	1.40	1.80	0.70	0.60
DBalP	n.d.	0.90	1.90	0.90	0.90	1.00	1.60	1.90	7.00	8.70	1.00	0.40	2.80	2.60	n.d.	4.20	0.80	2.20	3.00	2.20	1.10
DBaeP	n.d.	n.d.	0.60	0.30	0.30	0.50	0.60	0.50	2.40	1.70	n.d.	0.10	1.10	0.60	n.d.	0.90	0.30	0.80	0.80	0.40	0.20
DBaiP	n.d.	0.10	0.10	0.20	0.20	0.20	0.30	0.30	0.20	3.30	0.20	0.20	0.40	0.10	n.d.	n.d.	0.20	0.20	0.30	0.20	0.20
DBahP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BcFL	n.d.	2.20	n.d.	2.70	2.20	9.80	6.20	3.90	8.10	1.80	1.20	2.10	9.40	3.80	3.10	16.4	3.20	4.10	7.30	3.60	2.00
BbNdT	n.d.	0.90	7.40	1.70	1.60	5.40	5.70	2.40	4.90	1.40	1.10	0.90	6.80	2.60	2.80	12.7	2.20	0.30	3.40	1.30	0.80
ATR	1.40	n.d.	n.d.	0.00	0.10	0.10	0.10	0.10	1.10	n.d.	n.d.	n.d.	0.40	0.20	0.00	0.30	n.d.	0.20	0.20	0.00	n.d.

Naphthalene: *Nap*; Acenaphthylene: *ACL*; Acenaphthene: *AC*; Fluorene: *FL*; Phenanthrene: *PHE*; Anthracene: *AN*; Fluoranthene: *FA*; Pyrene: *PY*; Benzo(a)anthracene: *BaA*; Chrysene: *CHR*; Benzo(b)fluoranthene, Benzo(j)fluoranthene: *BbFA, BjFA*; Benzo(k)fluoranthene: *BkFA*; Benzo(a)pyrene: *BaP*; Indeno(1,2,3-c,d)pyrene: *IP*; Benzo(g,h,i)perylene: *BghiP*; Dibenzo(a,h)anthracene: *DBahA*; Cyclopenta(c,d)pyrene: *CPP*; 5-Methylchrysene: *5-MCH*; Dibenzo(a,l)pyrene: *DBalP*; Dibenzo(a,e)pyrene: *DBaeP*; Dibenzo(a,i)pyrene: *DBaiP*; Dibenzo(a,h)pyrene: *DBahP*; Benzo(c)fluorine: *BcFL*; Benzo(b)naphtho(2,1-d)thiophene: *BbNdT*; Anthanthrene: *ATR*.

In this study, T-PAH concentrations in the Strait are found in most cases higher compared to the previous data obtained from the Mediterranean region and Atlantic Ocean (Table 3.7).

Although, there are some Total PAHs (mussel tissue) analysis data collected by using Fluorescence spectrophotometry from the Marmara Sea mussels (2.3 – 21.6 μg/g wet weight Σ17 PAHs), those results are not comparable because of the analysis methods (Fluorescence spectrophotometry). It was observed that the fluorescence spectrophotometry assay gave concentrations which were of the order of 1000 times those obtained by HPLC. The fluorometric technique boosted by UNEP (1986) gives only approximate results in terms of chrysene equivalents. Any hexane soluble compound which fluorescent at the same wavelengths of chrysene, whether or not it is a PAH, will contribute to the observed concentration (Telli-Karakoç et al, 2002).

Table 3.7: General concentrations of T-PAHs in mussels (ng/g dry wt.)

Area Survey	year	Concentration	References
Spain and France, Mediterranean Sea	1996	25.1–82.2 (Σ18 PAHs)	Baumard et al. (1999)
Corsica and Sardinia, Mediterranean Sea	1995	26–390 (Σ18 PAHs)	Baumard et al. (1999)
Baltic Sea	1996	92.5–361 (Σ18 PAHs)	Baumard et al. (1999)
Arcachon Bay France	1995	279–2420 (Σ18 PAHs)	Baumard et al. (1999)
Northern Irish Sea	2000	95-184 (Σ13 PAHs)	Guinan et al. (2001)
Adriatic Sea, Croatia	2006	49.2-134 ng/g wet weight(Σ10 PAHs)	Bihari et al. (2006)
Izmit Bay, Marmara Sea, Turkey	1999	8.5-34 **μg/kg wet weight**(Σ17 PAHs) HPLC method 2.3-21.6 **μg/g wet weight**(Σ17 PAHs) Fluorescence method	Telli-Karakoç et al. (2002)
Istanbul Strait, Turkey	2007	601.1-42.9ng/g wet weight(Σ16 PAHs)	This study

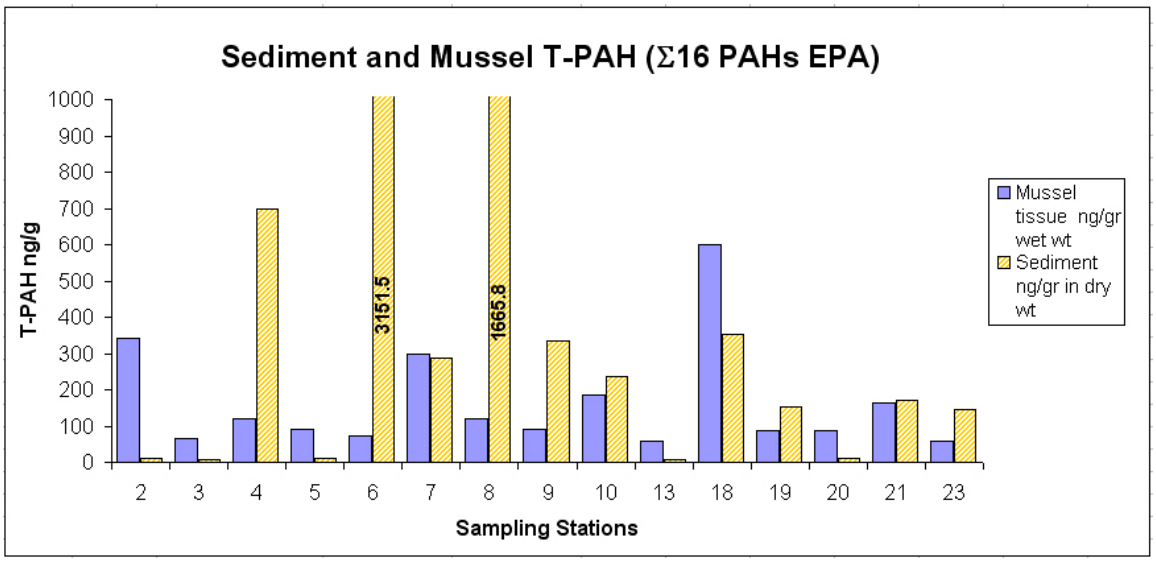


Figure 3.8: T-PAH concentrations of sediment and mussel samples

Table 3.8: T-PAHs concentration of mussels and sediments.

Sampling Stations	Mussel tissue ng/gr wet wt 16 EPA TPAHs	Sediment ng/gr in dry wt 16 EPA TPAHs
2	342	9.60
3	64.8	7.55
4	121	697
5	90.6	10.2
6	73.6	3152
7	299	286
8	121	1666
9	89.2	336
10	187	236
13	58.3	8.75
18	601	354
19	88.9	153
20	87.5	10.1
21	164	171
23	58.8	144

Total concentrations of PAHs in mussel tissues and sediments are not comparable (Figure 3.8 and Table 3.8). The main reason is that the sediments reflect the information about the long time period pollution while mussels show more recent information about pollution. Another reason may be that the suspended particles have no time to precipitate on sediment because of the high current flow but they can be filtered by mussels. Station 2 had high concentration of T-PAHs in mussel tissue and low concentration of T-PAHs in sediment. This station is placed in the Black Sea entrance and open to extreme weather conditions. The main wind direction is

Northern (N) and NorthEastern (NE) in the Strait (Meteor, 2007). Station 2 is open for N and NE wind directions and heavily affected by bad weather conditions in winter time. At that station sediments are well mixed by the waves. This may reduce the level of PAH accumulations in the sediments. According to PAHs source data (will be explained in Section 3.5.2), mussels are mostly affected by petrogenic PAHs at Station 2. Fishing boats at that site could be a possible reason for petrogenic PAH contamination. Stations of 4, 6 and 8 had very high concentrations of T-PAHs in sediments compared to mussel tissue concentrations. Those stations have been affected by the wastewater discharges for a long time period. As a result concentrations of T-PAHs in sediments are found higher than the mussel tissue concentrations.

Table 3.6 and Table 3.4 show the individual PAH concentrations in sediments and mussels respectively. The individual PAH concentrations differ for each site. Both sediment and mussel samples contain Benzo(b)fluoranthene (*BbFA*), Benzo(a)pyrene (*BaP*), Dibenzo(a,h)anthracene (*DBahA*) Anthanthrene (*ATR*) , Cyclopenta(c,d)pyrene (*CPP*) and Dibenzo(a,l)pyrene (*DBalP*) which are known as mutagenic and carcinogenic to mammals and fish (Jacob, 1996. EPA, 2001. Telli-Karakoç et al, 2002). The highest concentrations of BbFA, DBahA, ATR, CPP and DBalP were found at Station 2 (71 ng/g) in mussels and at Station 6 (400 ng/g) in sediments; at Station 2 (2.6 ng/g) in mussels and at Station 6 (29.9 ng/g) in sediments; at Station 2 (1.4 ng/g) in mussels and Station 6 (40.9 ng/g) in sediments; at Station 18 (21.2 ng/g) in mussels and at Station 6 (36.2 ng/g) in sediments; at Station 13 (8.7 ng/g) in mussels respectively. In sediment, Station 4, 6 and 8 had high carcinogenic PAHs concentrations. On the other hand, Station 2, 10, 15 and 18 had high concentrations of carcinogenic PAHs in mussels.

In sediment and mussel; Phenanthrene (*PHE*), Fluoranthene (*FA*), Pyrene (*PY*) and Benzo(b)fluoranthene, Benzo(j)fluoranthene (*BbFA, BjFA*) are the most abundant PAHs through the Istanbul Strait.

One of the most important and the most studied carcinogenic PAH is Benzo(a)pyrene (BaP). Human data specifically linking BaP to a carcinogenic effect are lacking. There are, however, multiple animal studies in many species demonstrating BaP to be carcinogenic following administration by numerous routes (IRIS, 2007). In this

study, BaP concentration was high at Station 4 (63.1 ng/g), 6 (291 ng/g) and 8 (126 ng/g) in sediments and at Station 2 (32.2 ng/g), 10 (12.2 ng/g) and 15 (11.2 ng/g) in mussels. The BaP levels in the mussels from those sites may be hazardous for the human health and consumption must be avoided.

The toxicity of PAHs may increase in the presence of UV-light, probably due to the production of highly destructive singlet oxygen, peroxides, and hydroxyl radicals, in the membranes of the organism following uptake into the tissue which may damage the cell constituents. Due to photomodification, PAHs are structurally changed into many different compounds that show, in most cases, more toxic effects on the organisms compared to the parent compounds (Okay and Karacık, 2007). The mussels and the coastal sediments of the Strait are exposed to the strong sun light during the summer and spring times and thus PAHs may be photomodified easily. Some of the well known potentially photomodifed PAHs are Acenaphthene (AC), Phenanthrene (PHE), Anthracene (AN), Fluoranthene (FA), Pyrene (PY), Chrysene (CHR) and Benzo(a)pyrene (BaP) which were found in the Strait sediment and mussel samples (Table 3.6 and Table 3.4) (Okay and Karacık, 2007; Huang et al, 1995). Sediment samples from Station 4, 6 and 8 and mussel samples from Station 10, 15 and 18 contain high amounts of photomodifed PAHs. Considering that photomodifed PAHs could be 100 times more toxic then the original PAH compounds, (Pelletier et al, 1997) mussels from those sites may be very toxic in case of photomodification.

3.5.2 Source of PAHs

PAHs may be produced either by organisms (biogenic) or derived from incineration processes (pyrolytic), from fossil fuels (petrogenic) or derived from transformation processes in soils and sediments (diagenic) (Hylland, 2006). Each process produce different PAH patterns and it is possible to identify their origins using molecular ratios based on the physical-chemical behaviour of them. Pyrolytic and petrogenic PAHs have a quantitative importance in marine ecosystems. In this study, PAHs are investigated to determine their sources of origin (pyrolytic or petrogenic origin) by using the LMW/HMW ratio (sum of the low molecular weight PAHs / the sum of higher molecular weight PAHs), Phe/Ant (Phenanthrene / anthracene) ratio and Flu/Pyr (Fluoranthene / Pyrene) ratio. The theory of this ratio index (Table 3.9) was based on the fact that the petrogenic contamination was characterised by the predominance of the lower molecular weight PAHs (tri- and tetra-aromatics), while the higher molecular weight PAHs dominate in pyrolytic PAH contamination (Tolun et al., 2006). In this study, The LMW/HMW ratio in the sediment samples range between 0.12 (Station 23) to 0.62 (Station 1). The results (Table 3.10) show for the majority of the samples that, the values of the ratio LMW/HMW are lower than 1, and indicating pollution of pyrolytic origin. In other studies carried out by Unlu et al.(2004) and Readman et al. (2002)shows that the general source for PAHs in the Istanbul Strait sediments is pyrolytic.

Table 3.9: Characteristic values of selected molecular ratios for pyrolytic and petrogenic origins of PAHs [a] Reference to (Qiao et al., 2006).

	Pyrolytic origin[a]	**Petrogenic origin[a]**
Phe/Ant	<10	>15
Flu/Pyr	>1	<1
LMW/HMW	Low	High

Phenanthrene and anthracene are two structural isomers. Because of their different physico-chemical properties, they could behave differently in the environment and could lead to different values for their Phe/Ant ratio that would give useful information on the PAH origin (Gschweng and Hites, 1981). Phenanthrene is

thermodynamically more stable than anthracene. Thus, Phe/Ant ratio is observed to be very high in case of petrogenic PAH pollution, but the ratio becomes lower in pyrolytic contamination cases (Soclo et al, 2000).

Table 3.10: PAHs source data for sediment of the Strait

Sampling Stations	Concentration: ng/gr dry wt			
	TPAH(16EPA)	Phe/Ant	Fla/Pyr	LMW/HMW
1	2.06	10.0	0.8	0.62
2	9.60	3.7	1.0	0.32
3	7.55	3.2	1.3	0.31
4	697	4.3	1.1	0.24
5	10.2	3.9	0.8	0.37
6	3152	3.9	0.9	0.18
7	286	4.7	1.1	0.25
8	1666	3.1	1.1	0.31
9	336	4.2	1.1	0.41
10	236	1.1	0.9	0.24
12	1.12	8.4	1.0	0.37
13	8.75	3.7	1.0	0.33
18	354	3.8	1.0	0.40
19	153	4.0	1.2	0.27
20	10.1	1.9	0.9	0.25
21	171	4.2	1.2	0.25
23	144	1.8	1.2	0.12

On the other hand, fluoranthene (Fla) and pyrene (Pyr) are often associated during natural matrices analyses and are considered as typical pyrolytic products derived from high temperature condensation of lower weight aromatic compounds. Fluoranthene is thermodynamically less stable than pyrene and predominance of fluoranthene over pyrene is characteristic for pyrolytic products, while in petroleum derived PAHs, pyrene is more abundant than fluoranthene (Tolun, 2006). In order to characterise PAH distribution, the molecular origin indices of Phe/Ant were also plotted against Fla/Pyr (Figure 3.9) (Budzinski et al., 1997; Baumard et al., 1999; Scolo et al., 2000; Tolun et al, 2006). The ratios of Phe/Ant <10 and Fla/Pyr>1 are characteristic of pyrolytic contamination.

In Figure 3.10, it is clearly seen that Fla/Pyr ratio is just below 1 for some of the stations (1, 5, 8, 10 and 20). When the other two ratios for those stations are investigated, the origin of the PAHs was also found as pyrolytic; The Phe/Ant ratio were below 10 for all sites except Station 1 (Figure 3.11). The concentration of T-PAHs in Station 1 is very low (2.06ng/g dry wt) compared to the other sites. Thus it may be not true to conclude about the origin of the PAHs measured at that station.

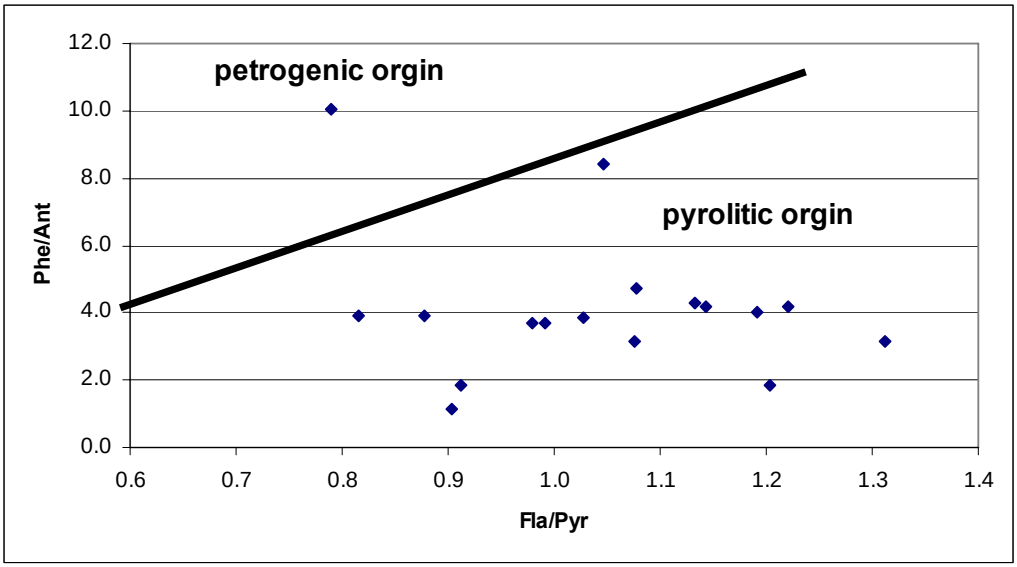


Figure 3.9: Plot of isomeric ratios of Phe/Ant against Fla/Pyr for sediment samples.

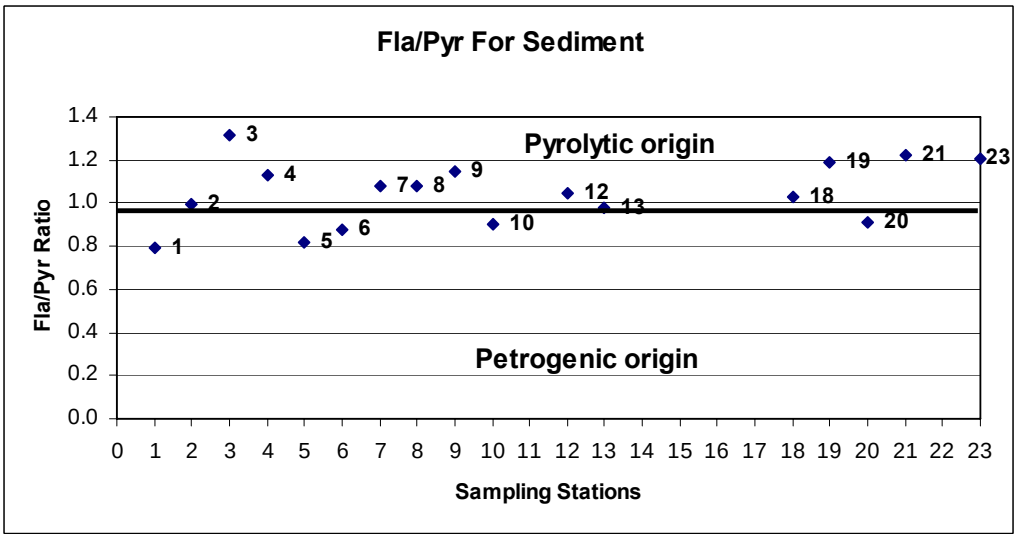


Figure 3.10: Fla/Pyr ratio of sediment samples.

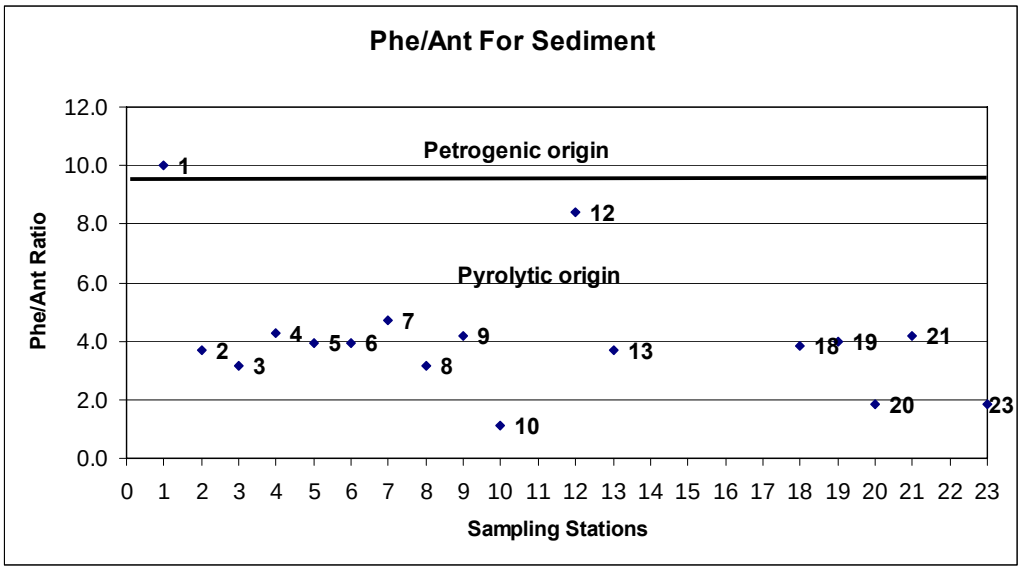


Figure 3.11: Phe/Ant ratio of sediment samples.

Source ratios of PAHs in mussel tissues are shown on Appendix C (Figure 3.12 3.13 3.14). The ratios data from mussel samples shows that the origin of the majority of the PAHs is pyrolytic. Although, mussels have low enzyme activity compared to the higher organisms, they can change the structure of bioaccumulated PAHs, i.e. PAH distribution shifted towards tri- and tetra-aromatics.(Baumard et. al, 1999) Thus it may be not true to decide about the origin of the PAHs according to the PAH concentrations measured at mussels tissue.

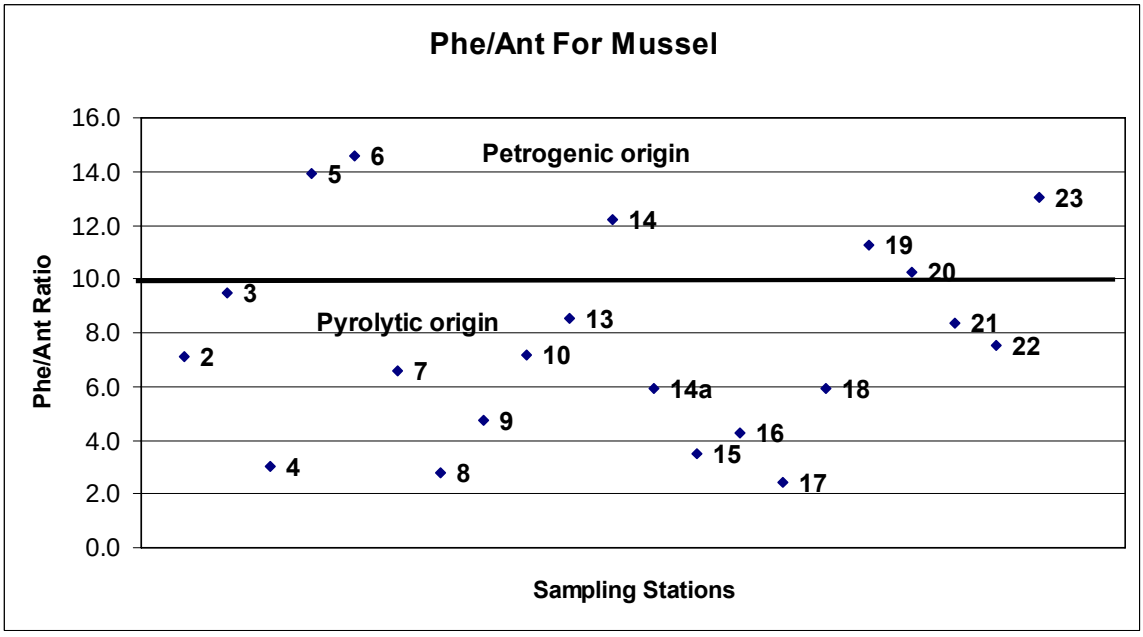


Figure 3.12: Phe/Ant ratio of mussel samples.

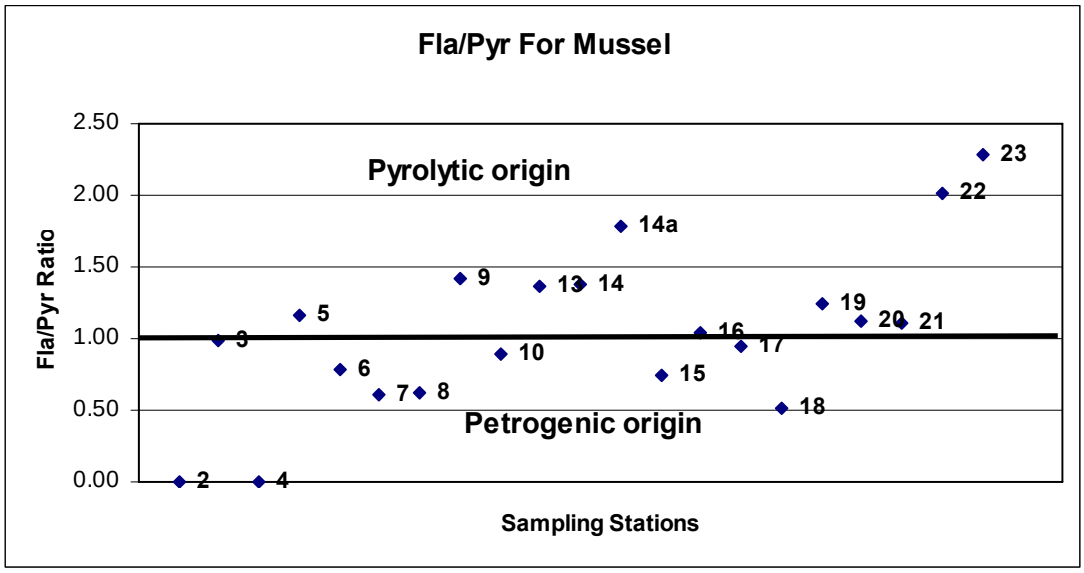


Figure 3.13: Fla/Pyr ratio of mussel samples.

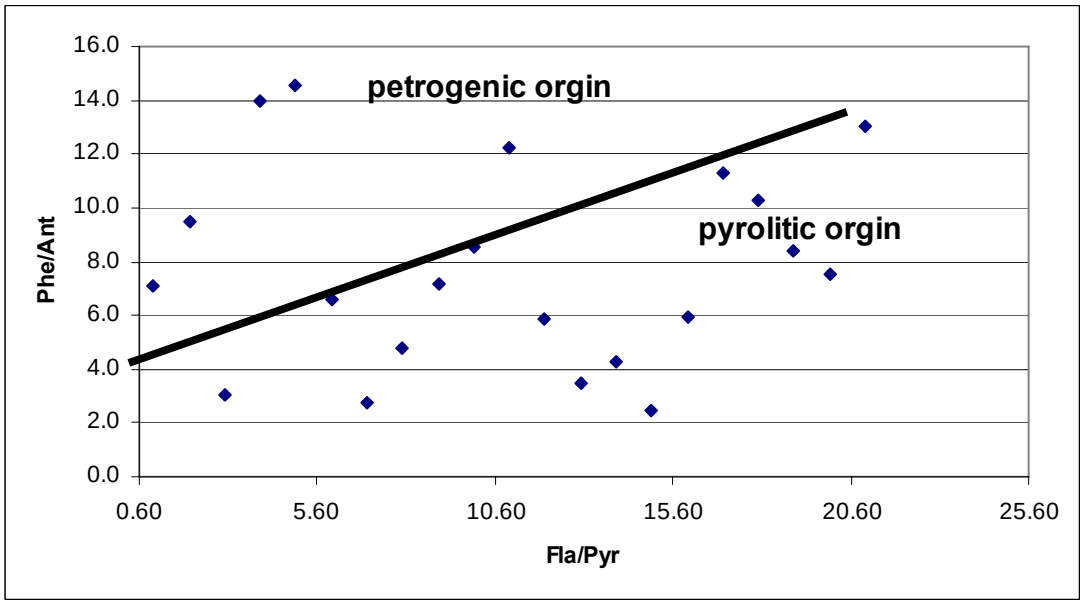


Figure 3.14: Plot of isomeric ratios of Phe/Ant against Fla/Pyr for mussel samples.

A variety of approaches have been developed to use the available ecotoxicological data on PAH to set numerical sediment quality guidelines (SQGs) (Chapman, 1989; MacDonald et al., 2000). Mainly, they involve weight of evidence approaches based on field and laboratory observations of biological effects (e.g. Long et al., 1998) or methods based on variations of the equilibrium partitioning (EqP) approach which calculates the interstitial water concentration at equilibrium and compares it with safe or effect concentrations for the relevant chemicals in water (Di Torro et al., 1991;

Swartz et al., 1995). Selection of the most appropriate SQGs for specific applications can be a daunting task for sediment assessors. In addition, the SQG selection process is further complicated due to uncertainties regarding the bio availability of sediment-associated contaminants, the effects of covarying chemicals and chemical mixtures and ecological relevance of the guidelines (MacDonald et al., 2000). In this study, the Threshold Effect Level (TEL) and Probable Effect Level (PEL) weight of evidence approach was used as SQGs (based on Macdonald et al., 1996; CCME, 1999) in order to evaluate PAH contamination of Istanbul Strait sediments. TEL represents the concentration below which adverse effects are expected to occur only rarely. PEL represents the concentration above which adverse effects are expected to occur frequently (MacDonald et al., 2000) (Tolun et. al 2006).

Sediment samples were predicted to be not toxic if the measured concentrations of a chemical substance were lower than the corresponding TEL. Similarly, samples were predicted to be toxic if the corresponding PELs were exceeded in field-collected sediments (MacDonald et al., 2000).

Individual PAH concentration which exceeds the PEL and TEL were shown in Table 3.11 and 3.12.

Only station 6 exceed the PEL indicated as total LMW concentration. And station 4, 6 and 8 most of the PAH values exceeds the TEL as well as the total LMW PAHs.

Table 3.11: Comparison of the LMW individual PAH contents in sediment with PEL guideline values.

	Ac	Fl	Phe	An	Fa	Py	Baa	Chr	Tot. LMW(ng/g)
PEL[1]	89	144	544	245	1494	1398	693	846	1442
1	0.0	0.1	0.4	0.0	0.3	0.4	0.1	0.1	1.4
2	0.2	0.2	0.8	0.2	0.9	0.9	0.7	0.7	4.5
3	0.3	0.0	0.3	0.1	1.2	0.9	0.2	0.6	3.8
4	1.0	9.7	88.3	20.6	139	121	51.6	43.1	476
5	0.1	0.2	1.1	0.3	1.3	1.7	0.0	0.0	4.8
6	9.9	25.3	322	81.9	539	615	246	211	**2050**
7	1.6	3.8	28.4	6.0	50.5	46.9	19.3	16.8	173
8	3.8	18.8	233	74.1	307	285	134	96.2	1152
9	1.5	3.5	31.8	7.6	53.0	46.3	20.5	17.7	182
10	3.4	3.1	11.1	9.8	34.9	38.6	16.3	14.2	131
12	0.0	0.0	0.1	0.0	0.2	0.1	0.1	0.1	0.6
13	0.0	0.2	1.1	0.3	1.1	1.2	0.4	0.5	4.8
18	1.9	8.3	56.8	14.8	62.4	60.7	21.9	18.6	246
19	1.2	2.4	18.0	4.5	27.5	23.1	10.2	9.7	96.7
20	0.0	0.2	0.7	0.4	1.0	1.1	0.3	0.2	4.0
21	2.2	2.2	19.3	4.6	33.4	27.3	10.4	9.9	109
23	3.2	0.4	7.0	3.8	25.8	21.4	11.4	10.9	83.8

[1]PEL = Probable Effect Level

Ac: Acenapthalene; Fl: Fluorene; Phe: Phenanthrene; An: Anthracene; Fa: Fluoranthene; Py: Pyrene; Baa: Benz(a)anthracene; Chr: Crysene.

Table 3.12: Comparison of the LMW individual PAH contents in sediment with TEL guideline values.

	Ac	Fl	Phe	An	Fa	Py	Baa	Chr	Tot. LMW(ng/g)
TEL[1]	6.7	21.2	86.7	46.9	113	153	74.8	108	312
1	0.0	0.1	0.4	0.0	0.3	0.4	0.1	0.1	1.4
2	0.2	0.2	0.8	0.2	0.9	0.9	0.7	0.7	4.5
3	0.3	0.0	0.3	0.1	1.2	0.9	0.2	0.6	3.8
4	1.0	9.7	**88.3**	20.6	**139**	121	51.6	43.1	**476**
5	0.1	0.2	1.1	0.3	1.3	1.7	0.0	0.0	4.8
6	**9.9**	**25.3**	**322**	**81.9**	**539**	**615**	**246**	**211**	**2050**
7	1.6	3.8	28.4	6.0	50.5	46.9	19.3	16.8	173.4
8	3.8	18.8	**233**	**74.1**	**307**	**285**	**134**	96.2	**1152**
9	1.5	3.5	31.8	7.6	53.0	46.3	20.5	17.7	182.1
10	3.4	3.1	11.1	9.8	34.9	38.6	16.3	14.2	131.4
12	0.0	0.0	0.1	0.0	0.2	0.1	0.1	0.1	0.6
13	0.0	0.2	1.1	0.3	1.1	1.2	0.4	0.5	4.8
18	1.9	8.3	56.8	14.8	62.4	60.7	21.9	18.6	245.6
19	1.2	2.4	18.0	4.5	27.5	23.1	10.2	9.7	96.7
20	0.0	0.2	0.7	0.4	1.0	1.1	0.3	0.2	4.0
21	2.2	2.2	19.3	4.6	33.4	27.3	10.4	9.9	109.4
23	3.2	0.4	7.0	3.8	25.8	21.4	11.4	10.9	83.8

[1]TEL = Threshold Effect Level

Ac: Acenapthalene; Fl: Fluorene; Phe: Phenanthrene; An: Anthracene; Fa: Fluoranthene; Py: Pyrene; Baa: Benz(a)anthracene; Chr: Crysene.

3.6 Filtration rate of mussels

Table 3.13 shows the filtration rate and neutral red-lysosomal stability results (Figure 3.15 3.16). The filtration rate of the mussels shows a decreasing trend from Station 2 to 5 and then increases gradually towards the Marmara Sea. The minimum values of filtration rate were found for stations 5, 6 and 7. Station 5 and 6 are situated in small bays which are busy with yachting/fishing activities and stations 6 and 7 are closer to the mouths of two small creeks carrying domestic wastewaters. Although there is a decreasing trend from station 13 towards station 18 (except station 16) in the filtration rate of the mussels collected from the Asian part, the results did not differ significantly. Tables are given in Appendix D.

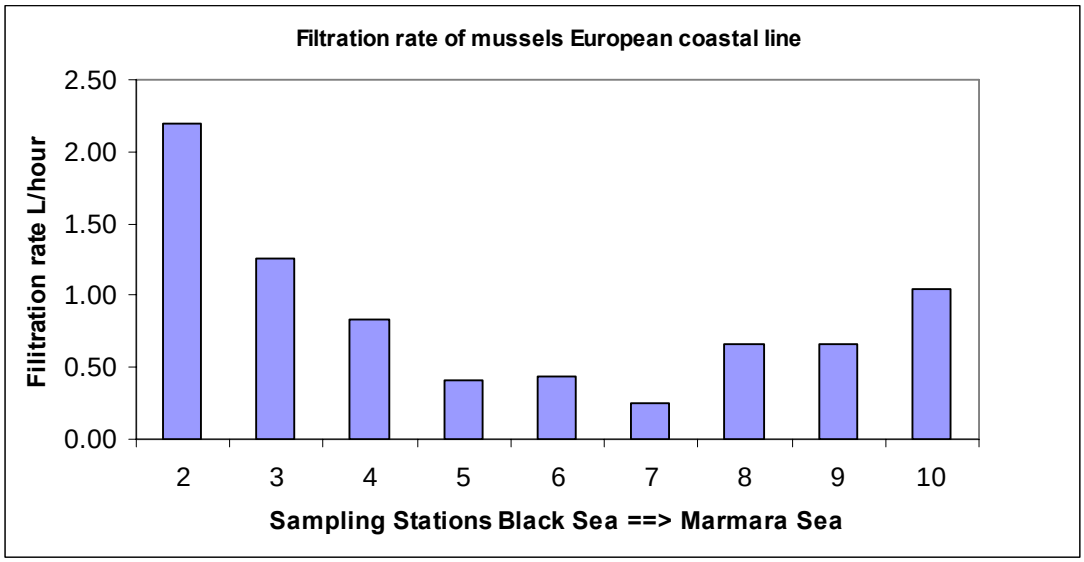


Figure 3.15: Filtration rate of mussels (European coastal line).

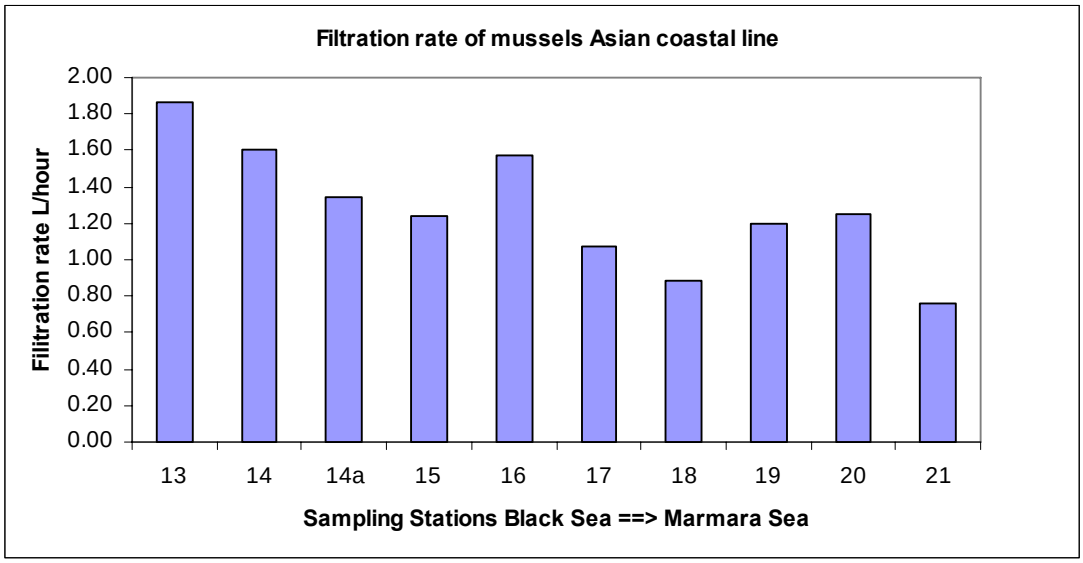


Figure 3.16: Filtration rate of mussels (Asian coastal line).

Table 3.13: The filtration rate and neutral red-retention (lysosomal stability) results with TPAHs concentrations.

Sampling Stations	Mussel ng/g wet wt 16 EPA TPAHs	FH L/hour	NR min.	Sediment ng/g dry wt 16 EPA TPAHs
2	342	2.19	141	9.60
3	64.7	1.26	135	7.55
4	121	0.83	148	697
5	90.6	0.41	84	10.2
6	73.6	0.43	56	3152
7	299	0.25	30	286
8	121	0.66	39	1666
9	89.2	0.67	29	336
10	186	1.04	87	236
13	58.3	1.86	63	8.75
14	42.8	1.60	77	
14a	72.8	1.34	86	
15	237	1.24	30	
16	116	1.57	57	
17	85.7	1.07	108	
18	601	0.88	45	354
19	88.9	1.20	50	153
20	87.5	1.25	26	10.1
21	164	0.76	27	171
22	98.2	0.94	62	
23	58.8	0.68	29	144

3.7 Neutral red- lysosomal stability

Table 3.13 shows the filtration rate and neutral red-lysosomal stability results (Figure 3.17 3.18). Similar to the results obtained for filtration rate, lysosomal stability has higher values from 2 to 4 and then starts to decrease. Those values obtained for stations 2, 3 and 4 are consistent with the lysosomal stability values obtained for the corresponding stations (13, 14,14a) situated on the European coast. Tables are given in Appendix D.

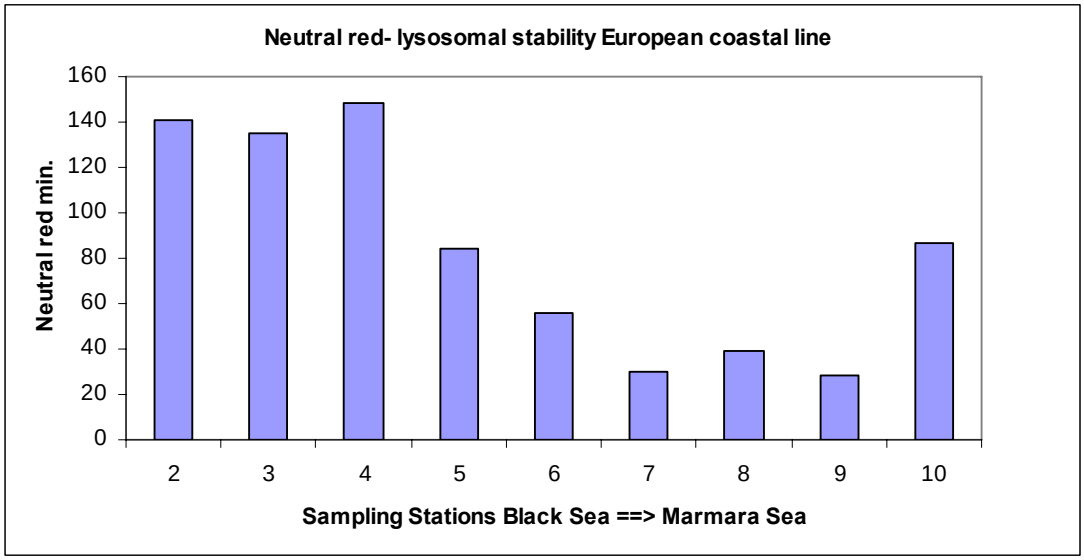


Figure 3.17: Neutral red- lysosomal stability (European coastal line).

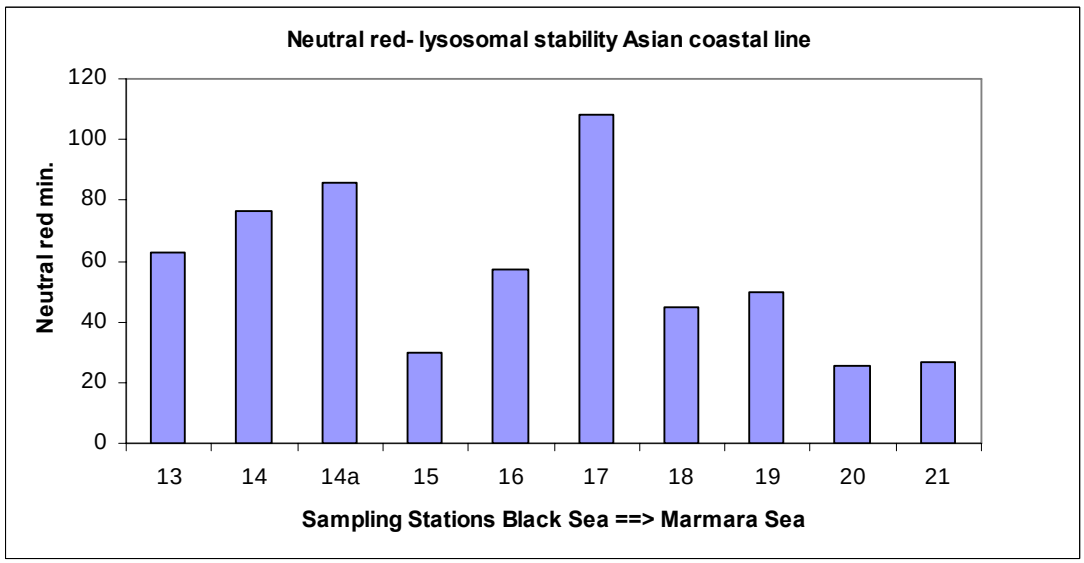


Figure 3.18: Neutral red- lysosomal stability (Asian coastal line).

3.8 Sediment toxicity

Percent inhibition of microalgal cultures were calculated by comparing the number of cells in the concentrated (undiluted) water elutriates of the sediments and in the control samples after incubation of 4 days. The inhibitions of algae incubated in sediment elutriates show an increasing trend and reach its maximum value at station 4 (54 %) and then start to decrease along the European coastline (Figure 3.19). Generally the values obtained from the five stations (1-5) closer to Black Sea side have higher toxicity compared to the stations (6-10) closer to Marmara Sea at the European coast. No inhibition was observed for the samples collected from station 8. Station 9 which has a higher toxicity value compared to the neighbouring stations is situated on a touristic site occupied with restaurants, cafes etc. which may cause a heavy local pollution on the coast.

The sediment samples could not be collected between the stations of 14 and 17 situated on the Asian part. Sediment toxicity values of Stations 12 and 13 which are closer to Black Sea are found higher similar to the corresponding stations (1 and 2) situated at the European part.

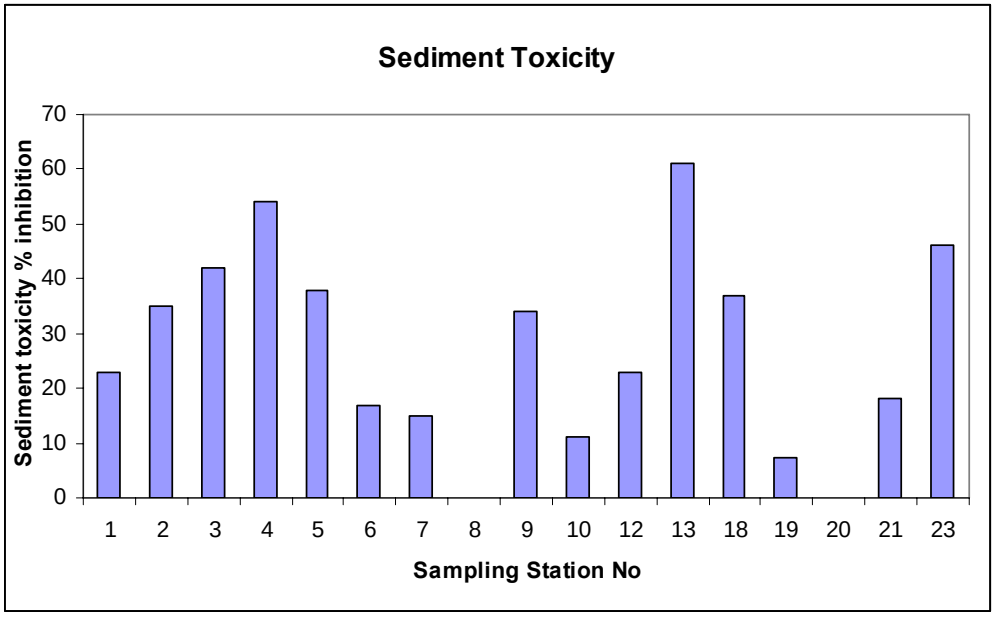


Figure 3.19: Sediment toxicity inhibition% for sampling sites.

The results shows that there is no significant correlation between the results of algal toxicity tests performed by sediment elutriates and threshold effect level (TEL) of

analyzed PAHs (Figure 3.20). This may explain by the sediment toxicity test is base on water soluble fraction of the sediment and PAHs have a very low solubility on water.

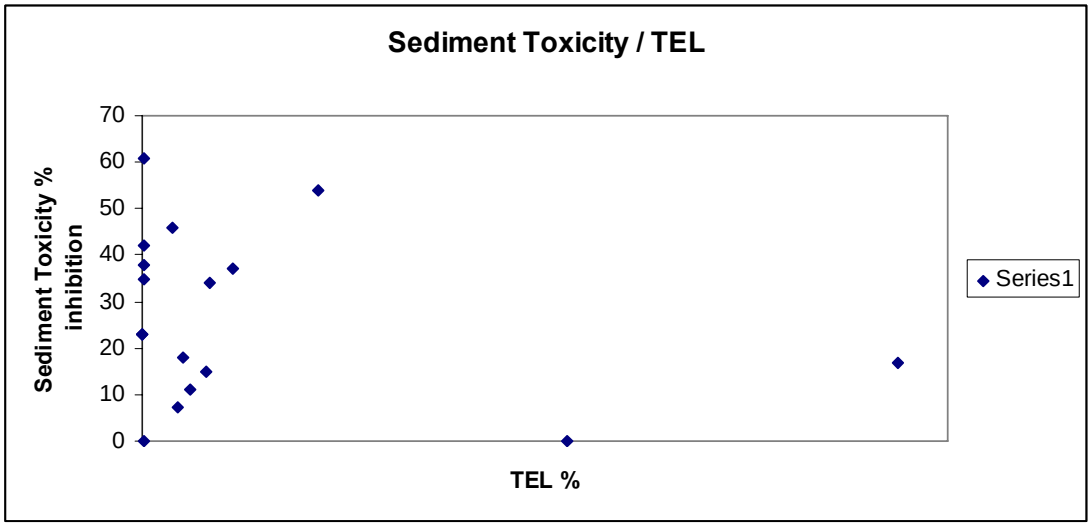


Figure 3.20: Sediment Toxicity / Threshold Effect Level.

4 CONCLUSIONS

This study documents the first known ecotoxicological monitoring study including the individual analysis of PAHs in sediments and mussels together with bioassay and biomarker techniques along the Istanbul Strait coast line.

Bottom topography of the Strait shows different properties. The coastline between the stations of 14-17 shows rocky characteristics.

Salinity levels found in this study were correlated with the values measured before. Nutrient data shows that there is an increase in nitrogen [(NO_3+NO_2) – N] (around 16-22μg/L increase in average) within the last ten years period while no change has been observed in the ortho-phosphate concentration. Chlorophyll-a concentration also showed an increase in those years that may be an indicator of eutrophication as a result of increase in nutrient levels. In this study, only the surface water samples were taken. Thus, more accurate nutrient information, water sampling thought to water column (euphotic zone ~0-30m depth) would give a more accurate date.

Carcinogenic PAHs (*ATR, DBahA, IP, BaP, BkFA, BbFA, Chr, BaA*) were found in sediment and mussel samples. Their contents are very high at Station 2, 10, 13, 15 and 18 in mussels and Station 6, 4 and 8 in sediments. These sites should be considered as a target area for further management strategies and risk assessment studies.

Sediment data shows that most of the PAHs contamination is originated from pyrolytic inputs. House heating system, car and ship exhausts may be the source of this contamination. Considering the 50000 ship/year cross the Strait, a new exhaust emission regulation may be useful for the Strait ecosystem.

The TEL/PEL analyses suggest that Station 4, 6 and 8 were contaminated by toxic PAH compounds. At those Stations, surface sediments will always create a risk for the ecology of the strait due to possible resuspension and water movements.

Majority of the PAHs source in mussel samples from the Strait are also pyrolytic like sediment samples. There is no direct correlation between the concentrations of T-PAHs in sediments and the mussels.

Biomarker techniques give us information about the general pollution. Filtration rate and lysomal stability of the mussel samples show a similar trend in most cases for both the European part and Asian part of the Strait. On the other hand, the sediment toxicity and biomarker results do not always correlate probably depending on the nature of the pollutants.

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APPENDIX A

Sediment Characteristic

Station 1 (Rumeli feneri)

Sampling depth: 3m.

Colour: Brown

Content: Lots of broken sea shell parts.

Station 2 (Garipçe köyü)

Sampling depth: 1m.

Colour: Brown-yellow

Content: Shells parts.

Station 3 (Rumeli Kavağı)

Sampling depth: 1m.

Colour: Brown colour.

Station 4 (Büyükdere)

Sampling depth: 2m.

Colour: Dark brown

Content: H_2S smell.

Station 5 (Tarabya)

Sampling depth: 1m.

Colour: Dark brown.

Station 6 (istinye)

Sampling depth: 3.9m.

Colour: Dark brown

Content: Small rocks particles.

Station 7 (Balta Limanı)

Sampling depth: 3.8m.

Colour: Dark brown

Content: H_2S smell.

Station 8 (Bebek)

Sampling depth: 4.8m.

Colur: Dark brown.

Station 9 (Ortaköy)

Sampling depth: 2.5m.

Colour: Black colour

Content: H_2S smell.

Figure A.1: Sediment of Station 9.

Station 10 (Beşiktaş)

Sampling depth: 1.4m.

Colour: Brown colour

Content: shells.

Station 12 (Anadolu Feneri)

Sampling depth: 2m.

Colour: Brown colour.

Content: shell particles.

Figure A.2: Sediment of Station 12.

Station 13(Poyraz)

Sampling depth: 1.9m.

Colour: Dark brown.

Content: light H_2S smell.

Figure A.3: Sediment of Station 13.

Station 18 (Kandilli)

Sampling depth: 2.8m.

Colour: Black colour.

Content: H_2S smell.

Figure A.4: Sediment of Station 18.

Station 19 (Kuzguncuk)

Sampling depth: 2m.

Colour: Black colour.

Content: H_2S smell.

Figure A.5: Sediment of Station 19.

Station 20 (Üsküdar)

Conditions: High current speed.

Sampling depth: 2.3m.

Colour: Brown

Content: broken shell particles.

Figure A.6: Sediment of Station 20.

Station 21 (Moda iskelesi)

Sampling depth: 1.6m.

Colour: Brown.

Content: Broken shell particles.

Figure A.7: Sediment of Station 21.

Station 23 (Büyük ada Plaj)

Sampling depth: 1m.

Colour: Brown colour.

Conditions: Relatively and visually clean site compared to the other sites. Station 23 can be effected by heybeli ada ISKI wastewater discharge. (Figure A.8)

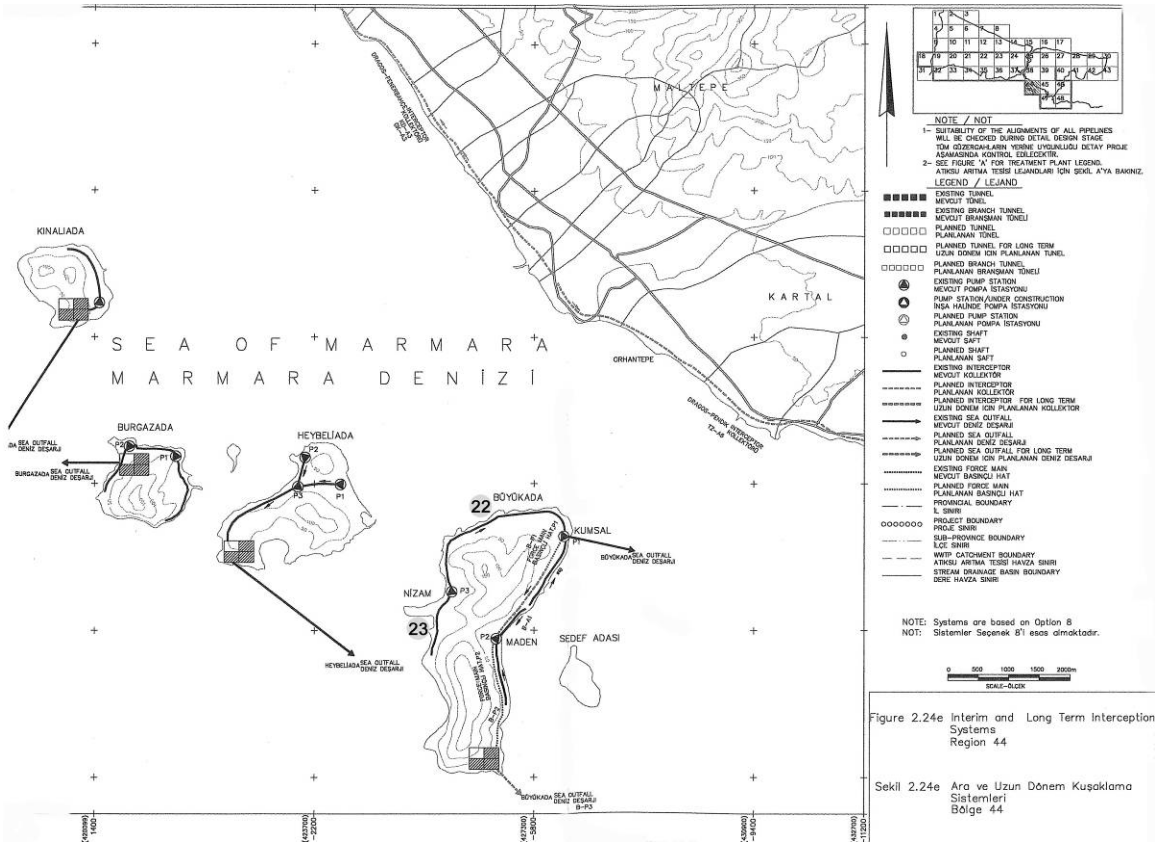

Figure A.8: Sampling station 23 and 22.

APPENDIX B

Nutrients results

Nitrite and nitrate nitrogen [(NO_3+NO_2) – N]

Table B.1: Nitrite and nitrate nitrogen [(NO_3+NO_2) – N)].

Sapmling Points	April 2006	june 2006	september 2006	january 2007
	N-(NO_2+NO_3)µg/lt	N-(NO_2+NO_3)µg/lt	N-(NO_2+NO_3)µg/lt	N-(NO_2+NO_3)µg/lt
1	62.9	8.38	39.9	16.4
2	48.2	32.1	43.4	369
3	11.5	37.1	29.8	14.8
4	15.9	39.6	36.2	11.5
5	24.7	27.1	31.1	23.0
6	57.1	30.9	50.3	19.7
7	8.53	27.1	28.1	6.57
8	7.06	13.4	17.3	14.8
9	7.06	20.9	25.1	21.4
10	8.53	22.1	24.4	18.1
11	74.7	25.9	52.1	31.2
12	4.12	7.13	9.84	8.21
13	27.6	7.13	19.0	13.1
14	20.3	9.63	18.1	14.8
15	23.2	22.1	30.0	18.1
16	14.4	10.9	16.3	8.21
17	5.59	13.4	14.0	18.1
18	12.9	14.6	21.7	13.1
19	20.3	24.6	29.4	11.5
20	24.7	23.4	31.4	13.1
21	10.0	10.9	17.6	23.0
22	12.9	43.4	42.5	9.86
23	1.18	13.4	18.7	13.1

Orthophosphate phosphate [(o-PO_4)-P]

Table B.2: Orthophosphate phosphate [(o-PO_4)-P].

Sapmling Points	April 2006	june 2006	september 2006	january 2007
	P-(PO_4) μg/lt	P-(PO_4) μg/lt	P-(PO_4) μg/lt	P-(PO_4) μg/lt
1	4.98	4.00	1.75	0.00
2	0.94	0.67	6.75	43.8
3	4.98	4.00	1.75	0.00
4	2.96	2.33	6.75	0.50
5	0.94	0.67	1.75	5.50
6	0.94	0.67	1.75	2.17
7	4.98	4.00	0.00	2.17
8	2.96	2.33	0.00	0.50
9	9.01	7.33	11.8	3.83
10	7.00	5.67	9.25	2.17
11	9.01	7.33	14.3	12.2
12	0.94	0.67	1.75	0.50
13	0.00	0.00	4.25	3.83
14	0.00	0.00	0.00	0.50
15	0.94	0.67	14.3	7.17
16	0.00	0.00	4.25	2.17
17	7.00	5.67	6.75	2.17
18	0.94	0.67	1.75	0.50
19	0.94	0.67	4.25	0.50
20	7.00	5.67	6.75	0.50
21	11.0	9.00	16.8	10.5
22	4.98	4.00	11.8	3.83
23	2.96	2.33	9.25	3.83

Silicate (Si)

Table B.3: Silicate.

Sapmling Points	April 2006	june 2006	september 2006	january 2007
	Si µg/lt	Si µg/lt	Si µg/lt	Si µg/lt
1	569	149	132	133
2	162	149	248	1566
3	256	74.6	190	100
4	225	149	393	167
5	225	187	161	167
6	287	224	190	167
7	225	448	219	133
8	381	448	161	100
9	319	336	190	100
10	319	261	190	133
11	287	299	248	100
12	350	149	132	133
13	225	149	104	133
14	256	112	104	233
15	256	187	190	267
16	319	187	132	200
17	319	112	161	167
18	194	187	104	167
19	225	187	161	133
20	2245	261	161	200
21	131	299	306	300
22	194	187	190	167
23	131	410	190	233

Chlorophyll a

Table B.4: Chlorophyll a concentrations.

		Chlorophyll a concentrations (Ch-a μg/L)			
Sampling Sites No	**Sampling Sites Name**	**April 2006**	**June 2006**	**September 2006**	**January 2007**
1	**Rumeli feneri ilerisi**	1.02	1.75	0.74	0.14
2	**Garipçe köyü**	2.28	2.31	0.60	0.77
3	**Rumeli Kavağı**	1.97	1.40	0.69	0.63
4	**Büyükdere**	1.74	2.34	1.22	1.08
5	**Tarabya**	1.71	2.61	0.70	1.43
6	**İstinye**	1.71	2.68	0.60	1.24
7	**Balta Limanı**	1.61	1.56	0.83	2.06
8	**Bebek**	1.36	0.99	0.73	1.44
9	**Ortaköy**	2.09	1.47	1.18	1.11
10	**Beşiktaş**	1.31	1.66	1.21	0.67
11	**Ahırkapı ilerisi**	1.10	1.53	0.86	3.93
12	**Anadolu Feneri**	0.83	0.60	0.44	0.50
13	**Poyraz**	1.13	1.11	0.53	0.81
14	**Anadolu Kavağı**	2.82	1.34	0.62	1.71
15	**Yalıköy- Beykoz**	1.89	1.66	0.52	0.47
16	**Çubuklu**	1.97	1.55	0.63	1.34
17	**Kavacık**	1.82	0.66	0.49	1.13
18	**Kandilli**	1.68	0.71	0.84	1.75
19	**Kuzguncuk**	1.26	1.11	0.58	1.08
20	**Üsküdar**	1.67	0.91	0.55	1.09
21	**Moda iskelesi**	1.44	2.99	1.34	0.43
22	**Büyük ada iskele**	1.35	0.86	0.70	1.51
23	**Büyük ada plaj**	1.18	1.30	1.60	2.88

APPENDIX C

Table C.1: PAHs source data for mussel tissue

Sampling Stations	**Concentration:** Benzo(a)pyrene	ng/gr wet wt 16EPA TPAHs	Phe/Ant ratio	Fla/Pyr ratio	LMW/HMW ratio *
2	32.15	342	7.1	n.d	1.30
3	0.87	64.8	9.5	0.98	0.53
4	4.67	121	3.1	n.d	0.83
5	1.96	90.7	13.9	1.16	0.34
6	2.30	73.6	14.6	0.79	0.22
7	3.21	299	6.6	0.61	1.74
8	3.60	121	2.8	0.62	0.24
9	3.42	89.2	4.8	1.42	0.18
10	12.22	186	7.2	0.89	0.17
13	0.89	58.4	8.6	1.37	0.38
14	0.82	42.9	12.2	1.37	0.41
14a	0.52	72.8	5.9	1.78	0.92
15	11.21	237	3.5	0.74	0.11
16	5.70	116	4.2	1.04	0.14
17	3.01	85.7	2.4	0.94	0.24
18	9.22	601	5.9	0.52	1.62
19	3.15	88.9	11.3	1.24	0.25
20	4.42	87.6	10.3	1.12	0.71
21	7.59	164	8.4	1.10	0.17
22	3.56	98.2	7.5	2.01	0.22
23	1.30	58.8	13.0	2.29	0.33

APPENDIX D

Filtration rate of mussels

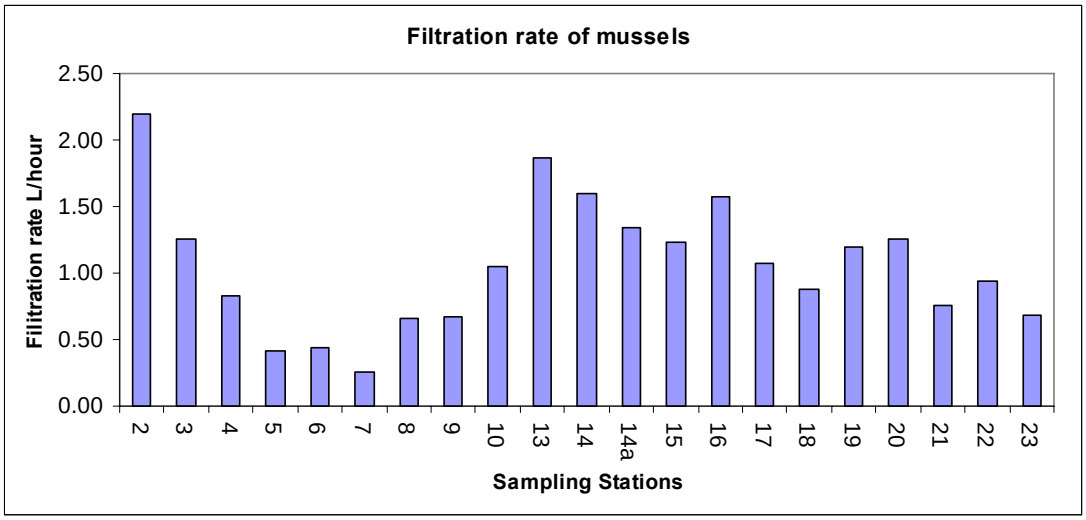

Figure D.1: Filtration rate of mussels from the Strait coastal line

Neutral red- lysosomal stability

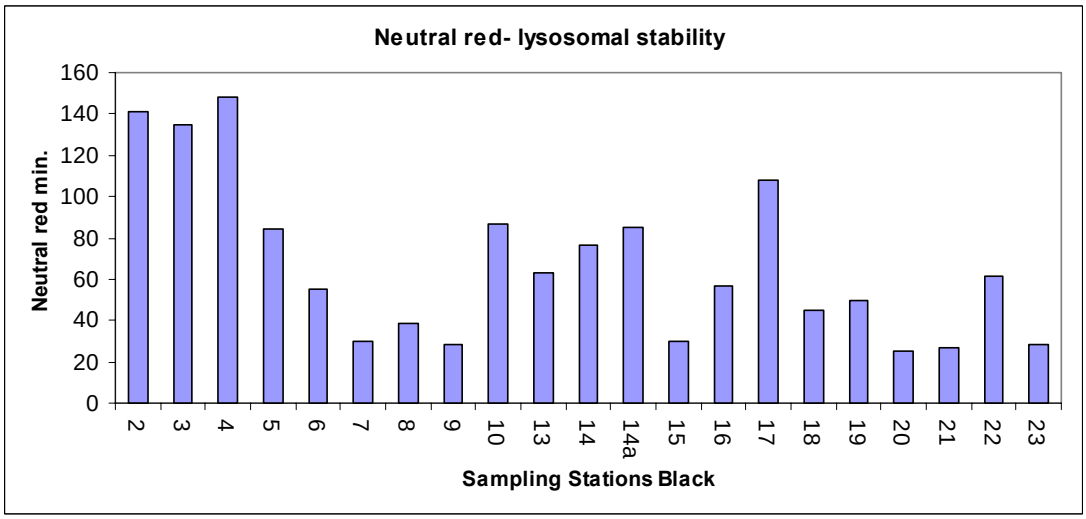

Figure D.2: Neutral red- lysosomal stability from the Strait coastal line.

RESUME

Burak Karacik was born in 1980 in Istanbul. He was graduated from Inönü Technical High School in 1998. Afterwards, he began his education at Istanbul Technical University, Faculty of Naval Architecture and Ocean Engineering in 1998, and was graduated in 2005. At present, he continues his education at the Istanbul Technical University, Institute of Science and Technology, Ocean Engineering Program and working as a research assistant at Naval Architecture and Ocean Engineering Faculty, Oceanography Division.