DOKUZ EYLUL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DISTRIBUTION OF ORGANIC POLLUTANTS IN SURFACE SEDIMENTS FROM AEGEAN COAST

by
Lütfi Tolga GÖNÜL

July, 2011
İZMİR

DISTRIBUTION OF ORGANIC POLLUTANTS IN SURFACE SEDIMENTS FROM AEGEAN COAST

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by
Lütfi Tolga GÖNÜL

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Ph.D. THESIS EXAMINATION RESULT FORM

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DISTRIBUTION OF ORGANIC POLLUTANTS IN SURFACE SEDIMENTS FROM AEGEAN COAST

ABSTRACT

Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (TALI) were determined in fourteen surface sediment with three replicates collected from the Eastern Aegean coast in 2008. Total concentrations of OCPs, PCBs, PAHs and TALI in sediments ranged from bdl to 17.8, bdl to 26.1, 73.5 to 2170 and 330 to 2660 ng/g dwt, respectively. The results indicated that the DDTs were the predominant contaminant in sediments. *p,p'*-DDE was the most often found OCP at all stations except Dardanelles Strait Entrance. DDTs in sediments may be derived from the aged and weathered agricultural soils and transported by surface run off from the rivers. OCPs and PCBs were present in noticeably higher concentrations at Izmir Inner Bay than the other sites. According to established sediment quality guidelines, DDTs at four sites and heptachlor at two sites would be more concerned for the ecotoxicological risk in the Eastern Aegean. In addition, the risk of adverse biological effects from the levels of PCBs at sites Candarli Bay and Izmir Inner Bay should be significant.

Both pyrolytic and petrogenic PAHs are present in most samples, although petroleum-derived PAHs are dominant at Izmir Inner Bay, Dardanelles Strait and pyrolytic sources are prevalent in other sampling sites. A high contribution of perylene to the total penta PAHs was found greater than 70 per cent in Meric River Estuary, Dikili, Candarli and Gokova Bays. The spatial distributions of TALI and PAHs indicated that urban run-off and transport from the continental shelf is the major input pathway of anthropogenic and biogenic hydrocarbons from terrestrial sources in the near-shore area. PAH levels at all sites were below the effects range-low (ERL) and effects range-median (ERM) values except fluorene. The average and maximum fluorene concentrations exceeded ERL, but below ERM in the Izmir Inner Bay. The results indicated that the sediments should have potential biological impact.

Keywords : Polycyclic aromatic hydrocarbons, aliphatic hydrocarbons, organochlorinated pesticides, PCBs, sediment, pollution, molecular ratios, risk assessment, Eastern Aegean coast

EGE KIYILARI YÜZEY SEDİMENTLERİNDE ORGANİK KİRLETİCİLERİN DAĞILIMI

ÖZ

Doğu Ege kıyılarından 2008'de üç tekrarlı toplanan ondört adet yüzey sediment örneğinde organoklorlu pestisitler (OCPs), poliklorlu bifeniller (PCBs), polisiklik aromatik hidrokarbonlar (PAHs) ve alifatik hidrokarbonlar (TALI) tayin edilmiştir. OCPs, PCBs, PAHs ve TALI'lerin toplam konsantrasyonları sırasıyla bdl-17.8, bdl-26.1, 73.5-2170 ve 330-2660 ng/g kuru ağırlık aralığında değişmektedir. Sonuçlar DDT'lerin sediment örneklerinde baskın tür olduğunu göstermiştir. Çanakkale Boğazı girişi haricindeki tüm istasyonlarda en sık rastlanan bileşik *p,p'*-DDE'dir. Sedimentte DDT'ler tarımsal alanlardan kaynaklanmaktadır ve nehirler ile taşınımları gerçekleşmektedir. OCPs ve PCB'ler İzmir İç Körfez'de diğer istasyonlardan daha yüksek seviyede bulunmuştur. Sediment kalite kılavuzlarına göre; Doğu Ege'de DDT türevlerinin dört istasyonda ve heptaklorun iki istasyonda ekotoksik risk taşıdığı ortaya çıkmaktadır. Buna ilaveten, Çandarlı ve İzmir İç Körfez istasyonlarında ölçülen PCB'lerin neden olduğu biyolojik etki riski önemli çıkmıştır.

Örneklerde hem pirolitik hemde petrol kökenli PAH'lar bulunmuştur. İzmir İç Körfez ve Çanakkale Boğazı'nda petrolden ileri gelen PAH lar yaygın olmasına karşın, diğer istasyonlarda pirolitik kaynaklı PAH'lar hakimdir. Meriç Deltası, Dikili, Çandarlı ve Gökova Körfezlerinde perilen bileşiğinin beş halkalı PAH'ların toplamına oranı yüzde 70'den fazla bulunmuştur. Toplam alifatik ve polisiklik aromatik hidrokarbonların bölgesel dağılımları, kıta sahanlığından ve evsel atıklardan gelen karasal kaynaklı antropojenik ve biyojenik hidrokarbonların başlıca giriş yolu olduğunu göstermiştir. Tüm istasyonlardaki PAH seviyeleri fluorene dışında düşük etki aralığı ve medyan etki aralığı değerlerinin altında bulunmuştur. Ortalama ve en yüksek fluorene konsantrasyonları İzmir İç Körfez'de düşük etki aralığını aşmıştır, ancak medyan etki aralığının altında bulunmuştur. Sonuçlar sedimentlerin potansiyel biyolojik etkisinin olması gerektiğine işaret etmektedir.

Anahtar Kelimeler: Polisiklik aromatik hidrokarbonlar, alifatik hidrokarbonlar, organoklorlu pestisitler, PCBs, sediment, kirlilik, moleküler oranlar, risk değerlendirmesi, Doğu Ege kıyıları

CONTENTS

Page

THESIS EXAMINATION RESULT FORM ii
ACKNOWLEDGEMENTS iii
ABSTRACT iv
ÖZ v

CHAPTER ONE – INTRODUCTION 1

CHAPTER TWO – ORGANIC POLLUTANTS 5

- 2.1 Pesticides 8
  - 2.1.1 Definition and Classification of Pesticides 8
  - 2.1.2 The current status of POP pesticides use 9
    - 2.1.2.1 Aldrin and Dieldrin 10
    - 2.1.2.2 DDT, DDE and DDD 12
    - 2.1.2.3 Heptachlor and Heptachlor Epoxide 13
    - 2.1.2.4 Hexachlorocyclohexane 14
    - 2.1.2.5 Hexachlorobenzene 16
    - 2.1.2.6 Endrin 17
  - 2.1.3 Pesticide Toxicity 18
    - 2.1.3.1 Acute Toxicity and Acute Effects 18
    - 2.1.3.2 Chronic Toxicity and Chronic Effects 19
- 2.2 Polychlorinated Biphenyls 19
  - 2.2.1 Physical and chemical properties 21
- 2.3 Petroleum Hydrocarbons 22
  - 2.3.1 Aliphatics (paraffins) 23
  - 2.3.2 Polycyclic Aromatic Hydrocarbons 24
    - 2.3.2.1 Chemistry of Petroleum Hydrocarbons 27
    - 2.3.2.2 Toxicity of Petroleum Hydrocarbons 29

CHAPTER THREE – STUDY AREA 30

3.1 Description of Study Area 30
3.2 Water Budget in the Aegean Sea 32
3.3 Hydrophysical Characteristic 32
3.4 Geological Characteristics of Aegean Sea 33
3.5 Chemical Characteristics of Aegean Sea 35

CHAPTER FOUR – MATERIAL AND METHODS 36

4.1 Sampling and Measurement of Environmental Parameters 36
4.2 Analytical Procedures 38
  4.2.1 Organochlorine Pesticides and PCBs Analysis 38
  4.2.2 Gas Chromotography Conditions for Halogenated Hydrocarbons 40
  4.2.3 Quality Assurance for OCPs 40
  4.2.4 Petroleum Hydrocarbon Analysis 41
  4.2.5 Gas Chromotography Conditions for Petroleum Hydrocarbons 42
  4.2.6 Quality Assurance for Petroleum Hydrocarbons 43
4.3 Statistical Analysis 44

CHAPTER FIVE – RESULTS AND DISCUSSION 51

5.1 Total hydrocarbons in sediment 51
5.2 Aliphatic hydrocarbons in sediment 51
  5.2.1 n-Alkanes 51
  5.2.2 Isoprenoid alkanes 59
5.3 PAHs in sediment 61
  5.3.1 PAH composition and sources 63
  5.3.2 Perylene origin 68
5.4 Statistical Analysis for aliphatics and PAHs 70
5.5 Assessment of Sediment Quality Using Biological Thresholds 78

5.6 Organochlorine pesticides in the sediments from the Aegean coast 79
    5.6.1 Contamination profiles of OCPs in sediment 79
    5.6.2 Characteristics of OCP Contamination in Sediments 85
    5.6.3 Data Analysis 90
    5.6.4 Potential biological effects of OCPs 94
    5.6.5 Ecotoxicological concerns for PCBs 97

CHAPTER SIX – CONCLUSIONS 98

REFERENCES 101

CHAPTER ONE

INTRODUCTION

Persistent organic pollutants (POPs) is the common name of a group of pollutants that are semivolatile, bioaccumulatative, persistent and toxic (Vallack et al., (1998); Jones & de Voogt, 1999). Organochlorines (OCs), such as polychlorinated biphenyls (PCBs) and chlorinated pesticides, represent an important group of POPs that have caused worldwide concern as toxic environmental contaminants (Bildeman & Olney, 1974; Tanabe, Tatbukawa, Kawano, & Hidaka, 1982; Wade, Atlas, Brooks, Garcia-Roero, & Defreitas, 1988; Iwata, Tanabe, Aramoto, Sakai, & Tatsukawa, 1994; Allen-gil et al., 1998; Wu, Zhang, & Zhou, 1999). Although the occurrence of POPs at elevated levels is of great environmental concern at contaminated hot spots, the regional and global significance of the problem has received increasing attention in the last decades (Wania & Mackay, 1993; UNECE, 1998; UNEP, 2001). Many POPs are believed to be possible carcinogens or mutagens and are of considerable concern to human and environmental health. The lipophilic nature, hydrophobicity and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues and subsequent magnification of concentrations in organisms progressing up the food chain (Swackhamer & Hites, 1988; Vassilopoulou & Georgakopoulous-Gregoriades, 1993).

The PCBs, commonly considered key representatives of the ‘industrial’ POPs (Breivik et al., 2004), are synthetic organic compounds obtained from chlorination of biphenyls, and, theoretically, up to 209 congeners can be generated in the process. These congeners differ widely in the toxicological and physicochemical properties, according to the member and possession of the chlorine atoms in the molecules. Commercial mixtures of PCBs are widely used as fluids in transformers and capacitors, hydraulic fluids, lubricating oils and as additives in pesticides, inks and paints due to their high chemical stability (Kennish, 1997). PCBs are very persistent in the environment and are now disseminated worldwide.

Coastal sediments act as temporary or long-term sinks for many classes of anthropogenic contaminants and consequently act as the source of these substances to the ocean and biota. Although most of the developed countries have banned or restricted the production and usage of many of these OCs during 1970s and 1980s, these chemicals are still being used in some developing nations for agricultural and aquacultural purposes (Dave, 1996; Li, 1999; Tanabe, Iwata, & Tatsukawa, 1994). The pesticides applied to land eventually find their way to the aquatic environment thus contaminating them. These are transported to aquatic bodies by rain run-off, rivers and streams and associated with biotic and abiotic macroparticles (Colombo, Khali, Horth, & Catoggio, 1990).

Studies on hydrocarbons in the aquatic environments can be based on the analysis of the water column, organisms and sediment. However, sedimentary hydrocarbons have received special attention because these compounds are readily adsorbed onto particulate matter, and bottom sediments ultimately act as a reservoir of hydrophobic contaminants (Volkman, Holdsworth, Neill, & Bavor, 1992). Among organic pollutants, polycyclic aromatic hydrocarbons (PAHs) are the most ubiquitous and constitute a major group of marine environmental contaminants. They contain two or more fused benzene rings. Two types of anthropogenic sources of PAHs are found petrogenic and pyrogenic sources. The study of the PAHs in coastal marine environments is of great importance as these areas are biologically active and receive considerable pollutant input from land-based sources via coastal discharge. The carcinogenic properties of some compounds, coupled with the stability of PAHs during their atmospheric and aquatic transport, and their widespread occurrence have, in recent years, generated interest in studying their sources, distribution, transport mechanisms, environmental impact and fate (Bouloubassi & Saliot, 1993).

The Mediterranean Sea is semi-enclosed sea which contamination from both anthropogenic and natural sources could generate pollution problems affecting the whole Mediterranean basin. The Aegean Sea is part of the Eastern Mediterranean. There are a number of rivers along the Eastern and Western coast of the Aegean Sea through which a large amount of contaminants is being transported into the marine ecosystem thereby causing a great concern for marine pollution. The present environmental problems are due to unmanaged shipping activity, river run-off (Gediz is the biggest river along the Eastern Aegean), and untreated sewage discharge by coastal settlements, dumping of toxic and industrial wastes from the western part of Turkey. The production and usage of many chlorinated compounds such as dieldrin, aldrin, endrin, chlordane, DDT, BHC, lindane and heptachlor were completely banned in Turkey in the 1990s. However, total pesticide usage in Turkey in 1995 was 37,000 ton, and this usage has shown a steady increase year by year (TCV, 1998). Although the use of PCBs was banned in Turkey in 1995, the import of PCBs continued illegally until the 2000s.

Substantial work has been carried out on heavy metal contamination in biotic and abiotic matrices in the Eastern Aegean coastal environment (Demirkurt, Uysal, & Parlak, 1990; Kucuksezgin, Çağlar, & Uslu, 1999; Parlak & Demirkurt, 1990; Sarı & Çağatay, 2001; Kucuksezgin, Uluturhan, Kontas, & Altay, 2002; Kucuksezgin, Kontas, Altay, Uluturhan, & Darilmaz, 2006; Dalman, Demirak, & Balcı, 2006). Zeri, Voutsinou, Romanov, Ovsjany, & Moriki (2000) and Voutsinou, Varnavas, Nakopoulou, & Moriki (1997) and Voutsinou & Zeri (2001) reported on dissolved trace elements in seawater. There is a lack of data pertaining to persistent organic pollutants in the sediments from the Eastern Aegean Sea.

The main objective of this study is;

- to investigate the occurrence and distribution patterns of organochlorinated pesticides, polychlorinated biphenyls, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons in sediments from the Eastern Aegean coast, which gave the information about status of contamination,
- to assess of the various biogenic and anthropogenic sources of hydrocarbons in the study area using related indices,
- to assess the importance and origins of human-related contamination from OCPs in the Eastern Aegean Sea,

- provide a better understanding of recent distribution, possible sources as well as potential biological risk of DDTs, PCBs and PAHs in this area,
- to compare the measured pollutants with those of other corresponding areas in the world,
- to assess the extent of contamination of sediment and will be useful reference for the development of any future studies.

CHAPTER TWO
ORGANIC POLLUTANTS

Aliphatic hydrocarbons (AHCs) and polycyclic aromatic hydrocarbons (PAHs) are two major classes of compounds that have attracted most investigations of petroleum related hydrocarbons (Benlahcen, Chaoui, Budzinski, Bellocq, & Garrigues, 1997; Guzzella & De Paolis, 1994). These compounds reach the marine environment by atmospheric transportation or by the direct input from oil spills and sewage discharge. Accidental oil spills, although most newsworthy, are not the only sources of those compounds in the marine environment. AHCs can be of both petrogenic and biogenic origin, while PAHs can be petrogenic, pyrolytic and biogenic. Both AHCs and PAHs are often used to identify hydrocarbon sources. The level of PAHs in the ecosystem, in particular, has received some attention because they potentially have carcinogenic and estrogenic effects. Due to their hydrophobic nature, these compounds tend to sorb onto particulate phase, making marine sediment a repository of these compounds (Karickhoff, 1984). Resuspension of sediment or bioturbation of sediment into the water column are believed to play a significant role in bioaccumulation of these compounds in the food web (Lee, Hsieh, & Fang, 2005).

N-alkanes are an important constituent of the aliphatic hydrocarbons that are present in petroleum and fossil fuels. *N*-alkanes are also the predominant constituent of biogenic hydrocarbons, and have been identified in many species of marine organisms (Reinhardt & Van Vleet, 1986; Cripps, 1990, Cripps & Priddle, 1991). *N*-alkanes from oil show no predominance of odd or even carbon chain lengths (NRC 1985, UNEP 1991) while n-alkanes from biogenic sources are variable depending on the organisms present in a given study area.

Polycyclic aromatic hydrocarbons (PAHs) are of special concern because they are widely distributed in the environment and many of them have toxic and carcinogenic properties (Pruell & Quinn, 1985). They can be generated and introduced into the environment by various processes: incomplete combustion at higher temperatures of recent and fossil organic matter (pyrolytic origin), slow maturation of organicmaterials under the geochemical gradient conditions (high temperatures and pressure, petrogenic origin) and short-term digenetic degradation of biogenic precursors (digenesis) (McElory et al. 1989). Terrestrial plant waxes, marine phytoplankton, volcanic eruptions, biomass combustion and natural oil seeps contribute natural inputs of hydrocarbons, including aliphatic and PAHs (Saliot, 1981).

Persistent organic pollutants (POPs) are organic compounds that, to a varying degree, resist photolytic, biological and chemical degradation. POPs are often halogenated and characterised by low water solubility and high lipid solubility, leading to their bioaccumulation in fatty tissues. They are also semi-volatile, enabling them to move long distances in the atmosphere before deposition occurs.

Although many different forms of POPs may exist, both natural and anthropogenic, POPs which are noted for their persistence and bioaccumulative characteristics include many of the first generation organochlorine insecticides such as dieldrin, DDT, toxaphene and chlordane and several industrial chemical products or by products including polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (dioxins) and dibenzo-p-furans (furans). Many of these compounds have been or continue to be used in large quantities and, due to their environmental persistence, have the ability to bioaccumulate and biomagnify. Some of these compounds such as PCBs, may persist in the environment for periods of years and may bioconcentrate by factors of up to 70,000 fold.

POPs are also noted for their semi-volatility; that property of their physico-chemical characteristics that permit these compounds to occur either in the vapour phase or adsorbed on atmospheric particles, thereby facilitating their long range transport through the atmosphere. These properties of unusual persistence and semi-volatility, coupled with other characteristics, have resulted in the presence of compounds such as PCBs all over the world, even in regions where they have never been used. POPs are ubiquitous.

They have been measured on every continent, at sites representing every major climatic zone and geographic sector throughout the world. These include remote regions such as the open oceans, the deserts, the Arctic and the Antarctic, where no significant local sources exist and the only reasonable explanation for their presence is long-range transport from other parts of the globe. PCBs have been reported in air, in all areas of the world, at concentrations up to 15 ng/m^3; in industrialized areas, concentrations may be several orders of magnitude greater. PCBs have also been reported in rain and snow.

Organic Pollutants are represented by two important subgroups including both the polycyclic aromatic hydrocarbons and some halogenated hydrocarbons. This latter group includes several organochlorines which, historically, have proven to be most resistant to degradation and which have had wide production, use and release characteristics. These chlorinated derivatives are generally the most persistent of all the halogenated hydrocarbons. In general, it is known that the more highly chlorinated biphenyls tend to accumulate to a greater extent than the less chlorinated PCBs; similarly, metabolism and excretion is also more rapid for the less chlorinated PCBs than for the highly chlorinated biphenyls.

Humans can be exposed to POPs through diet, occupational accidents and the environment (including indoor). Exposure to POPs, either acute or chronic, can be associated with a wide range of adverse health effects, including illness and death.

Laboratory investigations and environmental impact studies in the wild have implicated POPs in endocrine disruption, reproductive and immune dysfunction, neurobehavioural and disorders and cancer. More recently some POPs have also been implicated in reduced immunity in infants and children, and the concomitant increase in infection, also with developmental abnormalities, neurobehavioural impairment and cancer and tumour induction or promotion. Some POPs are also being considered as a potentially important risk factor in the etiology of human breast cancer by some authors.

2.1 Pesticides

2.1.1 Definition and Classification of Pesticides

Pesticides are organic chemicals (some synthesized and some extracted from plants such as nicotine) and inorganic chemicals (e.g synthesized from inorganic salts of arsenic compounds) used to combat agricultural pests (Castilho, Fenzl, Guillen & Nascimento, 2000). Almost any living creature can be a pest in certain circumstances.

Pesticide compounds are characterized by their toxicity, relatively high volatility, as well as by their capacity to interfere with cell biochemistry when accumulated in organic tissues (Castilho et al., 2000). Also organochlorine pesticides (OCPs) are known for their environmental persistence and global concerns. Residues of OCPs continue to detect in many areas (Doong, Peng, Sun, & Liao, 2002). Generally, the organochlorine pesticides are hydrophobic substances, with low water solubility, frequently at the μg or ng per liter level. Most of the OC pesticides have octanolwater partition coefficients (Kow) with log Kow comprised between 3.5 and 6 and, thus, are very soluble in lipids. As a consequence, these pesticides are highly concentrated by living organisms and concentrations can biomagnify along the food chain (Nhan et al., 2001).

Starting in the late 1800s, chemical pesticides containing arsenic, mercury, lead, and copper come into widespread use. Even in large amounts, sulfur and copper only partially controlled pests So the very effective synthetic insecticide dichlorodiphenyltrichloroethane (DDT) was introduced in 1940, it was quickly embraced. Many other synthetic chemical pesticides were quickly developed and saw widespread use (Hill, 1997).

Pesticides are compounds that are made of different elements or atoms bonded together chemically, so that the smallest unit of any pesticide is a molecule. The elements that are used frequently in pesticide construction are; Carbon(C), Hydrogen

(H), Nitrogen(N), Chlorine(Cl), Sulfur(S). And also there are metallic and semi metallic elements that may include in some pesticides. These are iron, copper, zinc, mercury, arsenic and others. Essentially all of the pesticides are organic compounds that contain carbon in their molecules.

Table 2.1 Classes of Organic Pesticides

A. Chlorinated hydrocarbons
1. Class I: oxygenated compounds (Dieldrin, methoxychlor, endrin)
2. Class П: benzenoid, nonoxygenated compounds (BHC, DDD (TDE), DDT, perthane)
3. Class Ш: nonoxygenated, nonbenzenoid compounds (Aldrin, chlordane, heptachlor, strobane, toxaphene)

B. Organophosphorus compounds
1. Aliphatic derivatives (Demeton, dimethoate, ethion, malathion, phosdrin, phorate)
2. Aromatic derivatives (Trithion, diazinon, EPN, fenthion, parathion, runnel)

C. Herbicides, fungicides, nematocides etc.
1. Phenoxyalkyl acids (2,4-D; 2,4,5-T, 2(2,4,5-TP)
2. Substituted ureas (Fenuran,manuran,diuron)
3. Substituted carbamates (IPC, CIPC, EPTC)
4. Symmetrical triazines (Simazine, atrazine)
5. Substituted phenols (PCP, DNBP, DNC)

A very few contain no carbon and are termed inorganic compounds (Ware, 1986). Organic pesticides are generally classified by use, i.e, insecticide, miticide, nematocide, rodenticide, fungicide, herbicide, etc. A more appropriate classification would be by chemical species. A list of some of the more important organic pesticides appears in Table 2.1 (Ciaccio, 1972).

2.1.2 The current status of POP pesticides use

Starting in the early 1970s, one country after another restricted or banned the use of POP pesticides, often with the use of DDT for public health applications (disease vector control) as the only exemption. The last known uses for each of the POPs pesticides are summarised in Table 2.2 (Mörner, 1996).

Table 2.2 The POP pesticides - examples of last known uses

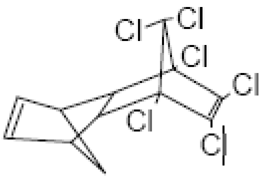
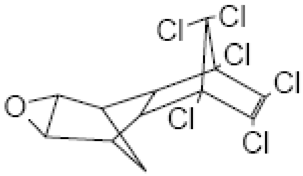
POP pesticide	**Last known uses**
Aldrin	Against termites and other soil pests, termites attacking building materials, in grain storage, and for vector control
Toxaphene	Control of insect pests in cotton and other crops
Chlordane	Against termites and other soil pests, termites attacking building materials
DDT	Control of medical and veterinary vectors, such as malaria-transmitting mosquitoes, plague-transmitting fleas and trypanosomiasis-transmitting flies
Dieldrin	Control of locusts, termites, human disease vectors
Endrin	Formerly used against insects and rodents. No current or recent uses are known
Heptachlor	Against termites and other soil pests, termites attacking building materials
HCB	Formerly used for seed treatment against fungal diseases, as well as for industrial purposes. No current or recent agricultural uses are known.
Mirex	Against leaf-cutting ants, termites in buildings and outdoors, and also as a fire retardant and for other industrial purposes

Data on the use of certain pesticides are difficult to obtain and may be unreliable. The table nevertheless provides some insight for what purposes the POPs pesticides have been or are being used. Production and use of the pesticides on the initially agreed list of POPs has, for all practical purposes, already ended in high-income countries, except for some products for termite control. Their use in low-income countries has been reduced, often because of growing trade restrictions on agricultural produce containing pesticide residues. DDT and possibly a few other POP pesticides are, however, still used in a number of countries. A significant portion of this use is that of DDT for the control of malaria vectors and of chlordane and heptachlor for termite control.

2.1.2.1 Aldrin and Dieldrin

Aldrin and dieldrin are the common names of two structurally similar compounds that were once used as insecticides (Table 2.3). They are chemicals that are made in the laboratory and do not occur naturally in the environment. The scientific name for aldrin is 1, 2, 3, 4, 10, 10-hexachloro-1, 4, 4α, 5, 8, 8α-hexahydro-1, 4-endo, exo-5, 8-dimethanonaphthalene. Technical-grade aldrin contains not less than 85.5% aldrin.

Table 2.3 Chemical Identity of Aldrin and Dieldrin

Characteristic	**Aldrin**	**Dieldrin**
Synonyms	1,2,3,4,10,10-Hexachloro-1,4,4*α* 5,8,8*α*-hexahydro-exo-1,4-endo-5,8-dimethano-naphthalene; HHDN	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4*α*,5,6,7,8,8*α*-octahydro-1,4-endo,exo-5,8-dimethanonaphthalene; HEOD
Chemical formula	$C_{12}H_8Cl_6$	$C_{12}H_8Cl_6O$
Chemical structured		

The scientific name for dieldrin is 1,2,3,4,10,10-hexachloro-6,7-epoxy-1, 4, 4α, 5, 6, 7, 8, 8α-octahydro-1, 4-endo,exo-5, 8-dimethanonaphthalene. The abbreviation for the scientific name for dieldrin is HEOD. Technical-grade dieldrin contains not less than 85% dieldrin. The trade names used for dieldrin include Alvit, Dieldrix, Octalox, Quintox, and Red Shield.

Pure aldrin and dieldrin are white powders, while technical-grade aldrin and dieldrin are tan powders. Aldrin and dieldrin slowly evaporate in the air. Aldrin evaporates more readily than dieldrin. Both aldrin and dieldrin have mild chemical odors. You might find aldrin and dieldrin in the soil, in water, or in homes where these compounds were used to kill termites. You might also find aldrin and dieldrin in plants and animals near hazardous waste sites.

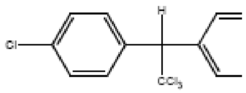
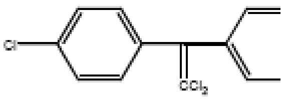
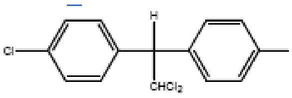
Aldrin and dieldrin are no longer produced or used. From the 1950s until 1970, aldrin and dieldrin were used extensively as insecticides on crops such as corn and cotton. The U.S. Department of Agriculture canceled all uses of aldrin and dieldrin in 1970. In 1972, however, EPA approved aldrin and dieldrin for killing termites. Use of aldrin and dieldrin to control termites continued until 1987. In 1987, the manufacturer voluntarily canceled the registration for use in controlling termites. In this profile, the two chemicals are discussed together because aldrin readily changes into dieldrin once it enters either the environment or your body.

2.1.2.2 DDT, DDE and DDD

DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) is a pesticide that was once widely used to control insects on agricultural crops and insects that carry diseases like malaria and typhus, but is now used in only a few countries to control malaria. Technical-grade DDT is a mixture of three forms, *p,p'*-DDT (85%), *o,p'*-DDT (15%), and *o,o'*-DDT (trace amounts).

The chemical formulas, structures, and identification numbers for *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *o,p'*-DDE, and *o,p'*-DDD are listed in Table 2.4. The latter five compounds are either impurities or metabolites of technical DDT.

Table 2.4 Chemical identity of *p,p*'- and *o,p*'-DDT, DDE, and DDD

Characteristic	***p,p*'-DDT**	***p,p*'-DDE**	***p,p*'-DDD**
Synonym(s)	4,4'-DDT; 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl) ethane; dichlorodiphenyl trichloroethane; DDT; 1,1'-(2,2,2-trichloroethylidene) bis(4-chlorobenzene)	4,4'-DDE; dichlorodiphenyl-dichloro ethane; 1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethylene; 1,1'-(2,2-dichloro-ethylidene)bis(4-chloro-benzene); DDE	4,4'-DDD; DDD; 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; 1,1-bis(4-chlorophenyl)-2,2-dichloroethane; TDE; tetrachlorodiphenylethane
Chemical formula	$C_{14}H_9Cl_5$	$C_{14}H_8Cl_4$	$C_{14}H_{10}Cl_4$
Chemical structure			

All of these are white, crystalline, tasteless, and almost odorless solids. Technical-grade DDT may also contain DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene) and DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethane) as contaminants. DDD was also used to kill pests, but to a far lesser extent than DDT. One form of DDD (*o,p'*-DDD) has been used medically to treat cancer of the adrenal gland. Both DDE and DDD are breakdown products of DDT.

DDT does not occur naturally in the environment. After 1972, the use of DDT was no longer permitted in the United States except in cases of a public health emergency. It is, however, still used in some other areas of the world, most notably for controlling malaria. The use of DDD to kill pests has also been banned in the United States.

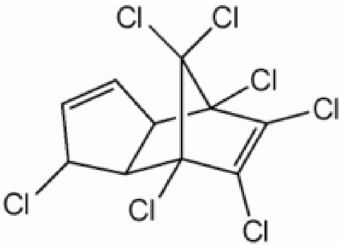
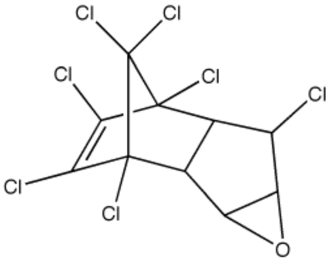
When we refer to DDT, we are generally referring to *p,p'*-DDT, which was produced and used for its insecticidal properties. However, technical grade DDT, the grade that was generally used as an insecticide, was composed of up to fourteen chemical compounds, of which only 65-80% was the active ingredient, *p,p'*-DDT. The other components included 15-21% of the nearly inactive *o,p'*-DDT, up to 4% of *p,p'*-DDD, and up to 1.5% of 1-(*p*-chlorophenyl)-2,2,2-trichloroethanol (Metcalf, 1995).

2.1.2.3 Heptachlor and Heptachlor Epoxide

Heptachlor is a manufactured chemical that was used in the past for killing insects in homes, in buildings, and on food crops. It has not been used for these purposes since 1988. There are no natural sources of heptachlor or heptachlor epoxide. Heptachlor is both a breakdown product and a component of the pesticide chlordane (approximately 10% by weight).

Pure heptachlor is a white powder. Technical-grade heptachlor is a tan powder and has a lower level of purity than pure heptachlor. Technical-grade heptachlor was the form of heptachlor used most often as a pesticide. Heptachlor smells somewhat like camphor. Heptachlor does not burn easily and does not explode. It does not dissolve easily in water (Table 2.5). Like pure heptachlor, heptachlor epoxide is a white powder that does not explode easily. It was not manufactured and was not used as an insecticide like heptachlor. Bacteria and animals break down heptachlor to form heptachlor epoxide. This profile describes these two chemicals together because about 20% of heptachlor is changed within hours into heptachlor epoxide in the environment and in your body.

Table 2.5 Chemical Identity of Heptachlor and Heptachlor Epoxide

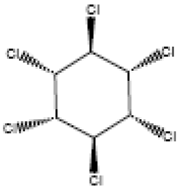
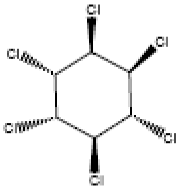
Characteristic	**Heptachlor**	**Heptachlor epoxide**
Synonyms	3-Chlorochlordene; 1,4,5,6,7,8,8a-hepta-chloro-3a,4,7,7a-tetrahydro-4,7-methanoindene; 1,4,5,6,7,8,8-heptachloro-3A,4,5,5a tetrahydro; alpha-dicylcopentadiene, 3,4,5,6,8,8a heptachloro, and others	Epoxyheptachlor; 1,4,5,6,7,8,8a-hepta-chloro-2,3-epoxy-3a,4,7,7a-tetra-hydro-4,7-methanoindene; 4,7-methanoindan, 1,4,5,6,7,8, 8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-
Chemical formula	$C_{10}H_5Cl_7$	$C_{10}H_5Cl_7O$
Chemical structure		

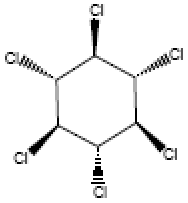
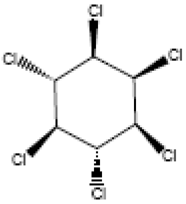
You might find heptachlor or heptachlor epoxide in the soil or air of homes treated for termites, dissolved in surface water or groundwater, or in the air near hazardous waste sites. You might also find heptachlor or its by-product, heptachlor epoxide, in plants and animals near hazardous waste sites. Heptachlor can no longer be used to kill insects on crops or in homes and buildings. However, heptachlor is still approved by EPA for killing fire ants in power transformers.

2.1.2.4 Hexachlorocyclohexane

Hexachlorocyclohexane (HCH), formally known as benzene hexachloride (BHC), is a synthetic chemical that exists in eight chemical forms called isomers. The different isomers are named according to the position of the hydrogen atoms in the structure of the chemical (Table 2.6). One of these forms, gamma-HCH (or γ-HCH, commonly called lindane), is produced and used as an insecticide on fruit, vegetables, and forest crops, and animals and animal premises. It is a white solid whose vapor may evaporate into the air. The vapor is colorless and has a slight musty odor when it is present at 12 or more parts HCH per million parts air (ppm). γ-HCH has not been produced in the United States since 1976. However, imported γ-HCH is available in the United States for insecticide use as a dust, powder, liquid, or concentrate. It is also available as a prescription medicine (lotion, cream, or shampoo) to treat and/or control scabies (mites) and head lice in humans.

Table 2.6 Chemical Identity of Hexachlorocyclohexane Isomers

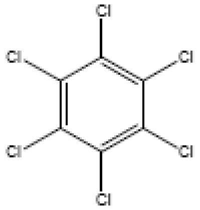
Characteristic	**γ-hexachlorocyclohexane**	**α-hexachlorocyclohexane**
Synonyms	Lindane; 1-α, 2-α, 3-β, 4-α, 5-α, 6-β hexachlorocyclohexane; benzene hexachloride γ-isomer; BHC; γ-BHC; γ-HCH; γ-lindane	1-α, 2-α, 3-β, 4-α, 5-β, 6-β-benzene transhexachloride; α 1,2,3,4,5,6 hexachlorocyclohexane; α-benzene hexachloride; α-BHC; α-HCH; α-hexachlorane; α-lindane
Chemical formula	$C_6H_6Cl_6$	$C_6H_6Cl_6$
Chemical structure		

Characteristic	**β-hexachlorocyclohexane**	**δ-hexachlorocyclohexane**
Synonyms	1-α, 2-β, 3-α, 4-β, 5-α, 6-β-hexachlorocyclo-hexane; β-lindane;	1-α, 2-α, 3-α, 4-β, 5-α, 6-β-hexachlorocyclo hexane; delta-BHC; delta-HCH;
Chemical formula	$C_6H_6Cl_6$	$C_6H_6Cl_6$
Chemical structure		

Technical-grade HCH, a mixture of several chemical forms of HCH, was also once used as an insecticide in the United States and typically contained about 10–15% of γ-HCH as well as the alpha (α), beta (β), delta (δ), and epsilon (ε) forms of HCH. Virtually all of the insecticidal properties reside in the gamma isomer. Technical-grade HCH has not been produced or used in the United States for more than 20 years. The scope of this profile includes information on technical-grade HCH, as well as the α, β, γ, and δ isomers.

HCH consists of eight isomers (Safe, 1993). Only γ-HCH, α-HCH, β-HCH, and δ-HCH are of commercial significance and considered in this profile. The pesticide lindane refers to products that contain >99% γ-HCH. The α-, β-, and δ-isomers, as well as technical-grade HCH are not synonymous with γ-HCH (Farm Chemicals Handbook, 1993). Technical-grade HCH is not an isomer of HCH, but rather a mixture of several isomers; it consists of approximately 60-70% α-HCH, 5-12% β-HCH, 10-15% γ-HCH, 6-10% δ-HCH, and 3-4% ε-HCH (Kutz, Wood, & Bottimore, 1991).

Table 2.7 Chemical Identity of Hexachlorobenzene

Characteristics	**Hexachlorobenzene**
Synonyms	Perchlorobenzene; HCB; pentachlorophenyl chloride
Chemical formula	C_6Cl_6
Chemical structure	

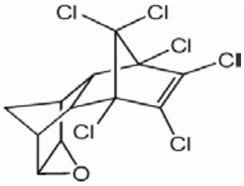
2.1.2.5 Hexachlorobenzene

Hexachlorobenzene is a white crystalline solid. This compound does not occur naturally. It is formed as a by-product during the manufacture of chemicals used as solvents, other chlorine-containing compounds, and pesticides. Small amounts of hexachlorobenzene can also be produced during combustion processes such as burning of city wastes. It may also be produced as a by-product in waste streams of chlor-alkali and woodpreserving plants (Table 2.7). Hexachlorobenzene was widely used as a pesticide until 1965. It was also used to make fireworks, ammunition, and synthetic rubber. Currently, the substance is not used commercially in the United States.

2.1.2.6 Endrin

Endrin is a cyclodiene insecticide used on cotton, maize, and rice. It also acts as an avicide. As a rodenticide, it is used to control mice and voles. It is a solid, cream to light tan to white, almost odorless substance. It melts and decomposes at 200 °C. It is moderately soluble in benzene and acetone, slightly soluble in alcohols, alkanes, and xylene, and almost insoluble in water.

Table 2.8 Chemical Identity of Endrin

Characteristic	**Perchloropentacyclodecane**
Synonyms	Octachloro-4,7-methanohydroindane
Chemical formula	$C_{12}H_8Cl_6O$
Chemical structure	

Endrin is a stereoisomer of dieldrin and is structurally similar to aldrin, and heptachlor epoxide (Table 2.8). It is likely to adsorb onto the sediments in surface water. It can bioaccumulate in tissues, particularly fatty tissues, of organisms living in water. Some estimates indicate its half-life in soil for over 10 years. Endrin may also be broken down by exposure to high temperatures (230 ºC) or light to form primarily endrin ketone, which is a product of endrin when it is exposed to light and endrin aldehyde. It is very toxic to aquatic organisms, namely fish, aquatic invertebrates, and phytoplankton.

Acute endrin poisoning in humans affects primarily the nerve system. Food contaminated with endrin caused several clusters of poisonings worldwide, especially affecting children. In comparison with dieldrin, the degree of persistence of endrin in organisms is lower, likely due to its rapid excretion in bile. It is eliminated mostly in feces.

2.1.3 Pesticide Toxicity

For all pesticides to be effective against the pests they are intended to control, they must biologically active, or toxic. Because pesticides are toxic, they are also potentially hazardous to humans and animals. Pesticides can cause skin or eye damage (topical effects) and can also induce allergic responses. However, if used according to label directions and with the proper personal protective equipment (PPE), pesticides can be used safely. The risk of exposure to pesticides can be illustrated with the following simple equation: **Hazard of pesticide use = Toxicity×Actual Exposure**

Toxicity is a measure of the ability of a pesticide to cause injury, which is a property of the chemical itself. Pesticide toxicity is determined by exposing test animals (usually rats, mice, rabbits, and dogs) to different dosages of the active ingredient. Tests are also done with each different formulation of the product (for example, liquids, dusts, and granular). Pesticide toxicities are listed in milligrams of exposure to kilograms of animal body weight.

2.1.3.1 Acute Toxicity and Acute Effects

The harmful effects that can occur from a single exposure by any route of entry are termed acute effects. Acute toxicity of a pesticide refers to the chemical’s ability to cause injury to a person or animal from a single exposure, generally of short duration. Acute toxicity is determined by three methods: (1) dermal toxicity is determined by exposing the test animal’s skin to the chemical; (2) inhalation toxicity is determined by having test animals breathe vapors of the chemical; and (3) oral toxicity is determined by feeding the chemical to test animals. In addition, the effect of the chemical as an irritant to the eyes and skin is examined under laboratory conditions.

Acute toxicity is usually expressed as LD50 (lethal dose 50) or LC50 (lethal concentration 50). This is the amount or concentration of a toxicant required to kill

50 percent of a test population of animals under a standard set of conditions. LD50 values of pesticides are recorded in milligrams of pesticide per kilogram of body weight of test animal (mg/kg), or in parts per million (ppm). LC50 values of pesticides are recorded in milligrams of pesticide per volume of air or water (ppm). The LD50 and LC50 values are useful in comparing the toxicity of different active ingredients as well as different formulations of the same active ingredient. The lower the LD50 value of a pesticide, the less it takes to kill 50 percent of the test population, and therefore the greater the acute toxicity of the chemical. Pesticides with high LD50 values are considered the least acutely toxic to humans when used according to the directions on the product label.

2.1.3.2 Chronic Toxicity and Chronic Effects

Any harmful effects that occur from repeated small doses over a period of time are called chronic effects. The chronic toxicity of pesticide is determined by observing symptoms of test animals, which result from long-term exposure to the active ingredient. Some of the suspected chronic effects from exposure to certain pesticides include birth defects (teratogenesis); fetal toxicity (fetotoxic effects); production of tumors (oncogenesis), either benign (noncancerous) or malignant (cancerous/carcinogenesis), genetic changes (mutagenesis), blood disorders (hemotoxic effects), nerve disorders (neurotoxiceffects), and reproductive effects. The chronic toxicity of a pesticide is more difficult to determine through laboratory analysis than is acute toxicity (Harvey, 1992).

2.2 Polychlorinated Biphenyls

PCBs are a class of organic compounds in which 2-10 chlorine atoms are attached to biphenyl which is a molecule composed of two benzene rings each containing six carbon atoms. The chemical formula for all PCBs is $C_{12}H_{10-x}Cl_x$.

Monochlorinated biphenyls (i.e., one chlorine atom attached to the biphenyl molecule) are often included when describing PCBs. The general chemical structure of chlorinated biphenyls is shown in Figure 2.1. It can be seen from the structure that a large number of chlorinated compounds are possible.

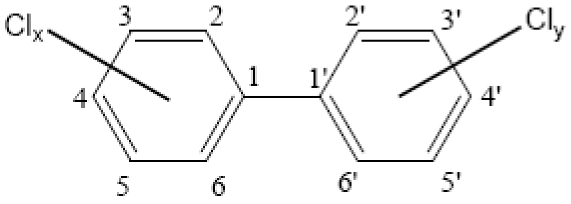


Figure 2.1 The general chemical structure of chlorinated biphenyls

The 209 possible compounds are called congeners. PCBs can also be categorized by degree of chlorination. The term “homolog” is used to refer to all PCBs with the same number of chlorines (e.g., trichlorobiphenyls). Homologs with different substitution patterns are referred to as isomers. For example, the dichlorophenyl homolog contains 12 isomers.

The numbering system for the PCBs is also shown above. Positions 2, 2', 6, and 6' are called ortho positions, positions 3, 3', 5, and 5' are called meta positions, and positions 4 and 4' are called para positions. The benzene rings can rotate around the bond connecting them; the two extreme configurations are planar (the two benzene rings in the same plane) and the nonplanar in which the benzene rings are at a 90 E angle to each other. The degree of planarity is largely determined by the number of substitutions in the ortho positions. The replacement of hydrogen atoms in the ortho positions with larger chlorine atoms forces the benzene rings to rotate out of the planar configuration. The benzene rings of non-*ortho* substituted PCBs, as well as mono-*ortho* substituted PCBs, may assume a planar configuration and are referred to as planar or coplanar congeners; the benzene rings of other congeners cannot assume a planar or coplanar configuration and are referred to as non-planar congeners.

PCBs were used as coolants and insulating fluids for transformers and capacitors, stabilizing additives in flexible PVC coatings of electrical wiring and electronic components, pesticide extenders, cutting oils, flame retardants, hydraulic fluids, sealants (used in caulking, etc), adhesives, wood floor finishes, paints, de-dusting agents, and in carbonless copy paper. PCB production was banned in the 1970s due to the high toxicity of most PCB congeners and mixtures. PCBs are classified as persistent organic pollutants which bioaccumulate in animals.

2.2.1 Physical and chemical properties

PCB congeners are odorless, tasteless and clear to pale-yellow, viscous liquids. They are formed by electrophilic chlorination of biphenyl with chlorine gas. There are theoretically 209 different PCB congeners, although only about 130 of these were found in commercial PCB mixtures. Commercial PCBs preparations are usually mixtures of 50 or more PCB congeners. Commercial PCB mixtures are clear to pale-yellow, viscous liquids (the more highly chlorinated mixtures are more viscous and more yellow - for example, Aroclor 1260 is a sticky yellowish resin).

PCBs have low water solubilities 0.0027-0.42 ng/L for Aroclors, and low vapor pressures at room temperature, but they have high solubilities in most organic solvents, oils and fats. They have high dielectric constants, very high thermal conductivity, high flash points (170-380°C) and are chemically almost inert, being extremely resistant to oxidation, reduction, addition, elimination, and electrophilic substitution. The density varies from 1.182 to 1.566 kg/L. Other physical and chemical properties vary widely across the class. As the degree of chlorination increases, melting point and lipophilicity increase, but vapour pressure and water solubility decrease.

PCBs readily penetrate skin, PVC (polyvinyl chloride), and latex (natural rubber); organic solvents such as kerosene increase the rate of skin absorption. PCB-resistant materials include Viton, polyethylene, polyvinyl acetate (PVA), polytetrafluoroethylene (PTFE), butyl rubber, nitrile rubber, and Neoprene.

PCBs are very stable compounds and do not degrade readily. They may be destroyed by chemical, thermal, and biochemical processes, though it is extremely difficult to achieve full destruction, and there is the risk of creating extremely toxic dibenzodioxins and dibenzofurans through partial oxidation. Because of the high thermodynamic stability of PCBs, all degradation mechanisms are difficult to sustain. Intentional degradation as a treatment of unwanted PCBs generally requires high heat or catalysis. Environmental and metabolic degradation generally proceeds quite slowly relative to most other compounds. Some commercial PCB mixtures are known in the United States by their industrial trade name, Aroclor. For example, the name Aroclor 1254 means that the mixture contains approximately 54% chlorine by weight, as indicated by the second two digits in the name.

2.3 Petroleum Hydrocarbons

Crude oil is a complex mixture of hydrocarbons with 4-26 or more carbon atoms in the molecule. Arrangements include straight chains, branched chains, or cyclic chains, including aromatic compounds (with benzene rings). Some polycyclic aromatic hydrocarbons (PAH) are known to be potent carcinogens.

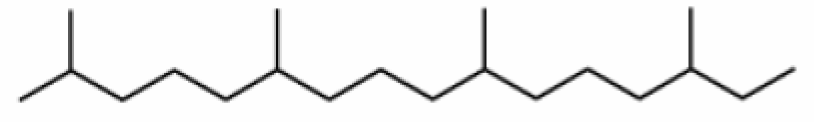
Table 2.9 Refinery “cuts” of crude oil

	Boiling Range (°C)	Molecular size (Number of carbon atoms)
Petroleum gases	30	3-4
Light gasoline, benzene	30-140	4-6
Naphtha	120-175	7-10
Kerosene	165-200	10-14
Gas oil (diesel)	175-365	15-20
Fuel oil and residues	350	20+

Crude oil must be refined before it can be used. Refining is esentially a distillation process with different fractions or cuts taken at different boiling ranges (Table 2.9). Light gasoline is the basis for petrol used in motor vehicles; naphtha provides feedstock for the petrochemical industry; the residue is used as bunker fuel in ships and power stations; and the higher fractions are used as tars, and so on. Many of the commercial are further refined, made into particular formulations, and receive additives of other materials to suit them for their various purposes.

All components of crude oil are degradable by bacteria, although at varying rates, and a variety of yeasts and fungi can also metabolize petroleum hydrocarbons. Small, straight- and branched-chain compounds degrade most rapidly, cyclic compounds more slowly. High molecular weight compounds, the tars, degrade extremely slowly (Clark, 1997).

Table 2.10 Chemical Structure of Identity of Pristane and Phytane

Characteristic	Pristane
Synonym(s)	2,6,10,14-tetramethylpentadecane
Chemical Formula	$C_{19}H_{40}$
Chemical Structure	
Characteristic	**Phytane**
Synonym(s)	2,6,10,14-tetramethylhexadecane
Chemical Formula	$C_{20}H_{42}$
Chemical Structure	

2.3.1 Aliphatics (paraffins)

These include *n*-alkanes and iso-alkanes in which carbon atoms are attached to hydrogen or other carbon atoms. They comprise 60 to > 90% of the hydrocarbon content of crude oils. Saturated hydrocarbons with fewer than five carbons are gases at room temperature. Those with 5 to 17 or 18 carbons are liquids. Paraffins with 20 to 35 carbon atoms per molecule are solids and are referred to as waxes (Wright, 2001). They are present in solution at elevated temperatures but may solidify at lower temperatures. *n*-C10, *n*-C12, *n*-C14, *n*-C16, *n*-C17, pristane, *n*-C18, phytane, *n*-C20, *n*-C21, *n*-C22, *n*-C24, *n*-C26, squalane, *n*-C28, *n*-C30, *n*-C32 and *n*-C34 were measured in this study. The structure of pristane and phytane are given in Table 2.10.

2.3.2 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds that consist of fused aromatic rings and do not contain heteroatoms or carry substituents. These compounds can be point source pollutants (e.g. oil spill) or non-point source (e.g. atmospheric deposition) and are one of the most widespread organic pollutants. Some of them are known or suspected carcinogens, and are linked to other health problems. They are primarily formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, tobacco, or other organic substances, such as incense and charbroiled meat. Tar also contains PAHs.

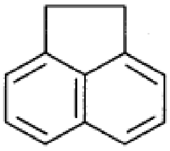
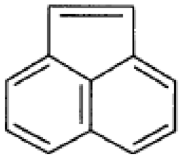
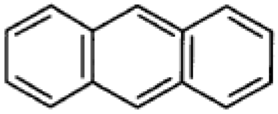
Table 2.11 The major PAH compounds

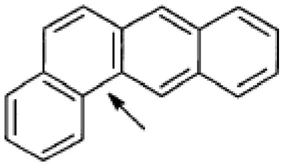
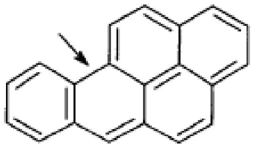
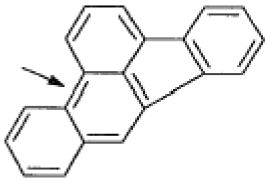
PAHs	Molecular Formula	Molecular Weight
Acenaphthene	$C_{12}H_{10}$	154
Acenaphthylene	$C_{12}H_8$	152
Anthracene	$C_{14}H_{10}$	178
Benzo[a] anthracene	$C_{18}H_{12}$	228
Benzo[a] pyrene	$C_{20}H_{12}$	252
Benzo[e] pyrene	$C_{20}H_{12}$	252
Benzo[b] f luoranthene	$C_{20}H_{12}$	252
Benzo[g.h.i] perylene	$C_{22}H_{12}$	276
Benzo[j] fluoranthene	$C_{20}H_{12}$	252
Benzo[k] fluoranthene	$C_{20}H_{12}$	252
Chrysene	$C_{18}H_{12}$	228
Dibenzo[a.h] anthracene	$C_{22}H_{14}$	278
Fluoranthene	$C_{16}H_{10}$	202
Fluorene	$C_{13}H_{10}$	166
Indeno[c.d] pyrene	$C_{22}H_{12}$	276
Phenanthrene	$C_{14}H_{10}$	178
Pyrene	$C_{16}H_{10}$	202

Since human civilization relies so heavily on combustion, PAHs (Table 2.11) are inevitably linked to our energy production. In this sense, PAH can be thought of as marker molecules as their abundance can be directly proportional to combustion processes in the region and therefore directly related to air quality. Different types of combustion yield different distributions of PAHs in both relative amounts of individual PAHs and in which isomers are produced. Thus, those produced from coal burning are different from those produced by motor-fuel combustion, which differ from those produced by forest fires. Some PAHs occur within crude oil, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. They are also found in the interstellar medium, in comets, and in meteorites and are a candidate molecule to act as a basis for the earliest forms of life.

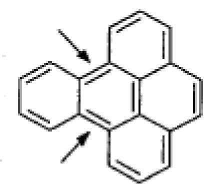
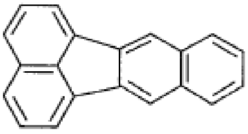
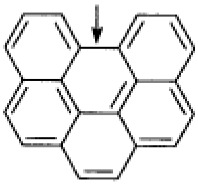
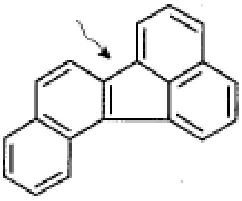
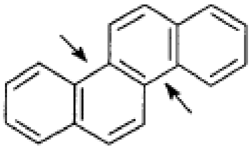
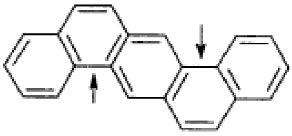
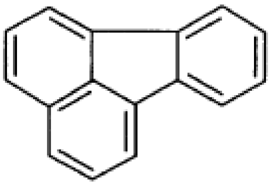
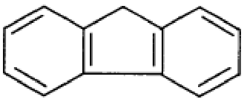
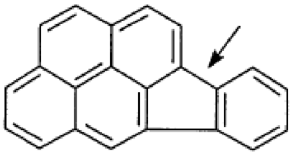
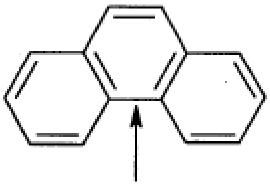
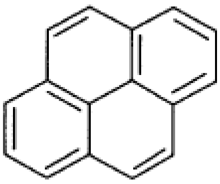
As pure chemicals, PAHs generally exist as colorless, white, or pale yellow-green solids. They can have a faint, pleasant odor. A few PAHs are used in medicines and to make dyes, plastics, and pesticides. Others are contained in asphalt used in road construction. They can also be found in substances such as crude oil, coal, coal tar pitch, creosote and roofing tar. They are found throughout the environment in the air, water, and soil. They can occur in the air, either attached to dust particles or as solids in soil or sediment. Although the health effects of individual PAHs are not exactly alike, the following 17 PAHs are considered as a group in this profile (Table 2.11 and Table 2.12).

Table 2.12 Chemical formula, Synonyms and structure of PAH compounds

Characteristic	Acenapthane	Acenaphthylene	Anthracene
Synonym(s)	1,2-Dihydroacenaphthylene;1,8-dihydroacenapthaline	Cyclopenta[d,e] naphthalene	Anthracin;green oil;paranaphthalene
Chemical Formula	$C_{12}H_{10}$	$C_{12}H_8$	$C_{14}H_{10}$
Chemical Structure			

Characteristic	Benzo[a]anthracene	Benzo[a]pyrene	Benzo[b]fluoranthene
Synonym(s)	BA;benz[a]anthracene;1,2-benzanthracene;tetraphene	BP;benz[a]pyrene;3,4-benzopyrene	2,3-Benzfluoranthene;B[b]F
Chemical Formula	$C_{18}H_{12}$	$C_{20}H_{12}$	$C_{20}H_{12}$
Chemical Structure			

Characteristic	Benzo[e]pyrene	Benzo[k]fluoranthene	Benzo[g,h,i]perylene
Synonym(s)	1.2-Benzopyrene;4.5 benzopyrene	8.9-Benzfluoranthene;2,3,1.8-binaphthylene	1,12-Benzoperylene
Chemical Formula	$C_{20}H_{12}$	$C_{20}H_{12}$	$C_{22}H_{12}$

Chemical Structure			
Characteristic	Benzo[j]fluoranthene	Chrysene	Dibenzo[a,h]anthracene
Synonym(s)	10.11-Benzofluoranthene;benzo-12.13-fluoranthene;7.8-benzofluoranthene	1.2-Benzophenanthrene;benzo[a]-phenanthrene;1,2,5,-dibenzonaphthalene	5,6-dibenz[a]anthracene;DBA; DB[a,h]A
Chemical Formula	$C_{20}H_{12}$	$C_{18}H_{12}$	$C_{22}H_{14}$
Chemical Structure			
Characteristic	Fluoranthene	Fluorene	Indeno[1,2,3-c,d]pyrene
Synonym(s)	1.2-[1,8-Naphthylene]benzene;1.2-benzacenaphthene;benzo[j,k]fluorene	Ortho-Biphenylene methane;diphenylene methane;2,2-methylenebiphenyl	Indenopyrene; ortho-phenylenepyrene;2,3-ortho-phenylene pyrene
Chemical Formula	$C_{16}H_{10}$	$C_{13}H_{10}$	$C_{22}H_{12}$
Chemical Structure			
Characteristic	Phenanthrene	Pyrene	
Synonym(s)	Phenanthrene, Phenantrin	Benzo[d,e,f]phenanthrene;8-pyrene	
Chemical Formula	$C_{14}H_{10}$	$C_{16}H_{10}$	
Chemical Structure			

There are more than 100 different PAHs. PAHs generally occur as complex mixtures (for example, as part of combustion products such as soot), not as single compounds. PAHs usually occur naturally, but they can be manufactured as individual compounds for research purposes; however, not as the mixtures found in combustion products.

2.3.2.1 Chemistry of Petroleum Hydrocarbons

The simplest PAHs, as defined by the International Union on Pure and Applied Chemistry (IUPAC) {G.P Moss, IUPAC nomenclature for fused-ring systems), are phenanthrene and anthracene. Smaller molecules, such as benzene and naphthalene, are not formally PAHs, although they are chemically related they are called one-ring (or mono) and two-ring (di) aromatics.

PAHs may contain four-, five-, six- or seven-member rings, but those with five or six are most common. PAHs composed only of six-membered rings are called alternant PAHs. Certain alternant PAHs are called "benzenoid" PAHs. The name comes from benzene, an aromatic hydrocarbon with a single, six-membered ring. These can be benzene rings interconnected with each other by single carbon-carbon bonds and with no rings remaining that do not contain a complete benzene ring.

PAHs containing up to six fused aromatic rings are often known as "small" PAHs and those containing more than six aromatic rings are called "large" PAHs. Due to the availability of samples of the various small PAHs, the bulk of research on PAHs has been of those of up to six rings. The biological activity and occurrence of the large PAHs does appear to be a continuation of the small PAHs. They are found as combustion products, but at lower levels than the small PAHs due to the kinetic limitation of their production through addition of successive rings. Additionally, with many more isomers possible for larger PAHs, the occurrence of specific structures is much smaller.

PAHs of three rings or more have low solubilities in water and a low vapor pressure. As molecular weight increases, aqueous solubility and vapor pressure decrease. The aqueous solubility decreases approximately one order of magnitude for each additional ring. PAHs with two rings are more soluble in water and more volatile. Because of these properties, PAHs in the environment are found primarily in soil and sediment, as opposed to in water or air. PAHs, however, are also often found in particles suspended in water and air. Natural crude oil and coal deposits contain significant amounts of PAHs, as do combustion products and smoke from naturally occurring forest fires.

PAHs may be small or large. One PAH compound, benzo[a]pyrene, is notable for being the first chemical carcinogen to be discovered (and is one of many carcinogens found in cigarette smoke). The EPA has classified seven PAH compounds as probable human carcinogens: benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene.

PAHs enter the environment mostly as releases to air from volcanoes, forest fires, residential wood burning and exhaust from automobiles and trucks. They can also enter surface water through discharges from industrial plants and waste water treatment plants, and they can be released to soils at hazardous waste sites if they escape from storage containers. The movement of PAHs in the environment depends on properties such as how easily they dissolve in water, and how easily they evaporate into the air. PAHs in general do not easily dissolve in water. They are present in air as vapors or stuck to the surfaces of small solid particles. They can travel long distances before they return to earth in rainfall or particle settling. Some PAHs evaporate into the atmosphere from surface waters, but most stick to solid particles and settle to the bottoms of rivers or lakes. In soils, PAHs are most likely to stick tightly to particles. Some PAHs evaporate from surface soils to air. Certain PAHs in soils also contaminate underground water.

The PAH content of plants and animals living on the land or in water can be many times higher than the content of PAHs in soil or water. PAHs can break down to longer-lasting products by reacting with sunlight and other chemicals in the air, generally over a period of days to weeks. Breakdown in soil and water generally takes weeks to months and is caused primarily by the actions of microorganisms.

2.3.2.2 Toxicity of Petroleum Hydrocarbons

The water-soluble components of crude oils and refined products include a variety of compounds that are toxic to a wide spectrum of marine plants and animals. Aromatic compounds are more toxic than aliphatics, and middle molecular weight constituents are more toxic than high molecular weight tars. Low molecular weight compounds are generally unimportant because they are volatile and rapidly lost to the atmosphere. A spillage of diesel fuel, with a high aromatic content, is therefore much more damaging than bunker fuel and weathered oil, which have a low aromatic content. A spillage of petrol may present a serious fire hazard, but has little impact on marine organisms in the water.

CHAPTER THREE
STUDY AREA

3.1 Description of Study Area

The Aegean Sea is one of the Eastern Mediterranean sub basins located between the Greek and Turkish coast and the island of Crete and Rhodes. It is an elongated basin and in the northeast it is connected to the Sea of Marmara through the Strait of Canakkale and Black Sea through the Strait of Istanbul (Figure 3.1).

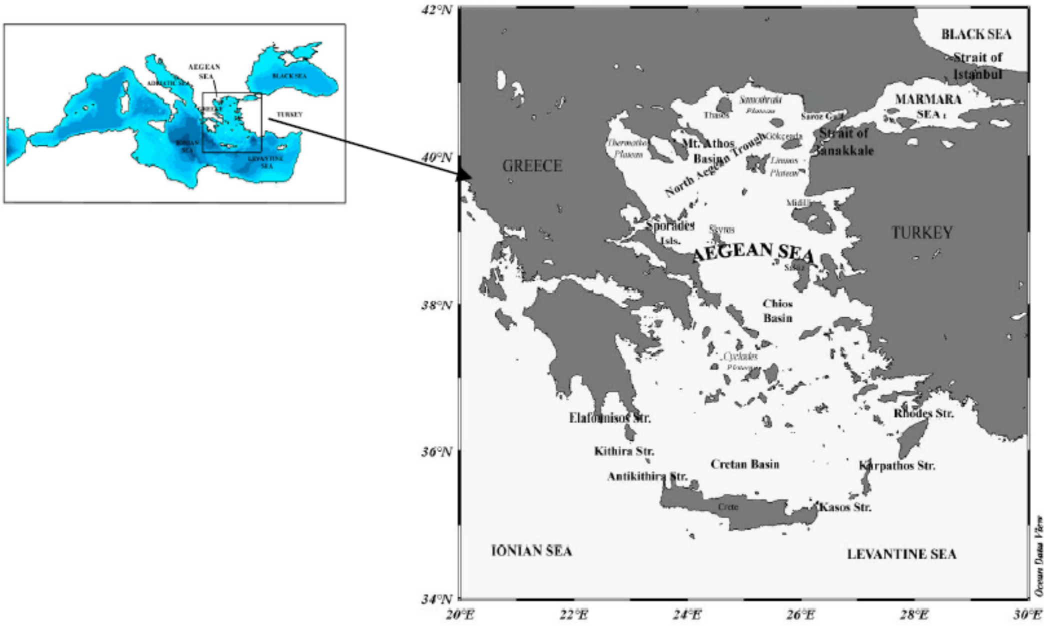


Figure 3.1 The location of the study area, major basins and islands

In the south it is bounded with the Cretan Island and several passages. It is connected to the Levantine Sea to the southeast via the Kassos Strait (sill depth: 1000 m, width 67 km), the Karpathos Strait (sill depth: 850 m, width: 43 km), and the Rhodes Strait (sill depth: 350 m, width 17 km). It joins to the Ionian Sea through three wide passages including the Antikithira Strait (sill depth: 700 m, width: 32km), the Kithira Strait (sill depth: 160 m, width: 33 km) and the Elafonissos Strait (sill depth: 180 m, width: 11 km) (Balopoulos et al., 1999).

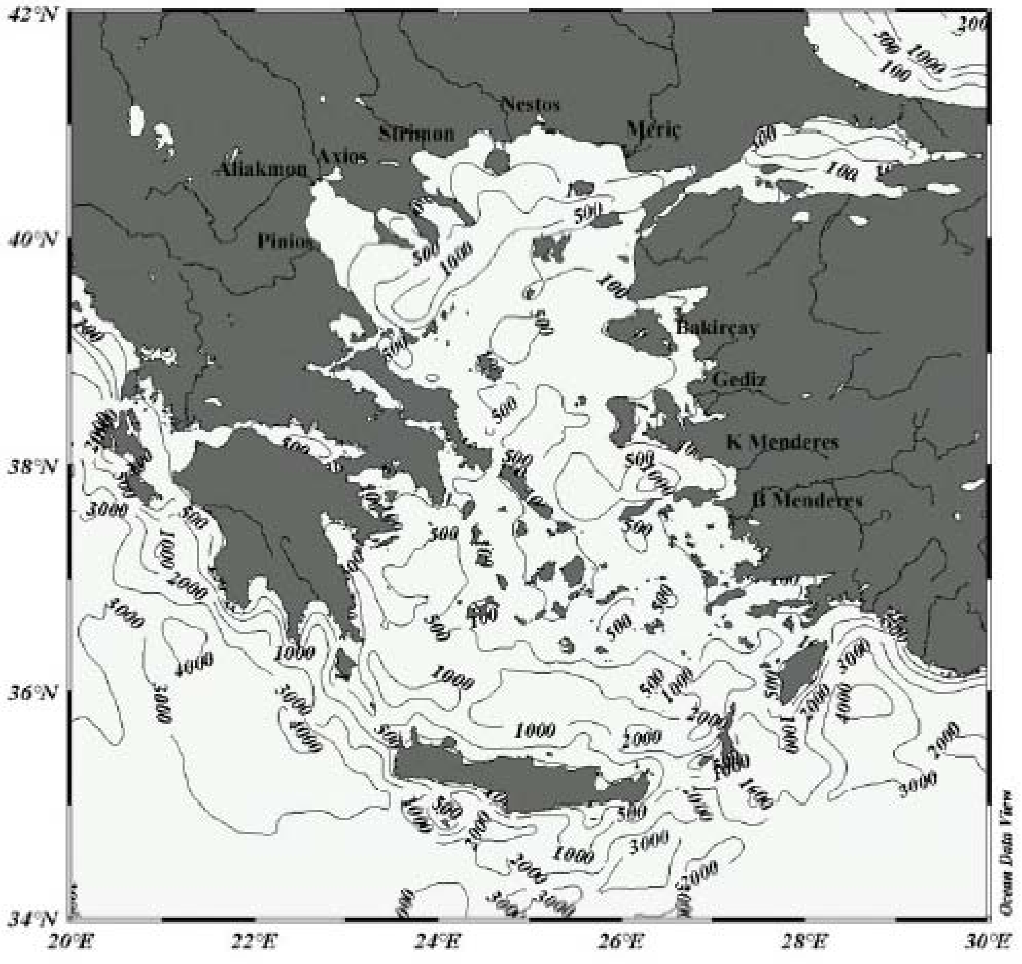


Figure 3.2 Bathymetry and major rivers discharging into the Aegean Sea (from Uckac, 2004)

It contains more than 200 islands forming small basins and narrow passages with very irregular coastline and topography. It covers an area of 2x10^5 km^2 and has a volume of 74.000 km^3 and a maximum depth of 2500 m. Bottom topography of the Aegean Sea is very complicated because of the fault block that occurred in the beginning of the Kuvaterner period (Figure 3.1, Figure 3.2). The North Aegean Trough is the deepest region, existing in the northern Aegean. It begins from Saroz Gulf, continues to the northeast-southwest direction including three depressions Samothraki Plateau, Mount Athos basin and Sporades basin. The sea further extends through the northwest-southeast direction and then it is curled to the northern part of the Create Island. Thus it is ‘S’ shaped and depths reach more than 1000 meters. The Cretan Sea is the deepest basin in the south Aegean reaching a depth of 2500 m. The Cretan Sea is bounded by the Cyclades Plateau with a 100-400 m in depth (Figure 3.2).

Several major rivers discharge into the Aegean Sea, such as Meric (Maritza River), Nestos, Strimon, Axios and Pinios discharge in the north and Bakırcay, Gediz, Buyuk and Kucuk Menderes in the east. These rivers drain Southeastern Europe and Western Turkey with a combined annual water discharge ranging between 400 and 2400 m^3 /s, or ~33 km^3 /yr through the Dardanelles. Most of this outflow occurs during the summer (peak in August), closely correlating with the maximum discharge of large rivers draining into the Black Sea, such as Dnieper, Dniester, Don, Danube and Bug.

3.2 Water Budget in the Aegean Sea

The annual evaporation is higher than the sum of rainfall and river inputs in the Aegean. But there is a positive water budget in the Aegean Sea because of the Black Sea originated waters entering from the Strait of Çanakkale. The water exchange in the Cretan straits is as much as 10 times bigger than the northern part and it varies seasonally depending upon exchanges with Eastern Mediterranean. In recent years, models show that 5000 km^3/year of water entering from Eastern Cretan Straits is balanced with the waters outflow through western straits (Oğuz & Tuğrul, 1998).

3.3. Hydrophysical Characteristic

Not only hydrochemical but also hydrophysical characteristics are different in the southern and northern parts of the Aegean. Lower salinity and temperatures were observed in the Northern Aegean due to the influence of Black Sea. Salty and warmer waters of the Eastern Mediterranean Sea affect Southern Aegean waters. In the beginning of the summer, Black Sea originated water masses move towards the Edremit Bay (MEDPOL, 1997).

Surface water mass in the Aegean Sea forms a counter-clockwise gyre. At present, warm (16-25 °C) and high salinity (39.2-39.5 ppt) Mediterranean water moves northward along the west coast of Turkey. This water mass is placed westward south the Strait of Dardanelle by the cooler and low salinity water mass initially moves west-northwest along the Northern Aegean Sea, then flows southwards along the east coast of Greece (Yaşar, 1994). Water masses:

1. Aegean Sea Surface Water forms a 40-50 m thick veneer, with summer temperatures ranging between 21-26 °C and winter temperatures ranging between 10-16°C in the Aegean Sea. Similar north-south gradient is also observed in salinities with summer salinity values ranging between 30-39.5 psu and winter salinities ranging between 36.1-39.2 psu.
2. Aegean Sea Intermediate Water mass (40-50 m to 200-300 m) has a smaller north-south temperature gradient ranging between 15-18 °C and 11-16 °C from the northern to southern Aegean Sea, respectively. The salinity observed with values between 39.0-39.1 psu Seasonal salinity variations is very low.
3. Aegean Sea Bottom Water (below 200-300 m) is very uniform in temperature (13-14 °C) and salinity (39.1-39.2 psu) with little variations between in summer and winter (Yaşar, 1994).

Table 3.1 Grain size distribution and sediment type of the easten Aegean Sea surficial sediments

Station	**Sand**	**Silt**	**Clay**	**Silt+Clay**	**Sediment Type**
Meric River Estuary (MRE)	15.62	73.79	10.59	84.38	Clayey silt
Dardanelles Strait Entrance (DSE)	85.35	9.85	4.80	14.65	Sand
Edremit Bay (EB)	-	88.36	11.64	100.0	Silt
Dikili Bay (DB)	34.90	60.66	5.04	65.70	Sandy silt
Candarli Bay (CB)	-	82.54	17.46	100.0	Silt
Izmir Outer Bay (IOB)	32.41	56.09	11.50	68.40	Sandy silt
Izmir Middle Bay (IMB)	10.79	75.43	13.78	89.21	Clayey silt
Izmir Inner Bay (IIB)	12.44	71.06	16.60	87.66	Clayey silt
Kusadasi Bay (KB)	12.25	80.15	7.60	87.75	Sandy silt
Menderes Region (MR)	-	91.27	8.73	100.0	Silt
Akbuk Bay (AB)	79.34	11.22	9.44	20.66	Silty sand
Gokova Bay (GB)	27.02	69.49	3.49	72.98	Sandy silt
Datca (D)	12.90	78.66	8.44	87.10	Sandy silt
Marmaris Bay (MB)	47.89	49.08	3.03	52.11	Silty sand

3.4. Geological Characteristics of Aegean Sea

Grain size analyses were performed using standard sieving and settling procedures (Hakanson & Jansson, 1983) in the Eastern Aegean Sea coast. Hydrometer method;

based on records of the variation in density of settling suspensions using a hydrometer. These sedimentation methods require inexpensive apparatus and cover a wide range of grain sizes. The hydrometer method is not applicable if less than 10% of the sample passes the 63 µm mesh. Textural classification of the sediment samples was based on the relative percentages of clay (<0.002 mm), silt (0.002-0.063 mm), sand (0.063-2 mm) and gravel (>2 mm). The grain size composition of the Eastern Aegean coast surficial sediments was given in Table 3.1.

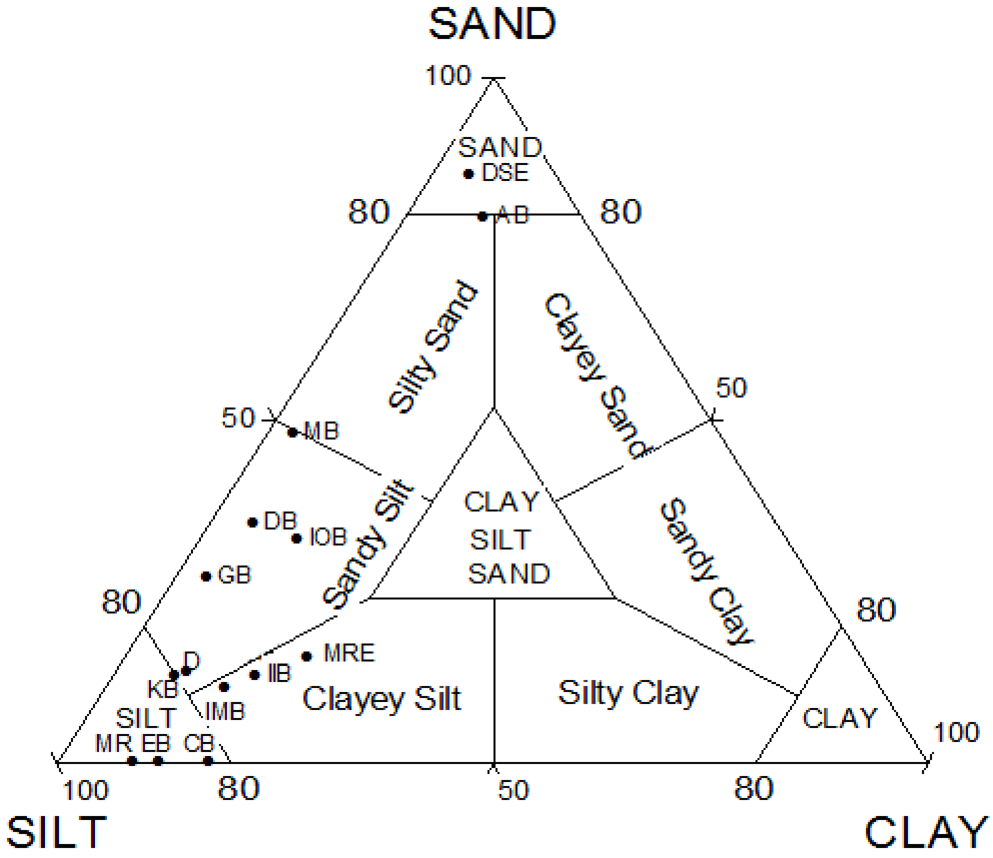


Figure 3.3 Textural compositions of the surface sediments from the Eastern Aegean Sea (According to Shepard, 1954).

The textural composition of the surface sediments from the Eastern Aegean Sea were shown in Figure 3.3. This classification was performed by grain size distribution. According to this classification Akbuk Bay and Marmaris Bay are covered by silty sand; Datca, Dikili Bay, Gokova Bay, Kusadasi Bay, Izmir Outer Bay sandy silt; Candarli Bay, Edremit Bay, Menderes Region are consists of silt while Meric River Estuary, Izmir Middle Bay and Izmir Inner Bay are floored clayey silt and Dardanelles Strait Entrance is only coverd by sand in the Aegean Sea.

3.5. Chemical Characteristics of Aegean Sea

The Aegean Sea is one of the most oligotrophic parts of the Mediterranean Sea. Although nitrogen and phosphorus levels are low in general, concentrations of nutrients are higher than the Mediterranean Sea in some regions.

Very few published data are available on nutrient concentrations in the Aegean. Distribution of nutrients was investigated by Friligos (1986a), Kucuksezgin, Balcı, Kontas, & Altay, (1995), UNEP, (1996) in the Aegean Sea. Nutrient levels are generally higher in the northern Aegean than in the southern part. This situation may result from water originating from the Marmara and the Black Sea. Nutrient values increase with increasing depth. There are many rivers, which transport nitrogen and phosphorus into the northern Aegean. The order of magnitude of the fresh water inputs is 1000 m^3/s in total along the Aegean coastline and this value is higher than in other Mediterranean regions (MEDPOL, 1997).

CHAPTER FOUR
MATERIAL AND METHODS

4.1 Sampling and Measurement of Environmental Parameters

Surface sediments were sampled on June 2008 (dry season) at fourteen sampling stations from the Aegean Sea. The location of sampling points and coordinates are given in Table 4.1 and Figure 4.1, respectively. Samples were collected using a small stainless steel Van-Veen grab sampler operated by handling from the middle of the grab to a depth of 1 cm, wrapped in aluminum foil and stored at -20°C for subsequent analysis in order to avoid degradation. The sediments were sampled in the framework of the IMST-165 (2008) project supported by the Ministry of Environment and Forestry.

Table 4.1.The coordinates of sampling stations of The Aegean Sea

Station	**Latitude (ºN)**	**Longitude (ºE)**
Meriç River Estuary (MRE)	40°44′00″	26°00′48″
Dardanelles Strait Entrance (DSE)	39°59′00″	26°00′00″
Edremit Bay (EB)	39°34′23″	26°55′07″
Dikili Bay (DB)	39°05′00″	26°51′52″
Candarli Bay (CB)	38°53′12″	26°59′00″
Izmir Outer Bay (IOB)	38°23′18″	26°46′43″
Izmir Middle Bay (IMB)	38°25′30″	27°00′06″
Izmir Inner Bay (IIB)	38°26′12″	27°07′48″
Kusadasi Bay (KB)	37°52′18″	27°13′00″
Menderes Region (MR)	37°32′	27°08′
Akbuk Bay (AB)	37°22′00″	27°22′21″
Gokova Bay (GB)	37°00′11″	28°09′15″
Datca (D)	36°38′20″	27°40′
Marmaris Bay (M)	36°49′	28°16′

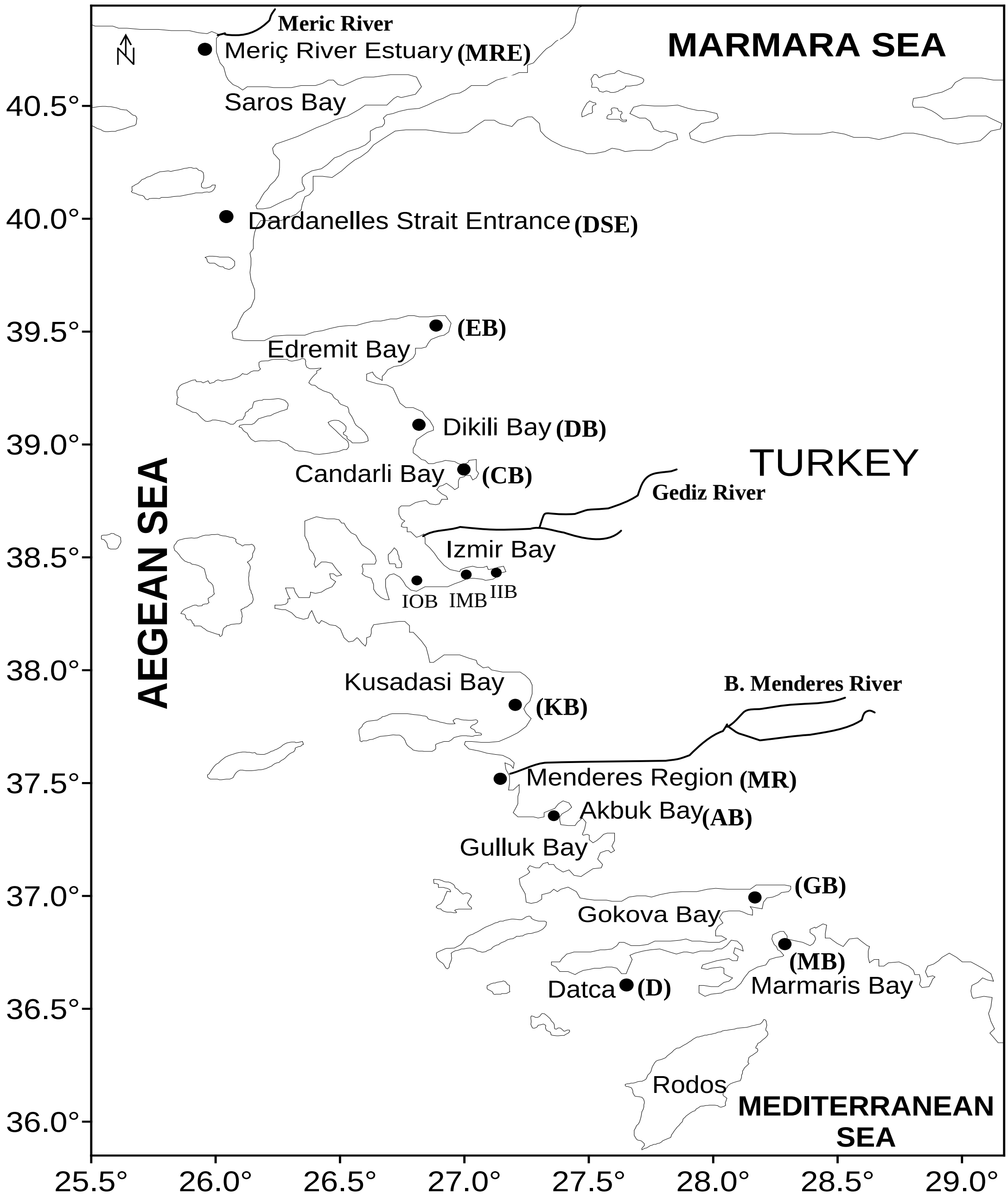


Figure 4.1 The Location of sampling sites on the Eastern Aegean coasts.

The samples were analyzed for organochlorinated pesticides (OCPs: DDTs, BHCs, HCB, cyclodienes), PCBs (Arochlor 1254 and Arochlor 1260) and petroleum hydrocarbons (aliphatic and polycyclic aromatic hydrocarbons).

Routine wet sediment sample analyses are performed at each sample such as the water content that is determined by oven drying of about 5-10 g wet sediments for 12 h (or to constant weight) at 105°C. The amount of organic carbon and organic matter are determined by spectrophotometrically in dried sediment samples following the sulfochromic oxidation method. The accuracy of this method is ±0.017 % organic matter (HACH Publication 3061, 1988). Water quality parameters such as dissolved oxygen (DO), pH, temperature and salinity are measured at sampling stations. During cruise, temperature and salinity are measured at each station using a SBE-9 CTD, equipped with pressure, temperature, conductivity and dissolved oxygen sensors and water samples are collected from discrete depths using a General Oceanics Rosette sampler attached to the CTD. The CTD salinities are calculated using the 1978 Practical Salinity Scale equations (1980). Sea Bird CTD sensors are calibrated by the northwest Regional Calibration Center (operating under contract to NOAA) once a year.

4.2 Analytical Procedures

4.2.1 Organochlorine Pesticides and PCBs Analysis

The samples are freeze-dried for 48 h and sieved to pass through 250 μm in a stainless steel sieve and powdered to homogenize in an agate mortar before the extraction and a pre-extraction procedure is applied to glassware, cellulose extraction thimbles, florosil and sodium sulphate using a soxhlet apparatus (UNEP/FAO/IAEA/IOC, 1991).

Twenty grams of homogenized sediment samples with three replicates are analyzed for OCPs and PCBs following well-established standard techniques of UNEP, IAEA and FAO (UNEP/IOC/IAEA, 1988, 1995, 1996; UNEP/FAO/IAEA/IOC, 1991; IOC, 1993). A series of internal standards comprising PCB29, PCB198, ε-HCH and α-endosulfan D_4 are added to the sediments for quantifying the overall recovery of the organochlorine fractions. Samples are extracted in a Soxhlet apparatus for 8 hours using 250 ml of glass distilled 1:1 DCM (dichloromethane): a hexane mixture. Extractable organic matter (EOM) is determined by evaporating a small measured volume of this extract on the pan of an electro balance. DCM:Hexane extracts are concentrated to about 15 ml using a rotary evaporator and they are evaporated to a few milliliters with a pure nitrogen gas. The extract is further treated with metallic mercury to remove sulfur compounds. This extract is evaporated to 1 ml using a rotary evaporator and then cleaned-up using florisil chromatography column to separate classes of compounds in different fractions as described below.

Table 4.2 Detection limits of OCPs (pg g^{-1})

Compounds	**DLs**
HCB	0.10
p,p'-DDE	0.35
p,p'-DDD	0.17
p,p'-DDT	0.57
γ-HCH	0.13
Dieldrin	0.17
Endrin	0.37
Aldrin	0.13
Heptachlor	0.27
Aroclor 1254	4.5
Aroclor 1260	2.4

The samples are then transferred into florisil column which is precleaned with dichloromethane and hexane for 8 hours and dried. Florisil is activated at 130°C for 8 hours and deactivated with 0.5 % water. Anhydrous sodium sulfate (*ca.* 1cm) is added to florisil column. From the florisil column, the first fraction is obtained by eluting the sample with 65 ml of hexane, this fraction contained mainly PCBs, DDE, heptachlor, HCB and aldrin. The second fraction is obtained with 50 ml of a freshly prepared mixture of 70:30 hexane: DCM and it contains DDD, DDT, BHCs. The third fraction containing endrin, dieldrin, endosulphan-I, endosulphan-II, endosulphan sulphate and heptachlor epoxide is eluted with 55 ml of DCM. A blank sample is prepared to determine any contamination during analyses and the same procedures are applied to the blank sample as to sediment samples. The method detection limits of OCPs and PCBs were described as 3:1 signal versus noise value (S/N). The detection limits were given in 0.10-0.57 pg g^{-1} for organochlorinated pesticides and 2.4-4.5 pg g^{-1} for PCBs (Table 4.2).

4.2.2 Gas Chromotography Conditions for Halogenated Hydrocarbons

DB-5MS Column 30m x 0.25mm, film thickness 0.25 µm

Carrier gas: Nitrogen (99.99 % pure), flow rate: 5 ml/min

Make-up gas flow rate: 25 ml/min

ECD Detector temperature: 300°C

Injector temperature: 280°C

Temperature program: Initial temperature 70°C, increases 3°C/min and after reaching to 300°C, analysis continues isothermally for 15 min.

Table 4.3 Observed and reference OCP values for reference material of IAEA-159

Compounds	**Observed value±SD**	**Reference value**
HCB	0.19±0.01	0.17
p,p'-DDE	0.88±0.051	0.89
p,p'-DDD	0.83±0.01	0.82
p,p'-DDT	0.71±0.021	0.71
γ-HCH	0.19±0.01	0.21
Dieldrin	0.46±0.006	0.48
Endrin	0.84±0.03	0.77
Aldrin	0.20±0.02	0.17
Heptachlor	0.29±0.03	0.31
Aroclor 1254	13.0±0.50	14.3
Aroclor 1260	5.97±0.42	5.54

4.2.3 Quality Assurance for OCPs

For every set of 10 samples, a procedural blank and spike sample consisting of all reagents is run to check for interference and cross contamination. The OCP recoveries are determined relative to the ratio of direct injection of extract and the working standards prepared in hexane. The recoveries for sediments fell with in a fairly narrow range, for internal standards between 70.0 and 96.1 %. The final results are cited on a dry weight basis. Also, the quality of the analytical data is assured using the reference material of IAEA-159 the sediment sample (from the International Laboratory of Marine Radioactivity, IAEA, Monaco). The values obtained (in ng g^{-1} dry wt) for the analyses of three replicates of this sample were given in Table 4.3.

4.2.4 Petroleum Hydrocarbon Analysis

Prior to extraction, about 10 g of freeze-dried sediment (250µm) samples with three replicates are placed in preextracted cellulose thimbles and internal, non-naturally occurring petroleum hydrocarbon standards (n-C_{19} d40, n-C_{32} d66, Hexamethylbenzene, Cadalene and Naphthalene-d8) are added for the quantitative calculations. All samples are extracted in a soxhlet apparatus for 8 hours, using n-hexane and dichlorometane (1:1), according to UNEP, (1991) then the extract is concentrated to 15 ml in rotary evaporator. The evaporation is achieved to 4-5 ml under a gentle stream of nitrogen. Finally activated copper is used to remove sulpfur from the extracts and activated copper is prepared daily. Copper is activated using %30 HCl, ultrasonic shaker, distilled water and acetone.

The sulpfur-free lipid extracts are then separated into two fractions, using a column chromatography on 5 g of deactivated silica (bottom), 10 g of deactivated alumina and 1 g of anhydrous Na_2SO_4 (top). The alumina and silica are precleaned by soxhlet extraction, first for 8 hours with methanol and then for 8 hours with hexane and then dried. Before use, they are activated at 200 ºC for 4 hours and partially deactivated with 5% water. The sample is added on top of the column. A first fraction is eluted with 20 ml hexane. The second saturated fraction is eluted with 30 ml solution of hexane:dichloromethane (90:10). All groups are collected in glass flasks, and first concentrated to 15 ml using a rotary evaporator then using a gentle stream of nitrogen gas to 1 ml. The first group has saturated aliphatic hydrocarbons, the second group has unsaturated and polycyclic aromatic hydrocarbons. The method detection limits (MDLs) of petroleum hydrocarbons were described as 3:1 signal versus noise value (S/N). Detection limits were 2.01-9.10 ng g^{-1}dw for aliphatics and 4.15-9.79 ng g^{-1}dw for PAHs (Table 4.4).

Table 4.4 Detection limits of aliphatic and polycyclic aromatic hydrocarbons (ng g^{-1})

Compounds	**DLs**	**Compounds**	**DLs**
n-C10	7.23	Naphthalene	4.76
n-C12	6.48	1-methylNaphthalene	4.89
n-C14	7.29	1-ethylNaphthalene	3.97
n-C16	6.21	Acenaphthene	6.11
n-C17	7.38	Acenaphthylene	4.15
Pristane	6.45	Fluorene	5.36
n-C18	7.27	Phenanthrene	5.88
Phytane	8.98	Anthracene	5.72
n-C20	5.96	2-methylPhenanthrene	9.47
n-C21	2.01	1-methylPhenanthrene	9.16
n-C22	6.09	3,6-dimethylPhenanthrene	9.71
n-C24	6.19	Fluoranthene	6.79
n-C26	6.10	Pyrene	6.99
Squalane	9.10	1-methylPyrene	9.19
n-C28	6.24	Chrysene	8.97
n-C30	6.26	Perylene	9.79
n-C32	6.95	Benzo(a)anthracene	6.29
n-C34	7.89	Benzo(b)fluoranthene	6.68
		Benzo(k)fluoranthene	6.96
		Benzo(e)pyrene	6.32
		Benzo(a)pyrene	8.39
		Indeno(1,2,3,c,d)pyrene	5.91
		Dibenzo(a,h)anthracene	7.96
		Benzo(g,h,i)perylene	5.26

4.2.5 Gas Chromatography Conditions for Petroleum Hydrocarbons

DB-5MS Column 30m x 0.25mm, film thickness 0.25 µm

Carrier gas: Nitrogen (99.99 % pure), flow rate: 1.6 ml/min

Make-up gas flow rate: 20 ml/min

FID Detector temperature: 300°C

Injector temperature: 270°C

Temperature program: Initial temperature 60°C, increases 3°C/min and after reaching to 300°C, analysis continues isothermally for 15 min.

Chromatograms of aliphatic and aromatic hydrocarbons for selected sampling points and standards are given in Figure 4.2, 4.3, 4.4, 4.5, 4.6 and 4.7.

Table 4.5 Observed and reference petroleum hydrocarbon values for reference material of IAEA-417

Compounds	**Observed value±SD**	**Reference value**
n-C17	210±21.50	200
Pristane	448±15.89	420
n-C18	239±17.01	230
Phytane	343±14.19	370
Naphthalene	137±3.61	150
Phenanthrene	4030±156.5	3900
Anthracene	641±48.69	630
Chrysene	3817±217	3600
Fluorene	222±14.47	230
Fluoranthene	7884±281.0	7700
Pyrene	6226±180	6000
Benzo(b)fluoranthene	4198±49.7	4100
Benzo(k)fluoranthene	1840±99.2	2000
Benzo(a)anthracene	3418±30.0	3200
Benzo(e)pyrene	2892±170.2	3000
Benzo(a)pyrene	2948±113.7	2800
Benzo(g,h,i)perylene	2252±80.3	2300
Indeno(1,2,3,cd)pyrene	2575±70.9	2700
Acenaphthylene	43.3±2.08	42
Acenaphthene	160.3±13.05	180

4.2.6 Quality Assurance for petroleum hydrocarbons

Compound identification was made by internal standards such as n-C_{19} d40, n-C_{32} d66 (normal and isoprenoid alkanes) and hexamethylbenzene, cadalene and naphthalene-d8 (PAHs). Appropriate blanks are analyzed with each set of analyses and in addition, sediment reference material IAEA-417 (from the International Laboratory of Marine Radioactivity, IAEA, Monaco) is analyzed simultaneously. The whole methodology is verified on this reference material, obtaining results in good agreement with the certified values. The results obtained (in ng g^{-1} dry wt) for the analyses of three replicates of this sample were given in Table 4.5. Blanks were run periodically during the analysis to confirm the absence of contaminants. The recoveries for sediments fell with in a fairly narrow range, for internal standards between 75 and 103 %.

4.3 Statistical Analysis

Statistical analyses were performed using STATISTICA for Windows, Release 6.0, Copyright StatSoft, Inc. 1995. Pearson's Product-Moment Correlation test used to check for significant relationships between organochlorine compounds and organic carbon in sediments. In all case, the level of significant was set at $p< 0.05$. Primer 5 for Windows Ver 5.2.9 software was used for cluster and principal component analyses. The first step in the multivariate statistical analysis was application of PCA with the aim of grouping the individual aliphatic hydrocarbons, aromatic hydrocarbons, organochlorinated compounds. Hierarchical cluster analysis which identifies homogenous groups of samples was engaged according to the complete linkage and group average between groups of stations and compounds in the sediment samples. The data set was normalized using log (x+1) transformation.

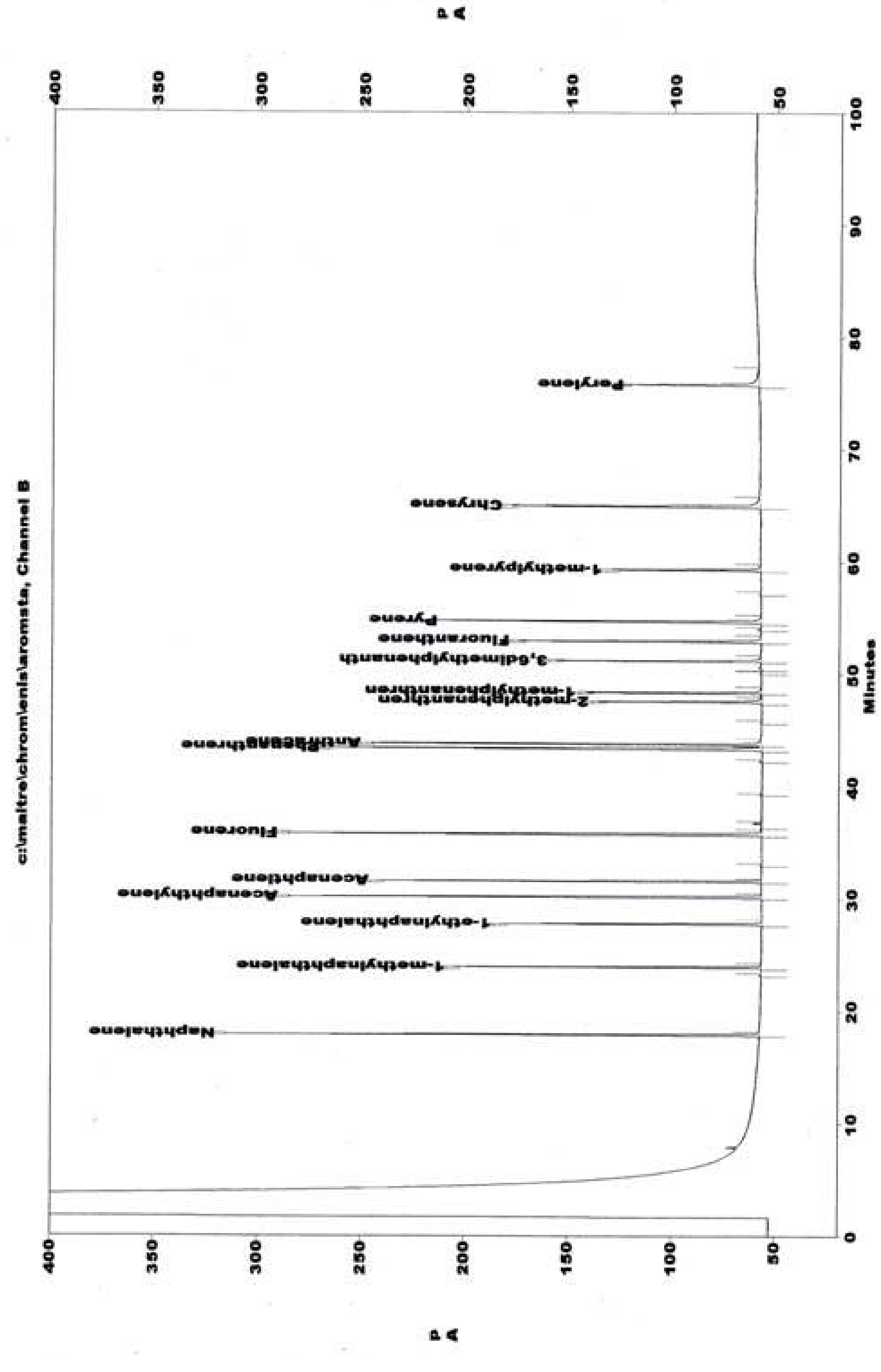


Figure 4.2 Chromatogram for standard polycyclic aromatic hydrocarbons.

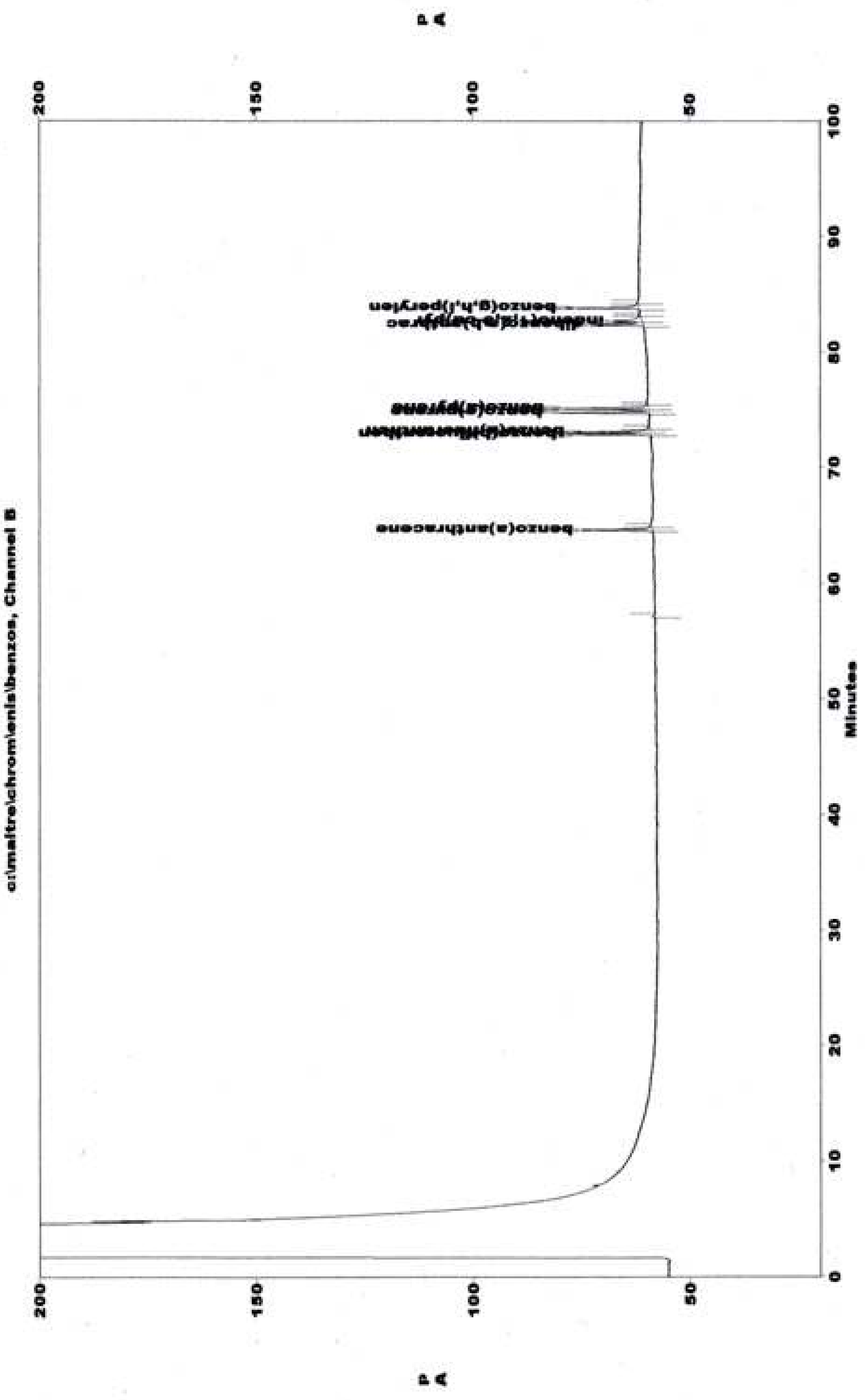


Figure 4.3 Chromatogram for standard benzo compounds.

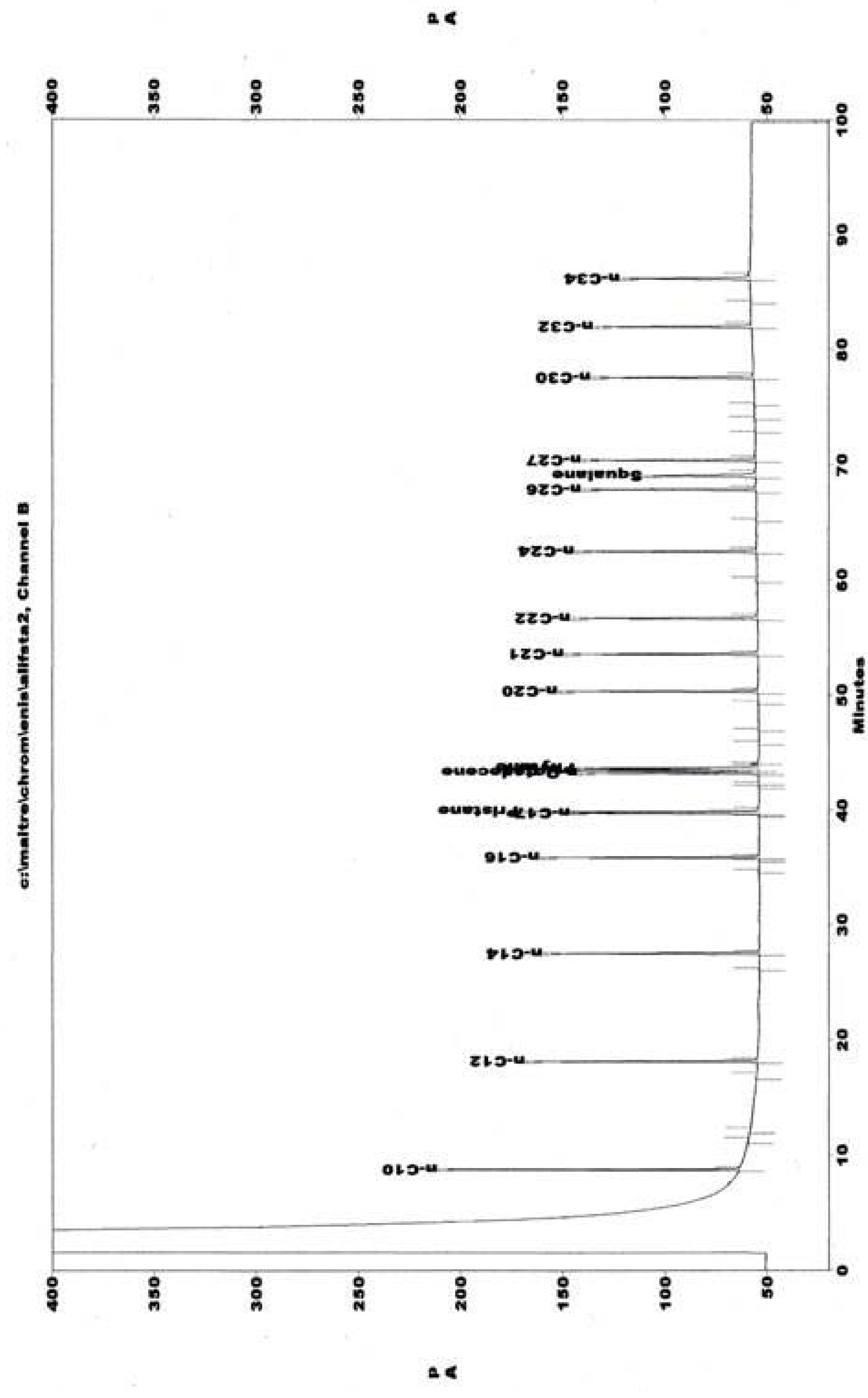


Figure 4.4 Chromatogram for standard aliphatic hydrocarbons.

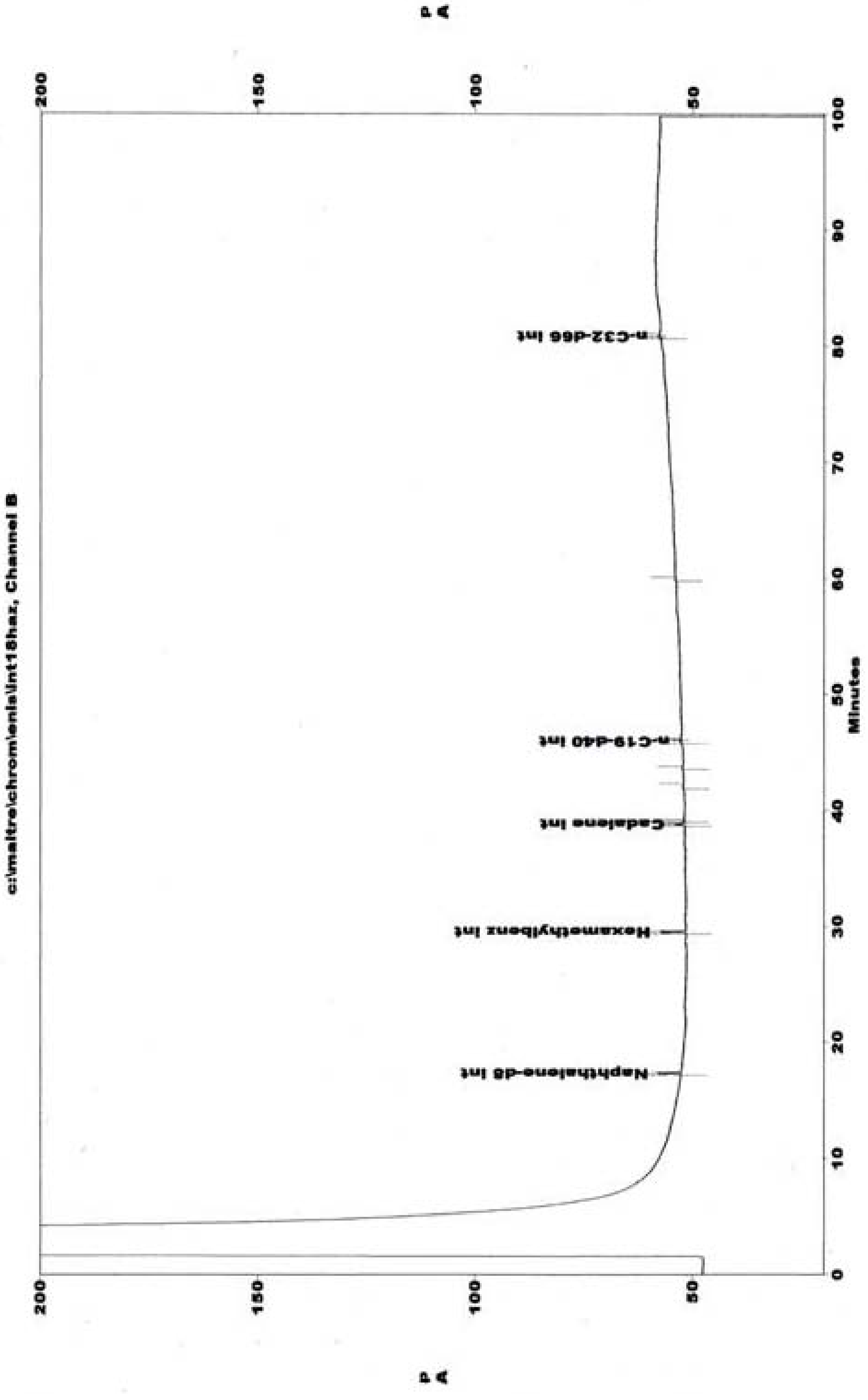


Figure 4.5 Chromatogram for internal satandards.

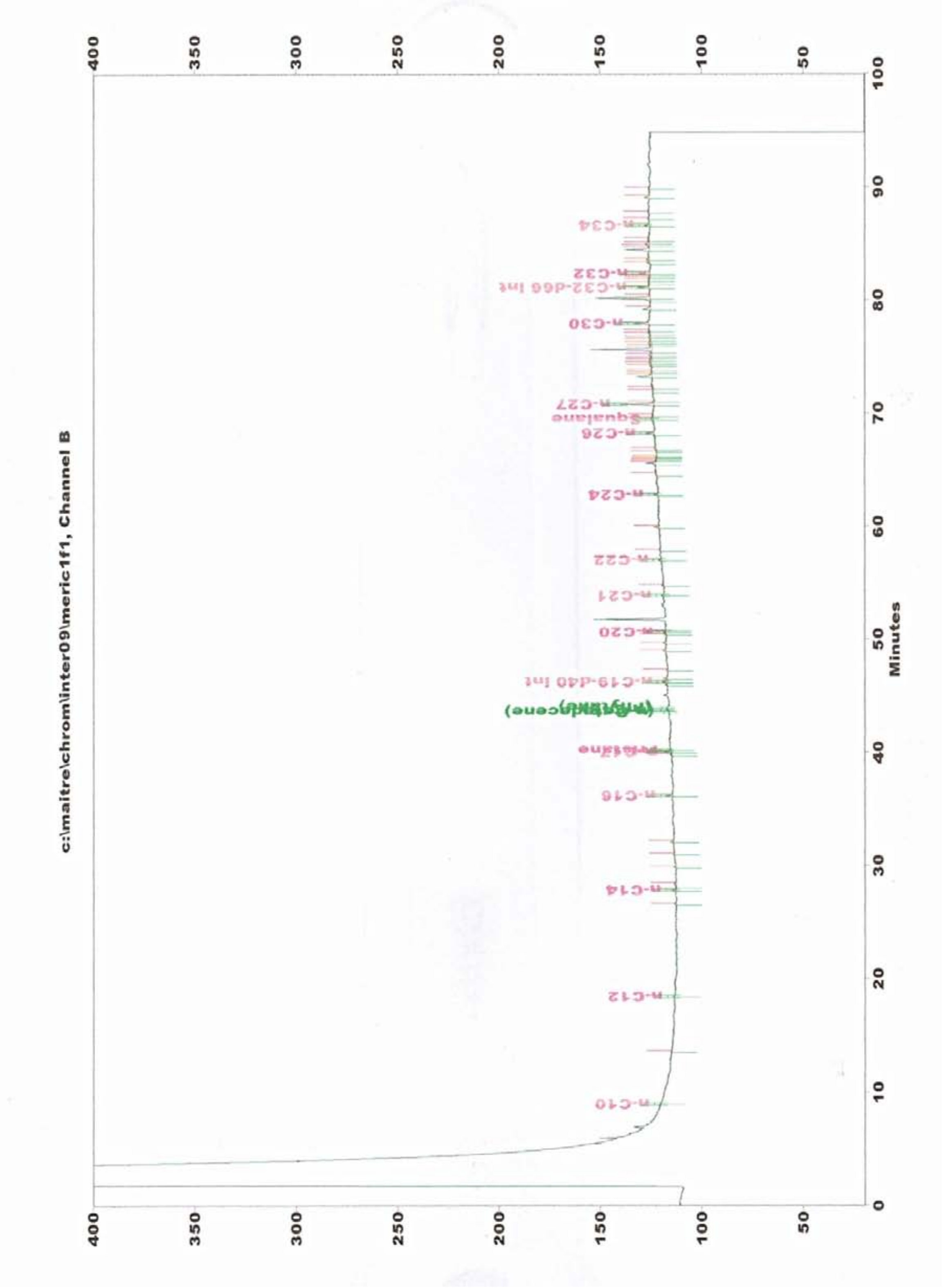


Figure 4.6 Chromatogram of aliphatic hydrocarbons for the Eastern Aegean Sea sediments.

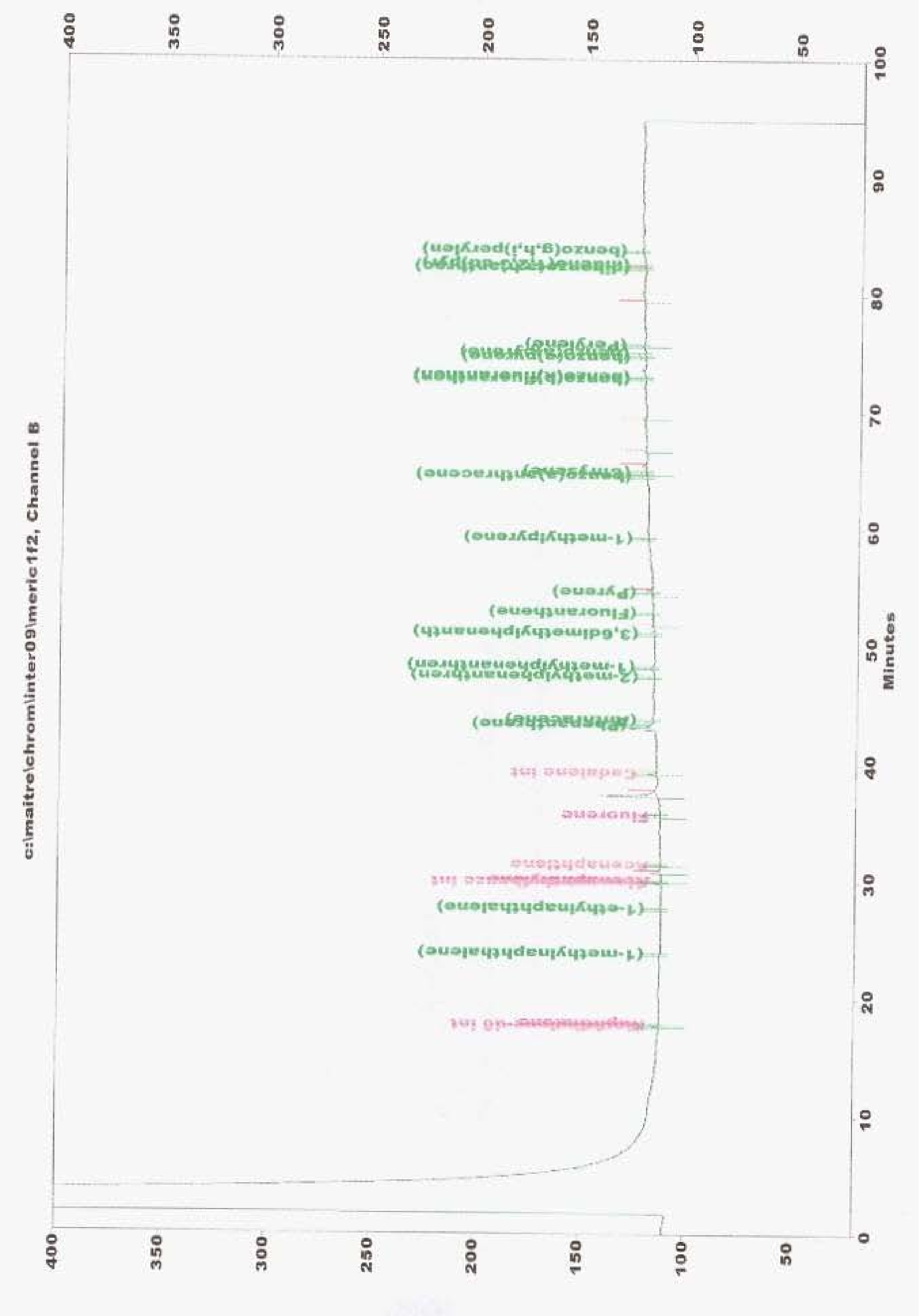


Figure 4.7 Chromatogram of polycyclic aromatic hydrocarbons for the Eastern Aegean Sea sediments.

CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 Total hydrocarbons in sediment

In terms of total hydrocarbons (Table 5.1), concentrations as the sum of total aliphatic and total aromatic hydrocarbons ranged from 0.52 to 4.85 µg g^{-1} dry wt, with the highest amounts in Izmir Inner Bay and the lowest in Izmir Outer Bay. Whereas total hydrocarbon concentrations higher than 500 µg g^{-1} are generally indicative of significant pollution, values below 10 µg g^{-1} are considered unpolluted sediments (Volkman et al., 1992). Samples taken from the Eastern Aegean Sea (Turkey) coastline showed comparatively little contamination (total hydrocarbon concentrations <10 µg g^{-1}). Compared to other regions of the world (Table 5.2), the total hydrocarbon concentrations observed in our study were within the same range of magnitude with those observed for sediments collected from areas, such as in Ukraine (2.1-6.6 µg g^{-1}, Readman et al., 2002), in Eastern Mediterranean (0.5-5.7 µg g^{-1}, Gogou, Bouloubassi, & Stephanou, 2000), in Australia (0.5-2 µg g^{-1}, Volkman et al., 1992) and in Izmir Bay (0.09-4.50 µg g^{-1}, Darilmaz & Kucuksezgin, 2007).

5.2 Aliphatic hydrocarbons in sediment

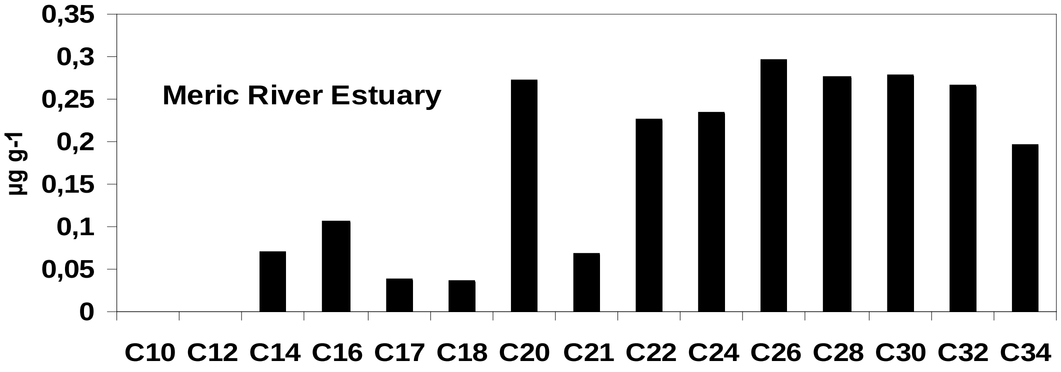
5.2.1 n-Alkanes

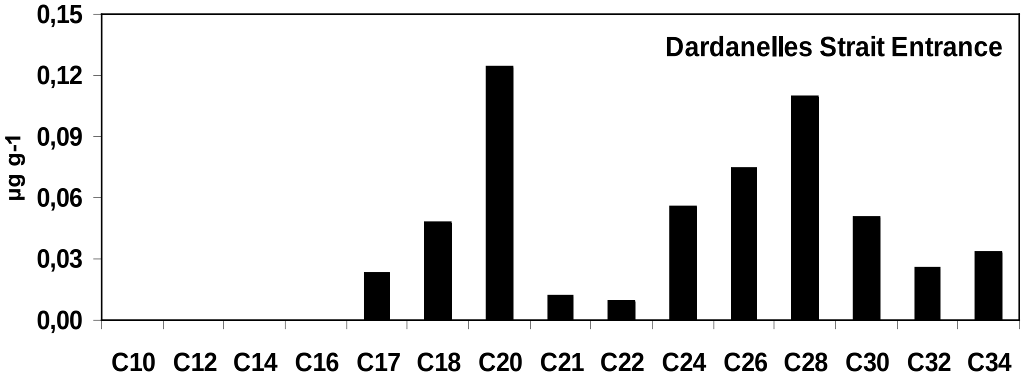
Resolved aliphatic hydrocarbons consisted mainly of C10-C34 *n*-alkanes with total concentrations ranging from 0.25 to 2.37 µg g^{-1} dry weight (Table 5.1). Concentrations of total *n*-alkanes ranged over 9-fold from 0.25 to 2.37 µg g^{-1}, with a mean of 1.22±0.65 µg g^{-1}. The concentrations of total *n*-alkanes in sediments from the Eastern Aegean coasts were lower than 2.00 µg g^{-1}, except for Meric River Estuary (2.37 µg g^{-1}) and Izmir Inner Bay (2.28 µg g^{-1}).

Table 5.1 Concentrations of aliphatic hydrocarbons (on a dry weight basis) and selected ratios recorded for Eastern Aegean sediments

	MRE	**DSE**	**EB**	**DB**	**CB**	**IOB**	**IMB**	**IIB**	**KB**	**MR**	**AB**	**GB**	**D**	**MB**
EOM (μg g^{-1})	2880	100	2760	4420	1860	2490	2420	6740	1200	2300	100	2220	100	2600
n-C17 (ng g^{-1})	38.3	23.5	76.7	72.3	68.8	47.9	21.2	124	47.8	46.8	63.4	58.3	48.5	82.1
Pri (ng g^{-1})	39.7	22.6	80.6	74.3	69.7	49.8	23.3	113	49.4	48.6	67.8	60.8	53.9	84.7
n-C18 (ng g^{-1})	35.4	48.3	60.7	48.0	68.3	33.4	20.3	234	37.4	36.8	50.6	47.3	26.0	79.5
Phy (ng g^{-1})	36.3	42.6	79.4	60.3	71.7	36.9	21.1	223	46.6	44.7	64.4	53.2	33.4	80.1
Squalane (ng g^{-1})	100	41.7	29.1	23.3	46.4	nd	nd	nd	41.4	36.6	68.6	29.0	29.1	46.2
Pri/Phy	1.09	0.53	1.02	1.23	0.97	1.35	1.10	0.51	1.06	1.09	1.05	1.14	1.61	1.06
n-C17/Pri	0.96	1.04	0.95	0.97	0.99	0.96	0.91	1.10	0.97	0.96	0.94	0.96	0.90	0.97
n-C18/Phy	0.98	1.13	0.76	0.80	0.95	0.91	0.96	1.05	0.80	0.82	0.79	0.89	0.78	0.99
C<24 (%)	34.5	38.3	49.9	50.1	41.2	47.8	57.3	48.6	54.6	62.1	53.7	64.8	51.7	47.2
Dominant Peaks	C26	C20	C20	C28	C28	C17	C22	C22	C18	C16	C28	C20	C20	C22
Total *n*-alk (μg g^{-1})	2.37	0.57	1.75	1.14	1.92	0.25	0.75	2.28	0.65	1.49	0.98	0.89	0.90	1.20
Σ ALI (μg g^{-1})	2.54	0.67	1.93	1.30	2.11	0.33	0.79	2.66	0.79	1.63	1.18	1.03	1.01	1.42
Σ PAHs (μg g^{-1})	0.28	0.23	0.075	0.088	0.17	0.19	0.25	2.17	0.11	0.41	0.14	0.074	0.086	0.26
T-HC (μg g^{-1})	2.82	0.90	2.01	1.39	2.28	0.52	1.05	4.85	0.89	2.04	1.32	1.10	1.10	1.69
%Aliphatics /EOM	0.09	0.67	0.07	0.03	0.11	0.01	0.03	0.04	0.07	0.07	1.18	0.05	1.01	0.05
%T-HC/EOM	0.10	0.90	0.07	0.03	0.12	0.02	0.04	0.07	0.07	0.09	1.32	0.05	1.10	0.06
%Aliphatics/T-HC	90.0	74.7	96.3	93.6	92.5	64.2	75.9	54.9	88.3	79.9	89.4	93.3	92.2	84.5
Organic C (mgg^{-1})	21.0	12.1	18.4	24.5	22.2	20.1	7.6	32.5	12.3	13.6	18.7	10.7	11.3	10.3

Abbreviations used: C<24: ΣC_{12-23}/total *n*-alk; Total *n*-alk: *n*-alkanes (*n*-C_{12}-*n*-C_{35}); T-ALI: Total Aliphatics; T-HC: Total hydrocarbons.





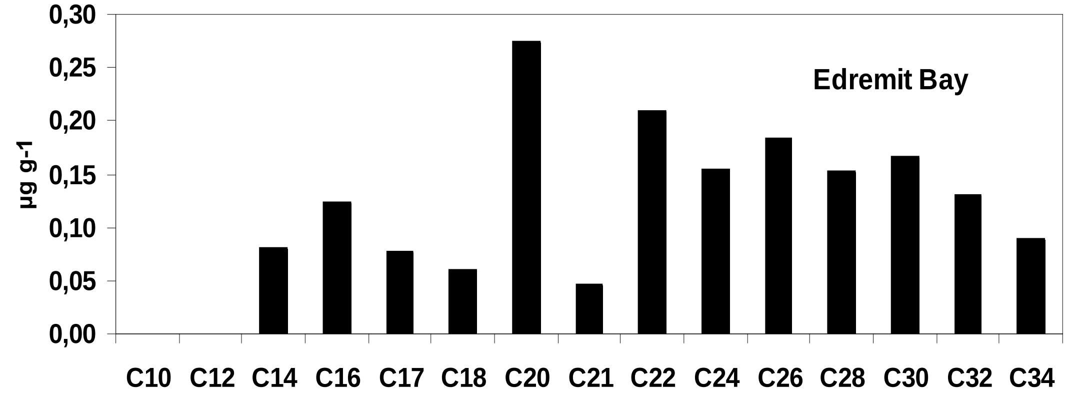


Figure 5.1a Distribution of individual *n*-alkanes in sediment samples of the Eastern Aegean coasts (MRE, DSE and EB).

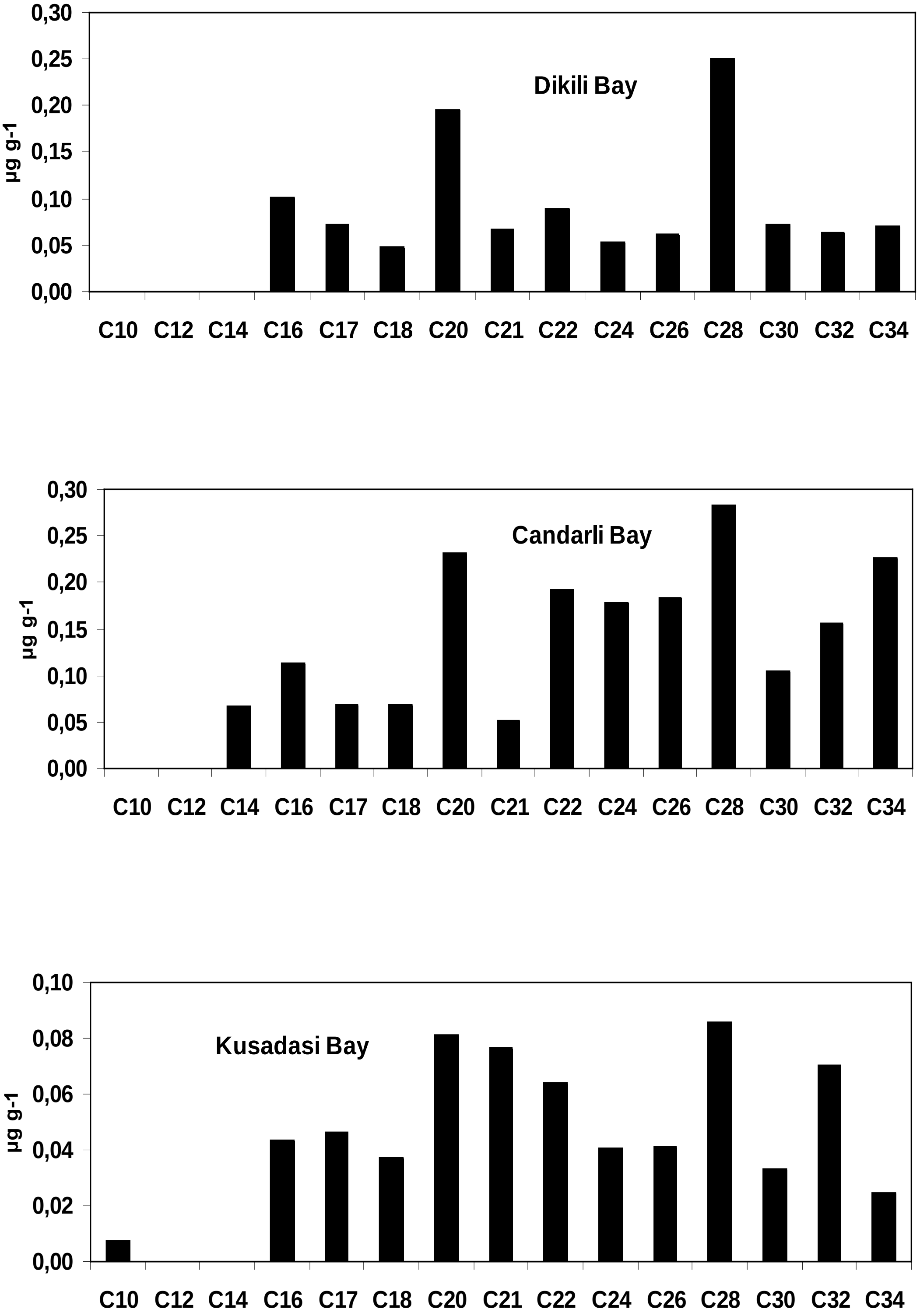
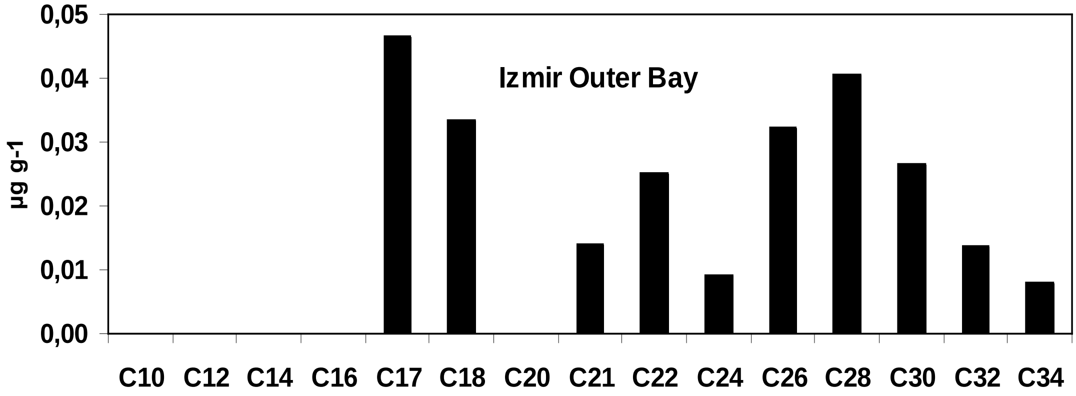
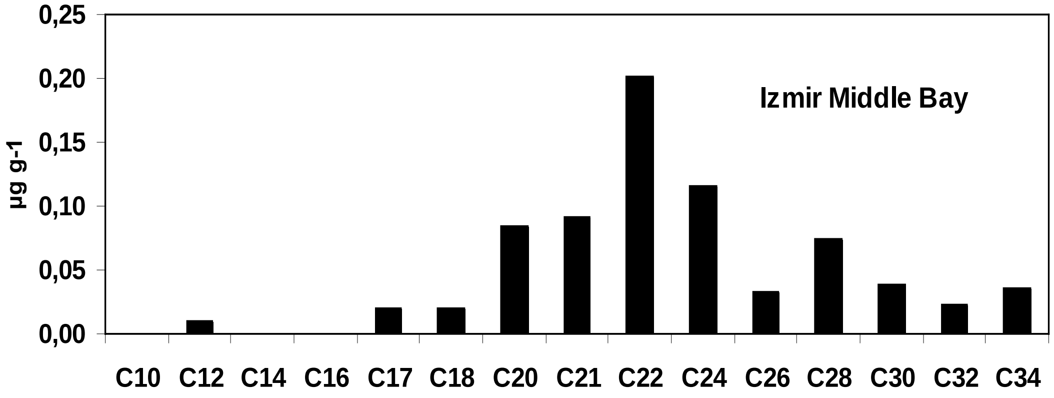


Figure 5.1b Distribution of individual *n*-alkanes in sediment samples of the Eastern Aegean coasts (DB, CB and KB).





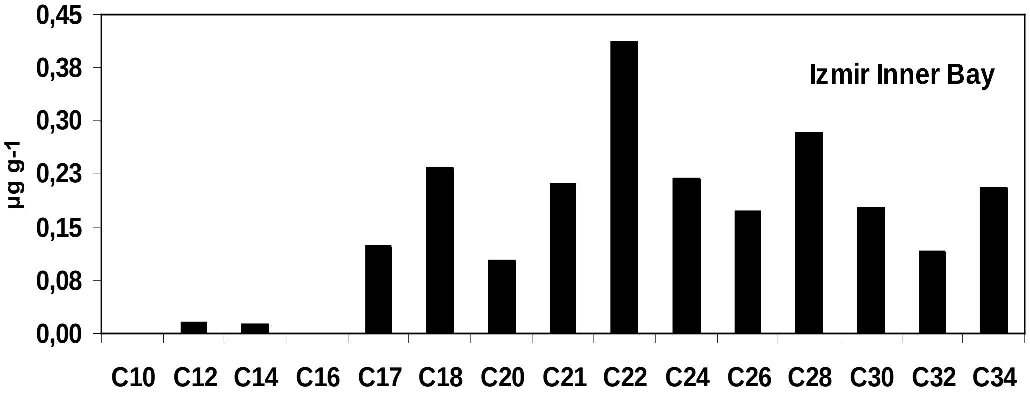


Figure 5.1c Distribution of individual *n*-alkanes in sediment samples of the Eastern Aegean coasts (IOB, IMB and IIB).

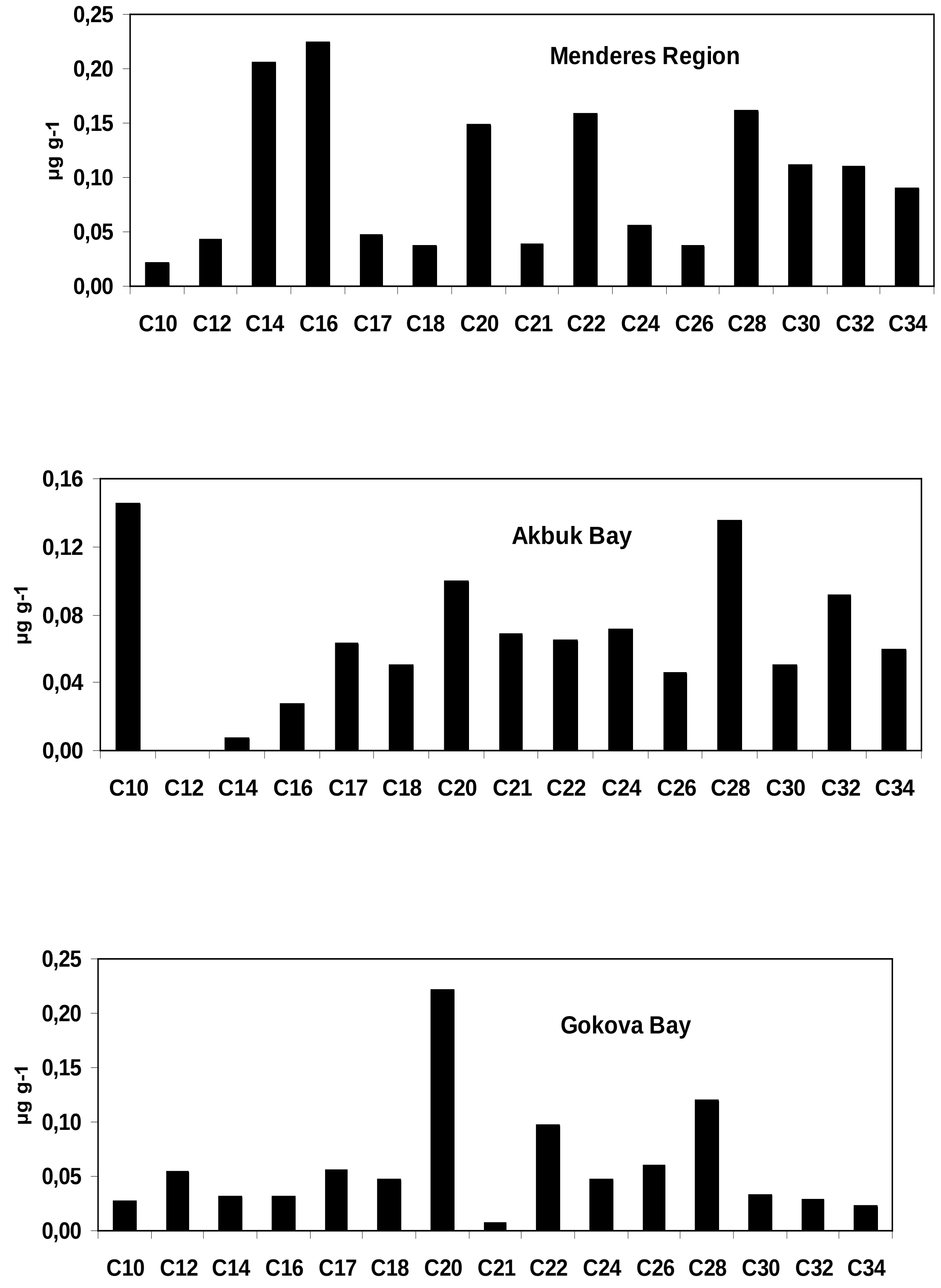
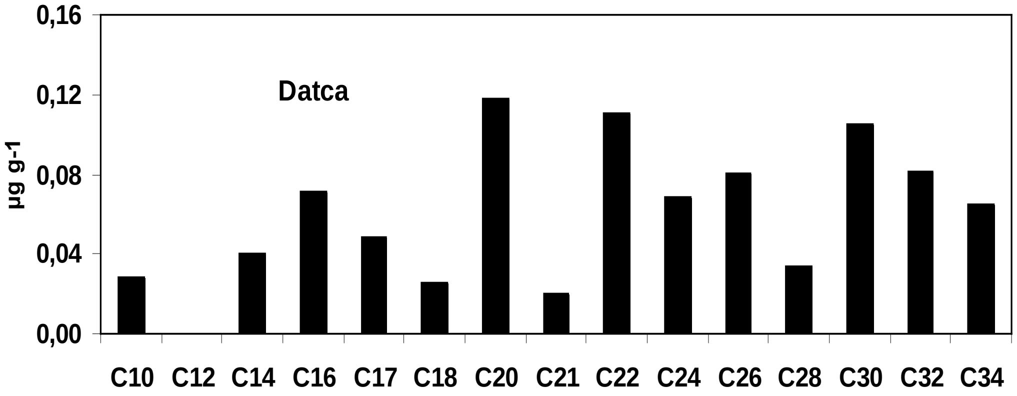


Figure 5.1d Distribution of individual *n*-alkanes in sediment samples of the Eastern Aegean coasts (MR, AB and GB).



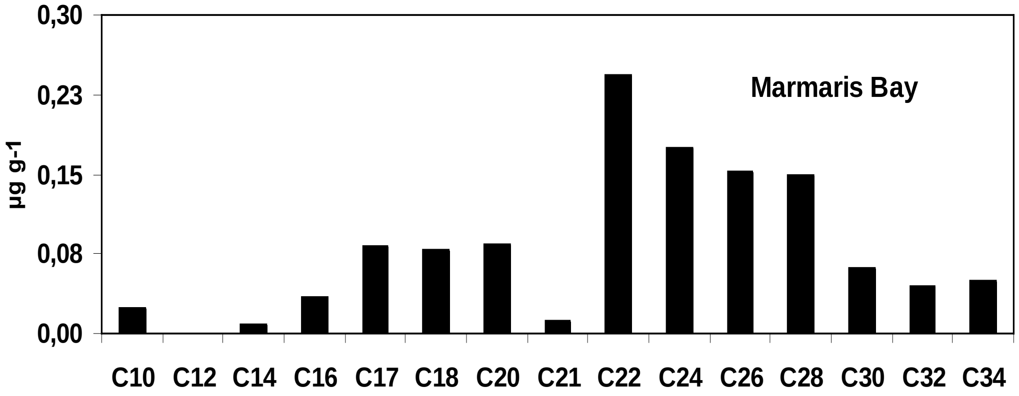


Figure 5.1e Distribution of individual *n*-alkanes in sediment samples of the Eastern Aegean coasts (D and MB).

High concentrations at station Izmir Inner Bay is probably related to anthropogenic sources as *n*-C22 was determined to be the dominant aliphatic hydrocarbon. The short-chain (C<24) *n*-alkane profile prevailed and accounted for >50% of the total *n*-alkanes at 7 out of 14 sampling sites (Table 5.1).

Marine phytoplanktonic hydrocarbons characterized by low odd carbon numbered *n*-alkanes (*n*-C17) were identified in all sampling sites. The long-chain (C≥25) *n*-alkane profiles occurred in variable concentrations. At stations Meric River Estuary, Dikili Bay, Candarli Bay and Akbuk Bay these long chain compounds prevailed with the C_{max} at C_{28} and C_{26} (e.g., Figure 5.1a, b, d). In general, the long-chain *n*-alkane distributions were observed along the Aegean coasts except Menderes region and Izmir Outer Bay.

Total aliphatic hydrocarbon ranged between 330 and 2660 ng g^{-1} along the eastern Aegean coast and distribution of total aliphatic hydrocarbon concentration were given in Figure 5.2. The highest level of total aliphatics was observed in Izmir Inner Bay.

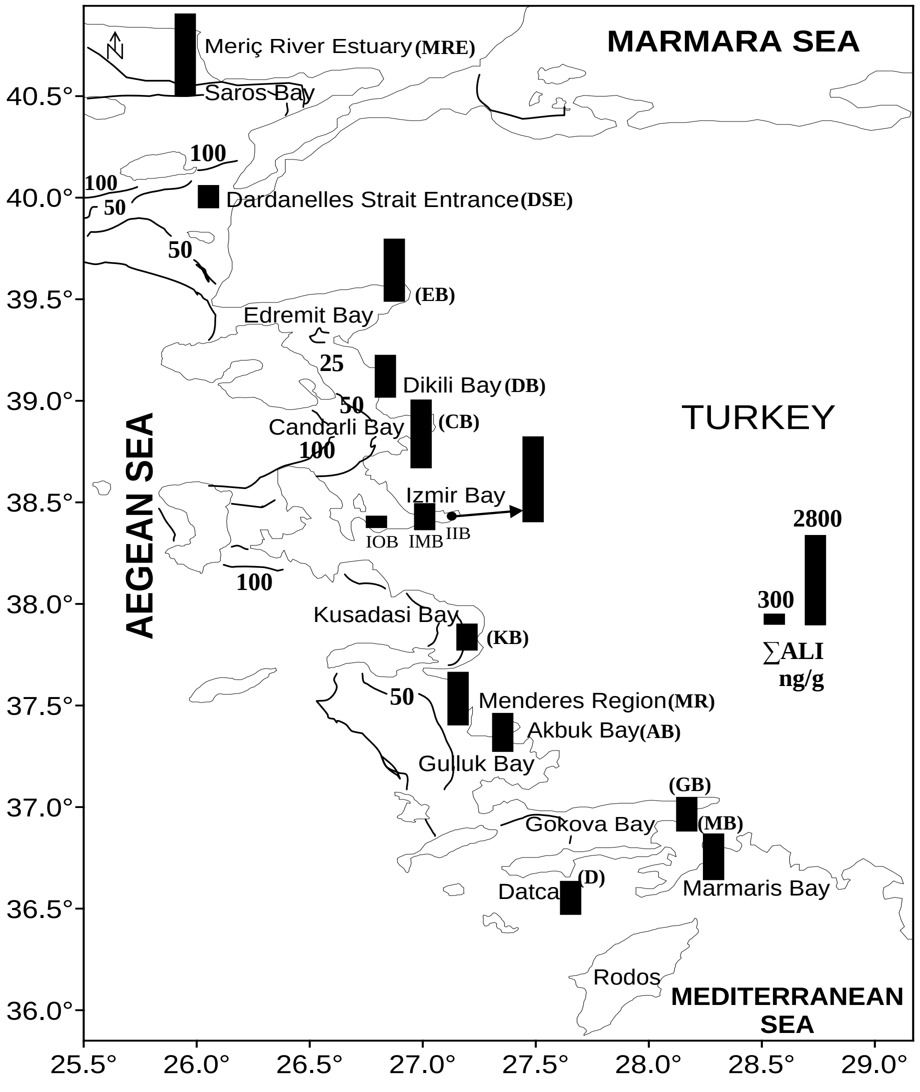


Figure 5.2 Distribution of total aliphatic hydrocarbon concentrations along the Eastern Aegean coasts.

5.2.2 Isoprenoid alkanes

Pristane (C19) and phytane (C20) are common isoprenoids detected in coastal marine sediments. Biogenic sources of the compounds are important, for example they derive from the phytol side chain of chlorophyll, either under reducing conditions (phytane) or oxidising conditions (pristane) and can also originate from lipids of zooplankton and bacteria (Le Dréau et al., 1997). As a rule, a high ratio of pristane to phytane or the predominance of a single isoprenoid (such as Pristane) indicates a biogenic source (UNEP/IOC/IAEA, 1992). In uncontaminated sediments, the ratio pristane/phytane (Pri/Phy) is higher than 1, typically between 3 and 5 (Steinhauer & Boehm, 1992). The Pri/Phy was greater than 1 in all samples except Dardanelles Strait Entrance and Izmir Inner Bay; this ratio showed slightly fluctuating values ranging from 1.02 to 1.61, indicating mainly a biogenic source (Table 5.1). Since the Pri/Phy was smaller than 1 in Dardanelles Strait Entrance and Izmir Inner Bay stations, they indicated reducing conditions.

In the Eastern Aegean coasts, the highest concentrations of pristane and phytane were recorded in Izmir Inner, Edremit and Marmaris Bays (pristane ranging from 80.6 to 113 ng g^{-1} dry wt and phytane from 79.4 to 223 ng g^{-1} dry wt; Table 5.1). *n*-C17 to Pristane (*n*-C17/Pr) ratios were ranging from 0.90 (D) to 1.10 (IIB) in the bay. In most of the sediment samples, it is noted that *n*-C17 dominates pristane indicating contributions derived from algae. Didyk, Simoneit, Brassell, & Eglinton, (1978) suggested that low *n*-C17/Pr ratio (<1) of a petroleum was evidence that terrigenous plants played a major role in the origin of the petroleum. The values of <1 for this study are consistent with this expectation about the source. *n*-C18 to Phytane (*n*-C18/Phy) ratios are variable, ranging from 0.76 (EB) to 1.13 (DSE). This ratio currently monitors the early effect of microbial degradation (Diez, Jover, Bayona, & Albaiges, 2007; Ezra, Feinstein, Pelly, Bauman, & Miloslavsky, 2000).

Table 5.2 Worldwide concentrations of Σ Hydrocarbons and Σ *n*-alkanes in sediments (μg g^{-1} dry wt^{-1})

Location	Σ Hydrocarbons	Σ *n*-alkanes	References
Bosphorus, Black Sea, Turkey	12–76	1.3–2.6	Readman et al., (2002)
Sochi, Black Sea, Russia	7.6–170	0.7–3.4	Readman et al., (2002)
Odessa, Black Sea, Ukraine	110–310	1.4–1.6	Readman et al., (2002)
Coastline, Black Sea, Ukraine	2.1–6.6	0.1–0.6	Readman et al., (2002)
Danube Coastline, Black Sea	49–220	1.2–2.1	Readman et al., (2002)
Crete, Eastern Mediterranean	0.5–5.7	0.1–0.9	Gogou et al., (2000)
Saudi Arabia, Gulf	11-6900	0.2–28	Readman et al., (1996)
Kuwait, Gulf	40–240	0.3–2.2	Readman et al., (1996)
Alexandria, Egypt	-	7–143	Aboul-Kassim & Simoneit, (1995)
Rhone River, France	25–170	2–12	Bouloubassi & Saliot, (1993)
Kuwait, Gulf	28	0.2	Fowler, Readman, Oregioni, Villeneuve, & Mckay, (1993)
UAE, Gulf	16	0.3–0.5	Fowler et al., (1993)
Oman, Gulf	6–22	0.1–1.2	Fowler et al., (1993)
Great Barrier Reef, Australia	0.5–2	-	Volkman et al., (1992)
Antartica (pristine)	<0.5	-	Lenihan, Oliver, Oakden, & Stephenson, (1990)
Dee Estuary, UK	-	1.8	Readman, Preston, & Mantoura, (1986a)
Tamar Estuary, UK	-	13	Readman et al., (1986a)
Mersey Estuary, UK	-	11	Readman et al., (1986a)
New York Bight, USA	35–2900	-	Farrington & Tripp, (1977)
Izmir Bay, Eastern Aegean Sea	0.09-4.50	-	Darilmaz & Kucuksezgin, (2007)
Danube River	-	1–40	Equipe Cousteau, (1993)
Bohai Sea, China	-	0.39-4.94	Hu, Guo, Feng, Yang, & Fang, (2009)
Mediterranean, Morocco	244-5281	-	Er-Raioui, Bouzid, Marhraoui, & Saliot, (2009)
Cienfuegos bay, Cuba	-	2.25-7.25	Tolosa, Mesa-Albernas, & Alonso-Hernandez, (2009)
Brazil	0.39-43.83	0.05-1.04	Maioli, Rodrigues, Knoppers, & Azevedo, (2010)
Eastern Aegean Sea	0.52-4.85	0.26-2.40	*This study*

The calculated *n*-C18/phytane ratios in the sediment samples were relatively low (0.76-1.13) indicating that microbial degradation processes were generally important in the sediments from Eastern Aegean coasts. Other unsaturated isoprenoid alkenes, e.g. squalene (a *n*-C30 isoprenoid), were also recorded in some samples (Table 5.1). This compound is usually attributed to animals (UNEP/IOC/IAEA, 1992) but is also ubiquitous in microalgae (Volkman et al., 1992).

5.3 PAHs in sediment

The total concentrations of 20 PAHs in sediment ranged from 73.5 ng g^{-1} at Gokova Bay to 2170 ng g^{-1} at Izmir Inner Bay, with a mean concentration of 323.7 ng g^{-1} (Table 5.3, Figure 5.3). The highest concentration was observed at Izmir Inner Bay, which is close to the Metropolitan of Izmir. Izmir having a population of nearly 3 million inhabitants is a densely populated area with industrial activities cover a large range of industries including food processing, tanneries, paint, chemicals, textile and petroleum refining. As a result, the high concentrations of PAHs in sediment could be caused by the large amount of soil run-off and sewage discharged from this area into seawater. Relatively high concentrations (> 200 ng g^{-1}) were also found at Meric River Estuary, Dardanelles Strait Entrance, Izmir Middle Bay, Menderes Region and Marmaris Bay. The specific PAHs Aceph, Ace and DBA were under the detection limits in all sampling sites. In addition, 1-methylPhe and 3,6-dimethylphe were measured below detection limit in most of the sampling sites.

Concentrations of ΣPAHs in the sediments of the Eastern Aegean coast did not exceed 1000 ng g^{-1} except Izmir Inner Bay where value reached up to 2170 ng g^{-1}. These levels can be compared to ΣPAHs in pristine areas, such as Antarctica (8 to 280 ng g^{-1}: Cripps, 1994), coastal areas of the Adriatic Sea (24-501 ng g^{-1}: Magi, Bianco, Ianni, & Di Carro, 2002), the Balearic Islands (30 ng g^{-1}: Baumard et al., 1998a), the sandy sediments from both the Gironde Estuary (19-252 ng g^{-1}: Budzinski, Bellocq, Pierard, & Garrigues, 1997) and the Shetland Islands (<40 ng g^{-1}: Webster, Fryer, Dalgarno, Megginson, & Moffat, 2001). Moderately to highly PAH-polluted sites are typified by Arcachon Bay in France (900-4100 ng g^{-1}:

Baumard, Budzinski, & Garrigues, 1998b); Fremantle Harbour in Western Australia (up to 3200 ng g^{-1}: Burt & Ebell, 1995) and the Gironde Estuary in France (up to 4900 ng g^{-1}: Budzinski et al., 1997). In highly industrialized areas, such as Lazaret Bay on the Mediterranean coast levels of ΣPAHs ranged from 1600 to 48,000 ng g^{-1} (Benlahcen et al., 1997). The worldwide concentrations of PAHs in sediments (ng g^{-1} dry wt) were summarized in Table 5.4.

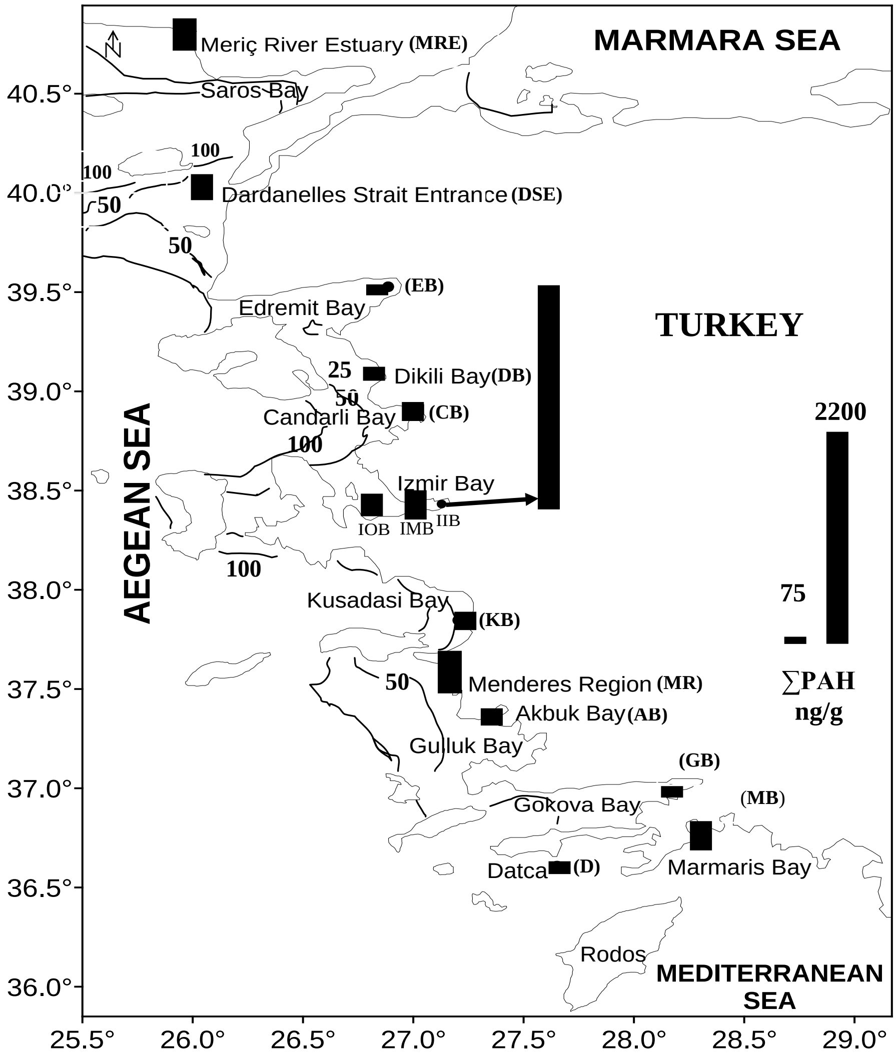


Figure 5.3 Distribution of total PAH concentrations along the Eastern Aegean coasts.

5.3.1 PAH composition and sources

Pyrolytic PAHs include all parent compounds other than perylene having MW> 178, namely fluoranthene, pyrene, 1-methyl pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indene[1,2,3-cd]pyrene, benzo[g.h.i]perylene, dibenzo[a.h]anthracene. Fossil PAHs are naphthalene, 1-methyl naphthalene, phenanthrene/ anthracene, 2-methyl phenanthrene, 1-methyl phenanthrene, 3,6-dimethyl phenanthrene, fluorene, acenaphthylene, and acenaphthene. Natural and/or diagenetic PAHs comprise perylene, it was detected in all sediment samples from Eastern Aegean coast (Table 5.3).

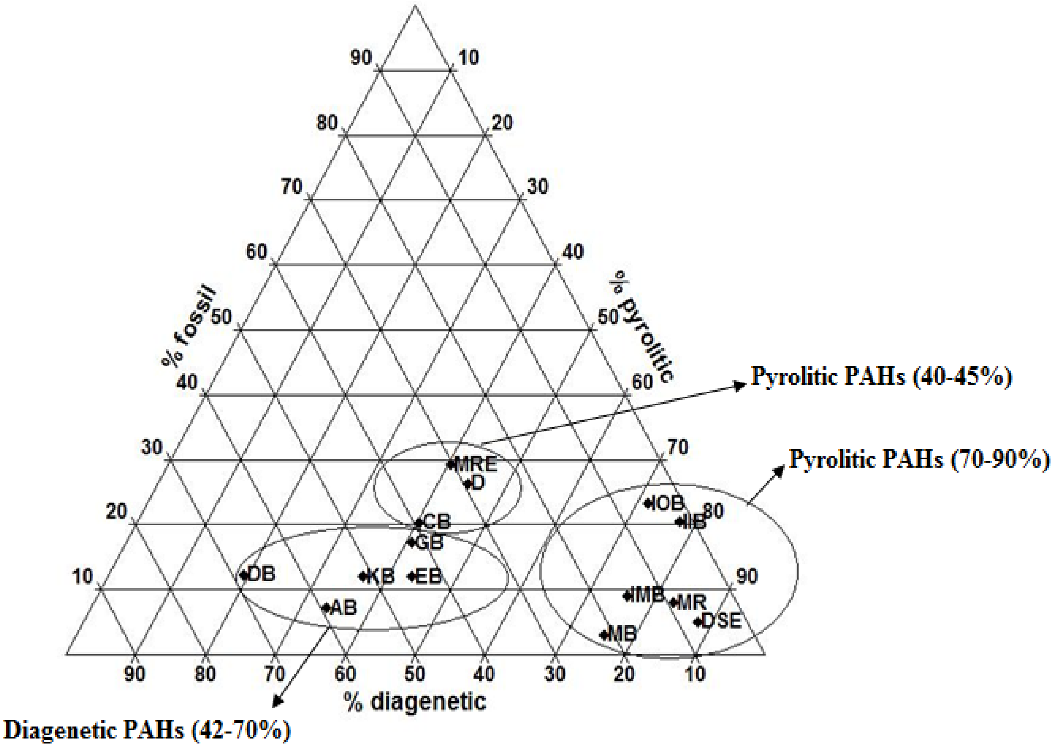


Figure 5.4 Ternary diagram showing the relative amounts of PAHs from different sources (fossil oil, combustion products and natural biological activity) in sediments from the Eastern Aegean coasts.

Table 5.3 Concentrations of PAHs (ng g^{-1} on a dry weight basis) and selected ratios recorded for the Eastern Aegean sediments

		MRE	**DSE**	**EB**	**DB**	**CB**	**IOB**	**IMB**	**IIB**	**KB**	**MR**	**AB**	**GB**	**D**	**MB**
2-3 ring	Nap	34.0	17.6	9.63	11.4	19.2	nd	nd	49.8	12.6	15.9	10.3	12.9	12.7	9.63
	1-methyl Nap	22.0	nd	nd	nd	5.46	12.1	nd	30.8	nd	nd	nd	nd	9.91	nd
	Fl	nd	nd	nd	nd	10.5	nd	nd	27.6	nd	nd	nd	nd	nd	nd
	Phe	6.1	nd	nd	nd	nd	16.4	12.2	223	nd	nd	nd	nd	nd	nd
	2-methyl Phe	16.3	nd	nd	nd	nd	nd	nd	62.2	nd	nd	nd	nd	nd	nd
	1-methyl Phe	nd	nd	nd	nd	nd	nd	nd	37.2	nd	nd	nd	nd	nd	nd
	3,6-dimethyl Phe	nd	nd	nd	nd	nd	nd	nd	nd	nd	18.0	nd	nd	nd	nd
	Ant	5.9	nd	nd	nd	nd	14.9	10.7	23.4	nd	nd	nd	nd	nd	nd
4-ring	Flu	22.3	38.6	nd	nd	nd	22.4	30.8	356	nd	64.6	nd	nd	nd	50.5
	Pyr	20.5	55.2	nd	nd	nd	12.8	20.2	379	nd	50.8	nd	nd	nd	46.5
	1-methyl Pyr	nd	nd	nd	nd	nd	nd	nd	34.2	nd	41.7	nd	nd	nd	nd
	BaA	nd	11	nd	nd	nd	7.93	26	107	nd	25.6	nd	nd	nd	18.5
	Chr	44.6	19.2	12.6	nd	35.5	43.2	20.3	260	nd	26.5	nd	nd	nd	20.3
5-ring	BbF	nd	12.6	nd	nd	nd	7.32	19.2	105	nd	22.7	nd	nd	nd	17.8
	BkF	nd	11	nd	nd	nd	nd	nd	63.1	nd	nd	nd	nd	nd	18.1
	BaP	16.1	13.4	19.7	17.1	19.2	14	25.4	46.5	38.6	24.8	47.3	8.97	38.4	23.5
	BeP	9.95	32.9	nd	nd	nd	10.2	14.3	171	nd	57.4	nd	nd	nd	nd
	BgP	nd	nd	nd	nd	nd	16.6	33.7	64.3	nd	nd	nd	nd	nd	nd
	Per	84.7	16.7	33.2	59.8	67.1	9.79	39.5	48.3	53.4	37.5	82.6	30.6	25.1	57.6
6-ring	Inp	nd	nd	nd	nd	14.3	nd	nd	81.4	nd	23.8	nd	21	nd	nd
	Σ 20 PAHs	283	228	75.1	88.3	171	188	252	2170	105	409	140	73.5	86.1	262
	LPAHs/HPAHs	0.44	0.11	0.30	0.67	0.43	0.25	0.13	0.22	0.33	0.07	0.22	0.43	0.33	0.05
	Phe/Ant	1.03	-	-	-	-	1.10	1.14	9.53	-	-	-	-	-	-
	Flu/Pyr	1.09	0.70	-	-	-	1.75	1.52	0.94	-	1.27	-	-	-	1.09
	Flu/Flu+Pyr	0.52	0.41	-	-	-	0.64	0.60	0.48		0.56				0.52
	BeP/Per	0.12	1.97	-	-	-	1.04	0.36	3.54	-	1.53	-	-	-	-
	%Per/Σpenta	76.5	19.3	62.8	77.8	77.8	23.7	40.1	9.7	58.0	26.3	63.6	77.3	39.5	49.2
	%Pyrolytic	40.2	85.0	43.0	19.4	40.3	71.7	75.3	76.9	36.9	82.6	33.7	40.8	44.6	74.4
	%Fossil	29.9	7.7	12.8	12.9	20.5	23.1	9.1	20.9	12.0	8.3	7.3	17.6	26.3	3.7
	%Diagenetic	30.0	7.3	44.2	67.7	39.2	5.2	15.7	2.2	51.1	9.2	58.9	41.6	29.1	21.9

Abbreviations**: naphthalene (Nap). fluorene (Fl). phenanthrene (Phe). anthracene (Ant). fluoranthene (Flu). pyrene (Pyr). chrysene (Chr). perylene (Per). benzo[a]anthracene (BaA). benzo[b]fluoranthene (BbF). benzo[k]fluoranthene (BkF). benzo[e]pyrene (BeP).benzo[a]pyrene (BaP). indeno[1.2.3-c.d]pyrene (Inp). benzo[g.h.i]perylene (BgP). **nd: not detected

Table 5.4 Worldwide concentrations of PAHs in sediments (ng g^{-1} dry wt^{-1})

Location	ΣPAHs	References
Lazaret Bay, France, Mediterranean Sea	1600-48,090	Benlahcen et al., (1997)
Santos Harbour, Brazil	80–42,390	Nishigima, Weber, & Bícego, (2001)
Naples' harbour, southern Italy	9–31,774	Sprovieri et al., (2007)
Izmit Bay, Turkey	2500–25,000	Tolun et al., (2001)
West Mediterranean Sea	1.5–20,440	Baumard, Budzinski, & Garrigues, (1998)
Gemlik Bay, Turkey	50.8–13,482	Ünlü & Alpar, (2006)
Gulf and the Gulf of Oman, Bahrain	13–6600	Tolosa et al., (2005)
France, Mediterranean Sea	900-4100	Baumard et al., (1998b)
Gironde Eustary, France	622-4888	Budzinski et al., (1997)
Western Coast, Australia	1-3200	Burt & Ebell, (1995)
Gulf of Mexico, USA	3–3230	Wade et al., (1995)
Caspian Sea sediments, Azerbaijan	338–2988	Tolosa et al., (2004)
Tabasco State, Mexico	454–3120	Botello, Gonzalez, & Diaz, (1991)
Hsin-ta coastal area, Taiwan	98.1–2048	Fang, Lee, & Yu, (2003)
Caspian Sea sediments, Iran	94–1789	Tolosa et al., (2004)
Daliao River watershed, China	61.9–840.5	Guo et al., (2007)
Coastline, Black Sea	7-638	Readman et al., (2002)
Gulf of Aden, Yemen	2.2–604.4	Mostafa, Wade, Sweet, Al-Alimi, & Barakat, (2009)
Danube Coastline, Black Sea	30.5-608	Readman et al., (2002)
Black Sea, Ukraine	66.9–635	Readman et al., (2002)
Bosphorus, Black Sea, Turkey	13.8-531	Readman et al., (2002)
Italy Coast, Adriatic Sea	27-527	Guzzella & DePaolis, (1994)
Coastal area of the Adriatic Sea	24-501	Magi et al., (2002)
Gao-Ping River, Taiwan	8–356	Doong & Lin, (2004)
Caspian Sea sediments, Russia	6–345	Tolosa et al., (2004)
Coastal areas, China	189–637	Liu, Chen, Lin, & Tao, (2007)
Sochi, Black Sea, Russia	61.2–368	Readman et al., (2002)
South Orkney Islands, Antarctica	8-280	Cripps, (1994)
Crete Sea, Eastern Mediterranean Sea	14.6-158.5	Gogou et al., (2000)
Coastline, Black Sea, Ukraine	7.2-126	Readman et al., (2002)
Gulf and the Gulf of Oman, Qatar	0.55–92	Tolosa et al., (2005)
North of the Shetland Islands	≤40	Webster et al., (2001)
Gulf and the Gulf of Oman, UAE	0.6–9.4	Tolosa et al., (2005)
Coastline, Eastern Aegean Sea	73.5-2169.8	*This study*

Using the traditional classification system of PAHs (Page et al., 1999; Tolosa et al., 2009), the relative amounts of pyrolitic, fossil and natural/diagenetic PAH compounds are shown in Figure 5.4. This ternary plot evidently shows the importance of pyrolitic as a source of PAHs in the Eastern Aegean coast. Excepting five sites (sites Dikili, Akbuk, Kusadasi, Edremit and Gokova bays), combustion derived PAHs contributed more than 40% of total PAHs and six sites (Izmir Outer Bay, Izmir Middle Bay, Izmir Inner Bay, Dardanelles Strait Entrance, Menderes Region and Marmaris Bay) exhibited a pyrolitic component higher than 70%. The second more important source was the diagenetic with percentages higher than 50% in Dikili, Akbuk and Kusadasi Bays. Fossil derived PAHs, with percentages always < 20% except for five sites (Meric River Estuary, Candarli Bay, Izmir Outer Bay, Izmir Inner Bay and Datca) (Table 5.3).

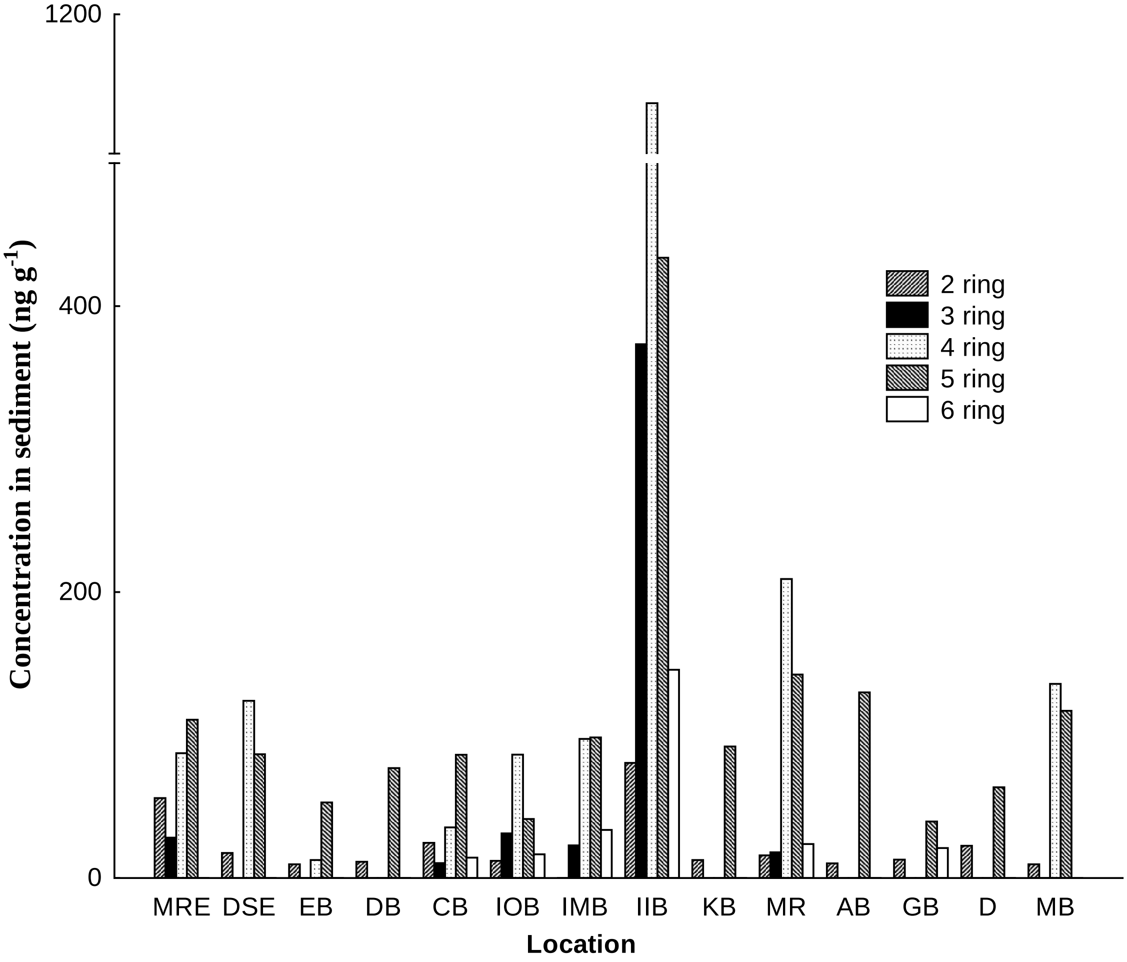


Figure 5.5 Concentration and composition pattern of parent PAHs in sediments of Eastern Aegean coast. Two ring PAHs include naphthalene, 1-methyl naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, 2-methyl phenanthrene, 1-methyl phenanthrene, 3.6 dimethylphenanthrene, phenanthrene, anthracene; four-ring PAHs include fluoranthene, pyrene, 1-methyl pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, dibenzo[a.h]anthracene and perylene; six-ring PAHs include indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene.

As far as the composition pattern of PAHs in sediments is concerned, it is mostly dominated by five-ring PAHs as shown in Figure 5.5. In addition, four-ring PAHs also showed dominance at sites Dardanelles Strait Entrance, Izmir Outer Bay, Izmir Inner Bay, Menderes Region and Marmaris Bay.

Molecular indices based on ratios of selected PAH concentrations may be differentiate PAHs from pyrogenic and petrogenic origins. Three specific PAH ratios were calculated for the studied samples: Phe/Ant, Flu/Pyr and Flu/(Flu+Pyr). The Phe/Ant index reflects that phenanthrene (Phe) is more thermodynamically stable than anthracene (Ant). Because of their different physico-chemical properties, they might behave differently in the environment with characteristic Phe/Ant values for the identification of the PAH origin. Similarly, fluoranthene (Flu) is less thermodynamically stable than pyrene (Pyr); they are often associated with each other in natural matrices and a predominance of Flu over Pyr is characteristic of a pyrolytic process, while in petroleum-derived PAHs, pyrene is more abundant than fluoranthene. Generally, a Phe/Ant ratio <10 and Flu/Pyr ratio >1 indicates that the contamination by PAHs results from a combustion process (Soclo, Garrigues, & Ewald, 2000). Nevertheless, for both ratios, the limits between the two processes are not precise and the two indices must be considered simultaneously to provide a good estimate of the different PAH sources (Budzinski et al., 1997). Some typical values of these indices are given in Table 5.5.

Table 5.5 Characteristic values of selected molecular ratios for pyrolytic and petrogenic origins of PAHs

Diagnostic Ratio	Pyrolytic Origin	Petrogenic Origin	*This Study*	References
LPAHs/HPAHs*	Low	High	0.05-0.67	Soclo et al., (2000); Rocher, Azimi, Moilleron, & Chebbo, (2004); Wang, Sun, Ma, & Liu, (2006)
Phe/Ant	<10	>15	1.03-9.53	Soclo, (1986); Baumard et al., (1998)
Flu/Pyr	>1	<1	0.70-1.75	Sicre et al., (1987); Baumard et al., (1998)
Flu/(Flu+Pyr)	>0.5	<0.5	0.41-0.64	Budzinski et al., (1997); Gogou, Apostolaki, & Stephanou, (1998)

*LPAHs/HPAHs: sum of (Nap, Aceph, Ace, Fl, Phe and Ant) concentrations against sum of (Flu, Pyr, BaA, Chr, BbF, BkF, BaP, Inp, DBA and BgP) concentrations.

The entire investigated samples (Meric River Estuary, Izmir Outer Bay, Izmir Middle Bay and Izmir Inner Bay) exhibited pyrolytic input (Table 5.3). Phenanthrene to anthracene ratios in the sediment samples consistently demonstrated the classical value of pyrogenic sources (<10). However, Flu/Pyr ratio showed slightly higher value than unity. In a majority of sites except Dardanelles Strait Entrance and Izmir Inner Bay the Flu/Pyr ratios were >1, indicating important pyrolytic inputs. Sediment samples from Izmir Outer Bay and Izmir Middle Bay with Phe/Ant <10 and Flu/Pyr >1 showed strong pyrolytic origin. Sediment samples of the Izmir Inner Bay (Phe/Ant=9.53, Flu/Pyr=0.94) with Phe/Ant <10 and Flu/Pyr~1 were characteristic of a pyrolytic source. The different ratios might also relate to the degree of photo-degradation or biodegradation and also to grain size of the sediment samples (Tam, Ke, Wang, & Wong, 2001).

To estimate the origin of the PAHs in the Eastern Aegean sediment samples, the LPAHs/HPAHs ratio (the sum of the low molecular weight PAH concentrations to the sum of higher molecular weight PAH concentrations; i.e., Naph+Aceph+Ace+Fl+Phe+Ant /Flu+Pyr+BaA+Chr+BbF+BkF+BaP+Inp+DBA+BgP). The choice of this index for source identification was based on the fact that the PAHs from a petrogenic origin consist predominantly of those with lower molecular weights (three to four rings), while the PAHs from a pyrogenic origin generally have higher molecular weights (Soclo et al., 2000). Data in Table 5.3 showed that for the majority of samples, the LPAHs/HPAHs ratios were relatively low (0.05-0.67) to support the pyrolytic origin (Soclo et al., 2000). The Flu/(Flu+Pyr) ratios were from 0.41 to 0.64 and could be indicative of pyrolytic origin, or coal combustion.

5.3.2 Perylene origin

In addition to pyrolytic and petrogenic sources, perylene is also produced by in situ degradation of biogenic precursors (Venkatesan, 1988; Wakeham, 1996; Baumard et al., 1998). Indeed, perylene is probably the most important diagenetic PAH encountered in sedimentary environments and, thus, a high abundance of perylene relative to the other

PAHs can indicate an important natural origin of the compound. Perylene has been frequently associated with inputs from rivers and estuaries (La Flamme & Hites, 1978; Baumard et al., 1998). These authors have suggested that concentrations of perylene which are higher than 10% of the total penta-aromatic isomers indicate a probable diagenetic input whereas those in which perylene is less than 10% indicate a probable pyrolytic origin of the compound. Concentrations of perylene relative to the penta-aromatic isomers (expressed as % composition) for the Eastern Aegean Sea sediments are given in Table 5.3 and are shown in Figure 5.6. In the present study perylene was found in all sediment samples and its concentration varied from 9.8 to 85 ng g^{-1} which accounted for up to 78% of the total penta PAHs (Table 5.3).

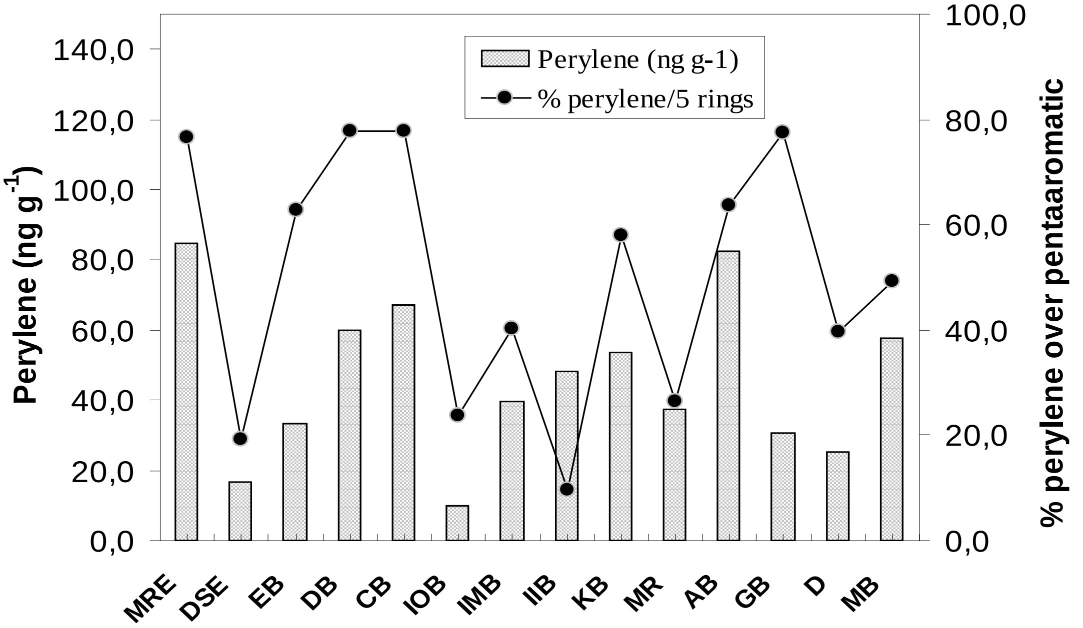


Figure 5.6 Plot of perylene concentration and percentage of perylene relative to the combined concentration of all penta-aromatic isomers for stations in the Eastern Aegean Coasts.

Concentrations of perylene relative to the penta-aromatic isomers indicated most of the values were higher than 10%, indicating a diagenetic origin. Only one value was lower than 10%, indicating a pyrolytic input at Izmir Inner Bay impacted by the industrial city of Izmir. High values were, however, observed in most of the samples from the Eastern Aegean Sea-Dikili and Candarli Bays (77.8%), Gokova Bay (77.3%), Meric River Estuary (76.5%), Akbuk Bay (63.6%), Edremit Bay (62.8%), Kusadasi Bay (58%), Marmaris Bay (49.2%) and Datca (39.5%), indicating a diagenetic origin for the presence of perylene at these locations. Most probably, the diagenesis of terrestrial organic matter draining into the Aegean Sea produces the majority of the perylene present. Compared to benzo[e]pyrene, a characteristic pyrolytic PAH of the same MW, perylene showed higher relative abundance at Meric River Estuary, Izmir Outer Bay and Menderes Region sampling sites (see BeP/Per in Table 5.3) which further supports the assumption of natural perylene inputs in the area close to the land.

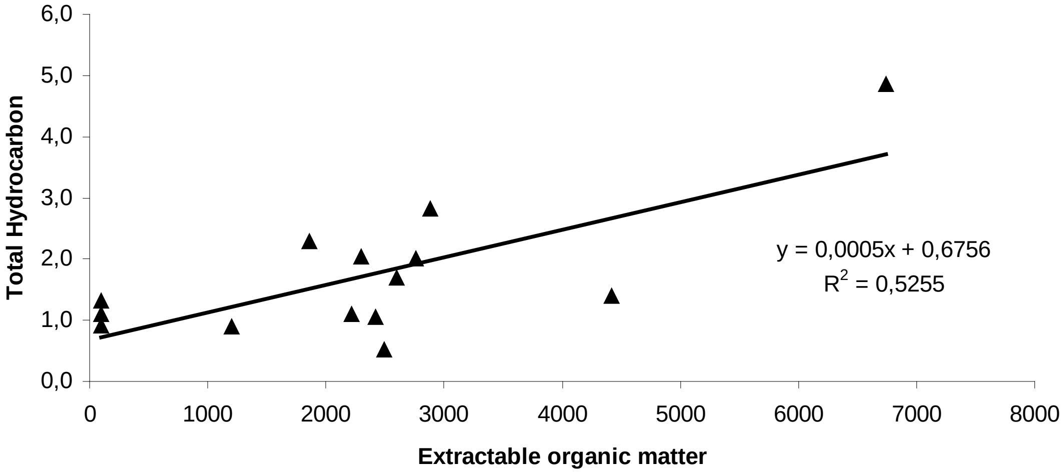


Figure 5.7 Plot of total hydrocarbons (μg g^{-1} dry weight) against extractable organic material (μg g^{-1} dry weight) for sediment samples taken from Aegean Sea.

5.4 Statistical Analysis for aliphatics and PAHs

Total extractable organic matter (EOM) in the sediments from the Eastern Aegean Sea ranged from 100 to 6740 μg g^{-1} dry wt^{-1} along the Eastern Aegean coast. The EOM content was higher at Station Izmir Inner Bay than the other stations due to domestic inputs. In most of these samples, total hydrocarbons accounted for a minor part of the EOM (from 0.02% to 1.32%) (Table 5.1). Total hydrocarbon concentrations in sediments were related to the concentrations of EOM (R^2=0.52, n=14, p<0.05) (Figure 5.7).

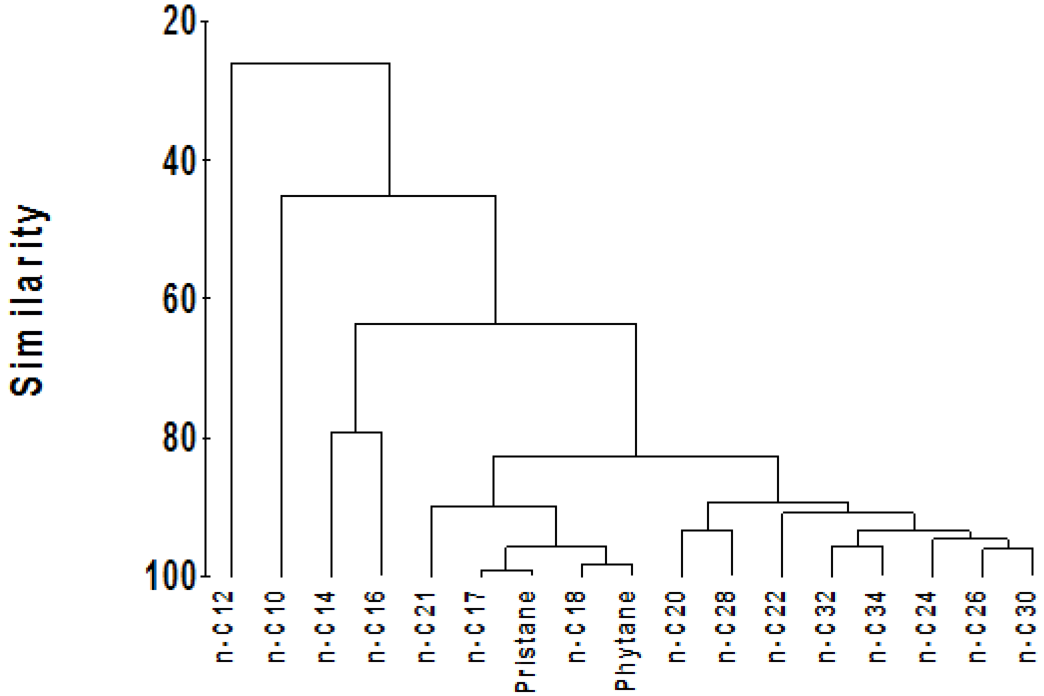


Figure 5.8 Hierarchical dendogram for aliphatic hydrocarbons in sampling sites from the Eastern Aegean coasts.

Cluster analysis was performed to identify the complete linkage groups of individual aliphatics in sediment from the Eastern Aegean coast. The data set was normalized using log (x+1) transformation. Two major clusters of aliphatics with sub-groups were identified in sediment samples. The first group included *n*-C12, *n*-C10, *n*-C14, *n*-C16. The second major group was comprised of two sub-groups. The first group contained maximum concentrations of *n*-C21, *n*-C17, Pristane, *n*-C18, Phytane and the second group indicated that other aliphatics were present in the sediment samples. The third group generally contained compound of high molecular weight; the second included isoprenoid alkanes and the first group of lower molecular weight (Figure 5.8).

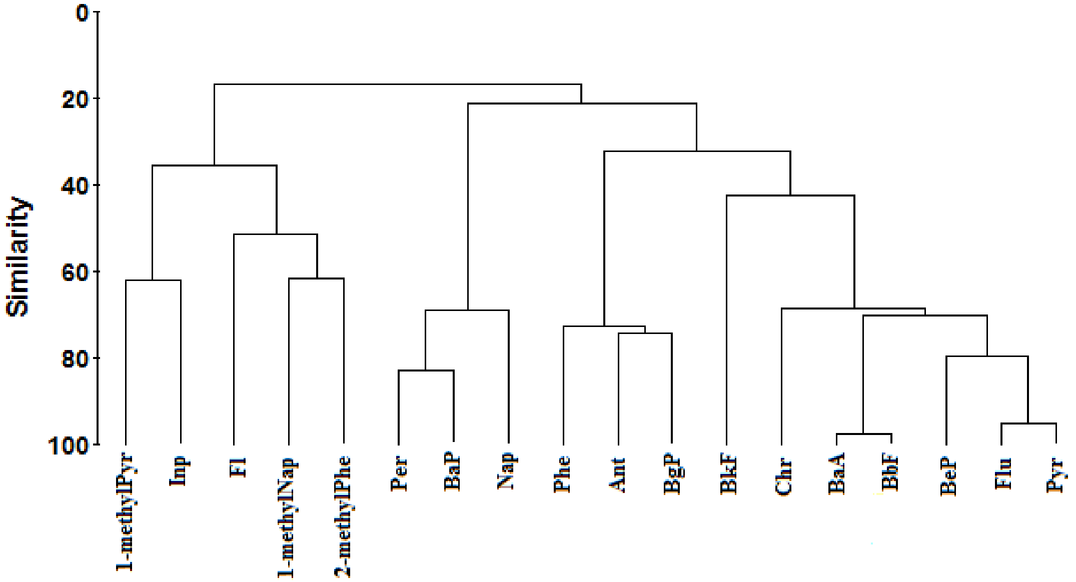


Figure 5.9 Hierarchical dendogram for PAHs in sampling sites from the Eastern Aegean coasts.

Cluster analysis was performed to identify the homogeneous groups of individual PAHs occurring in sediments. The individual PAHs were divided into two major groups. The first major group included 1-methylPyr, Inp, Fl, 1-methylNap, 2-methylPhe. These are mainly PAHs of low molecular weight with 2-4 rings (except Inp) and the PAHs from petrogenic origin. The second group contained Per, BaP, Nap, Phe, Ant, BgP, BkF, Chr, BaA, BbF, BeP, Flu and Pyr. Since BaP is usually detected in pyrogenic sources, such as those derived from the combustion of coal, wood, vehicle fuel and waste tire (Arias et al., 2009), it is difficult to understand why Nap was assigned to this group. The second group generally includes PAHs with 4-5 rings an exception being Nap, Phe and Ant (Figure 5.9).

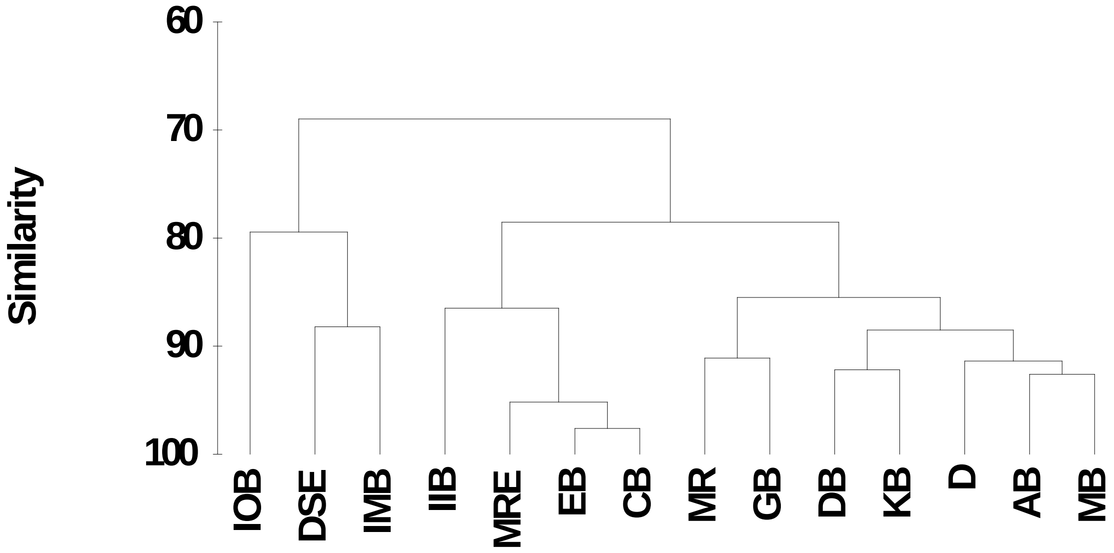


Figure 5.10 Hierarchical dendogram for aliphatic hydrocarbons in different sampling sites from the Eastern Aegean coasts.

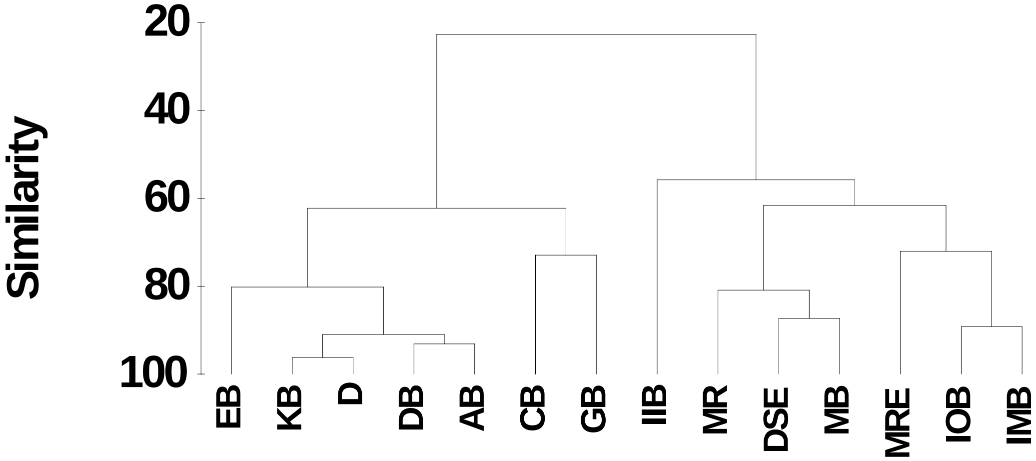


Figure 5.11 Hierarchical dendogram for polycyclic aromatic hydrocarbons in sampling sites from the Eastern Aegean coasts.

The cluster analysis was engaged according to the complete linkage between groups method on the transformated (log x+1) aliphatic data from the different sites of the Eastern Aegean. Three big clusters with sub groups were identified; the first group represents Izmir Outer Bay, Dardanelles Strait Entrance, Izmir Middle Bay; the second group polluted sites from the Aegean coast (Izmir Inner Bay, Meric River Estuary, Edremit Bay, Candarli Bay); the third group contains several sites from the southern parts of the Aegean (Menderes Region, Gokova Bay, Kusadasi Bay, Datca, Akbuk Bay, Marmaris Bay) and mainly unpolluted areas (Figure 5.10). The HCA results indicated that the stations clustered into two groups, and Figure 5.11 shows their PAH compositional pattern. Group 1 included sample from Edremit Bay, Kusadasi Bay, Datca, Dikili Bay, Akbuk Bay, Candarli Bay, Gokova Bay and group 2 contained polluted sites from the Eastern Aegean coast (Izmir Inner Bay, Menderes Region, Dardanelles Strait Entrance, Marmaris Bay, Meric River Estuary, Izmir Outer Bay, Izmir Middle Bay).

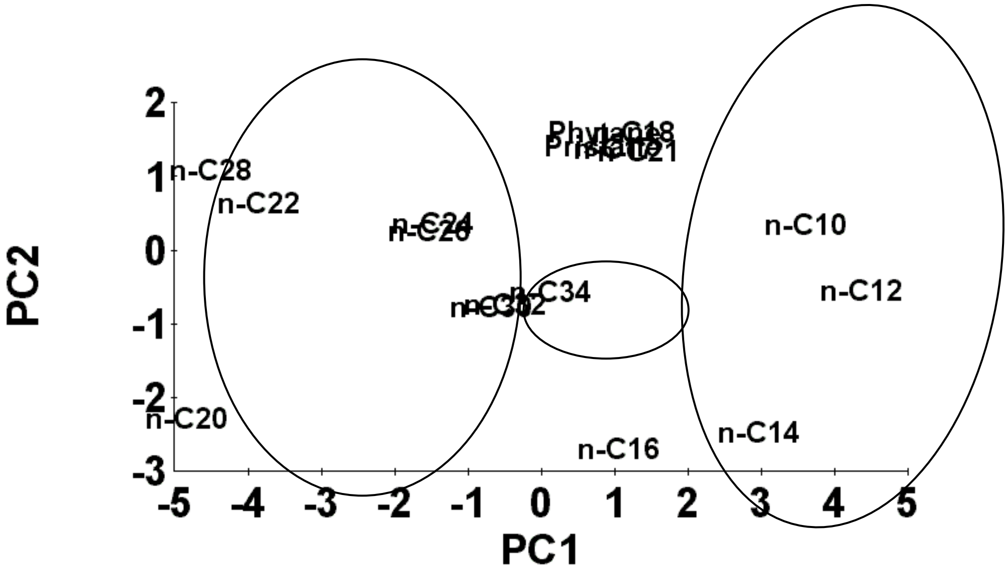


Figure 5.12 Principal component analysis loading plots for sediment samples collected in sampling sites of the Eastern Aegean coasts for aliphatics.

In this study, principal component analysis (PCA) was deployed in order to analyze the data. The first step in the multivariate statistical analysis was application of PCA with the aim of grouping the individual aliphatic hydrocarbons. The PCA results were generally similar to those of the cluster analysis discussed in the previous paragraph. The first three principal components explained 75.4 % of the total variability in sediments. These three principal components were highly weighted due to the contributions of aliphatic hydrocarbons. After auto scaling, the two significant components were identified giving account for 49.7 % and 14.7 % of the total variation, respectively. The third component takes into account only 11.0 % of the total variation. The horizontal axis PC1 correlated with *n*-C10, *n*-C12, *n*-C14, *n*-C16, *n*-C17, *n*-C18, *n*-C21, Pristane, Phytane in the positive part. The vertical axis PC2 represented *n*-C30, *n*-C32, *n*-C34 in the negative part. PC3 represented *n*-C22, *n*-C24, *n*-C26 in the positive part and *n*-C20, *n*-C28 in the negative part (Figure 5.12).

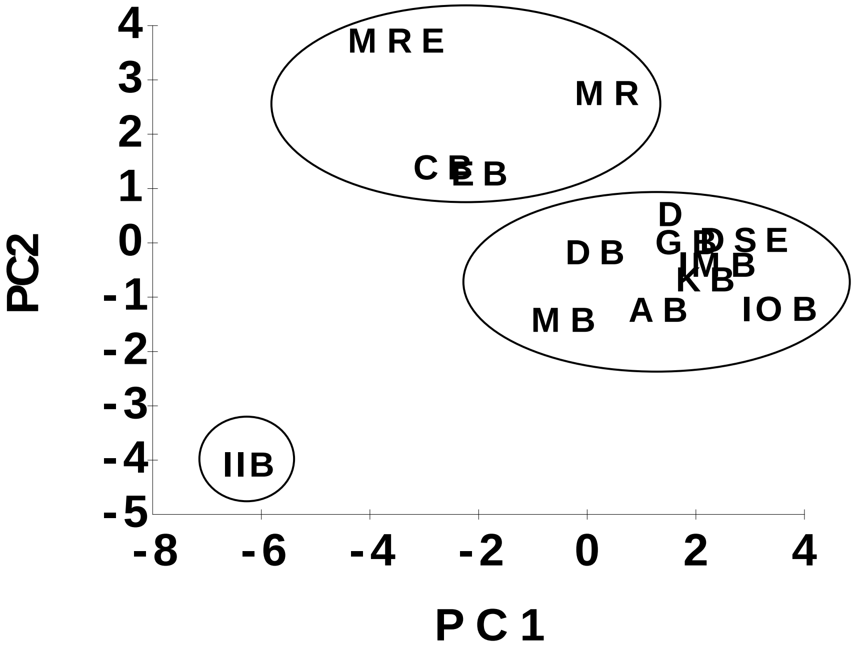


Figure 5.13 Principal component analysis loading plots for sediment samples collected in the different sites of the Eastern Aegean coasts for aliphatics.

The score plot of first two components allowed for the characterization of the sampling stations according to the first and second component for aliphatics. The three principal components explained 77.9 % of the total variance with the values for PC1, PC2 and PC3 of 45.7 %, 21.5 % and 10.7%, respectively. Station Izmir Inner Bay sediments were well differentiated by the higher scores on the first component in the negative part. Samples from Meric River Estuary, Edremit Bay, Candarli Bay and Menderes Region exhibited high pollution extent and they were grouped together, and were clearly separated from the other stations in the positive part of the second component. PC3 represented Dardanelles Strait Entrance, Izmir Outer Bay, Izmir Middle Bay, Kusadasi Bay, Datca, Marmaris Bay in the negative and Dikili, Akbuk, Gokova Bays in the positive part (Figure 5.13).

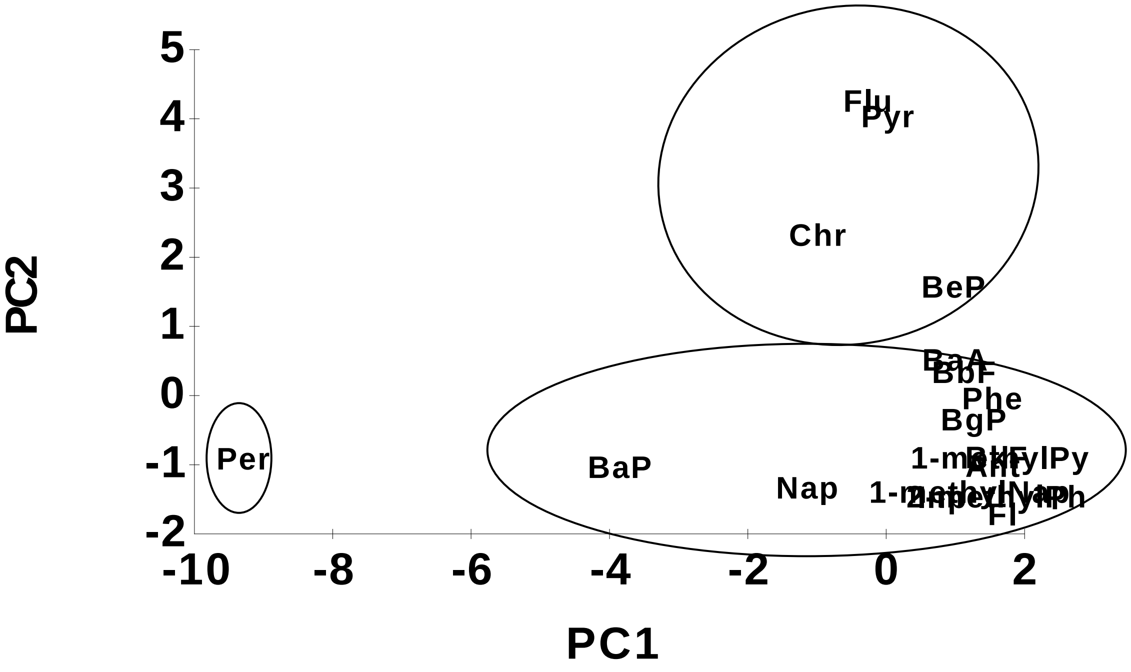


Figure 5.14 Principal component analysis loading plots for sediment samples collected in sampling sites of the Eastern Aegean coasts for polycyclic aromatic hydrocarbons.

The score plot of first two components allowed for the characterization of the aromatic compounds in terms of the first and second component. Three principal components accounted for 85.4 % of the total variation, with values for PC1, PC2 and PC3 of 52.9 %, 24.5 % and 8.0 %, respectively. PC1 represented Per in the negative part. Per generally dominated at sampling stations and was clearly separated from the other compounds by its ubiquity. Component 2 was represented by compounds Flu, Pyr, Chr and BeP in the positive part. Flu and Pyr are typical markers for pyrolysis or incomplete combustion. Other aromatic compounds are differentiated by having the higher scores on the third component (Figure 5.14). PAHs are the result of the combustion and/or pyrolitic processes and this is absent in crude oil or refined products (Wang, Fingas, & Page, 1999).

The PCA calculation for PAHs at 14 sites resulted in three principal components describing almost 88.9 % of the total variance of the data. Principal components described 75.1 %, 8.2 % and 5.6 %, respectively of the data. The component 1 was represented by station Izmir Inner Bay in the negative part. The highest levels of the component 2 can be observed at stations Meric River Estuary, Candarli Bay, Akbuk Bay, Kusadasi Bay in the positive part while Izmir Outer Bay in the negative part. Other sites grouped together on the PC3 (Figure 5.15).

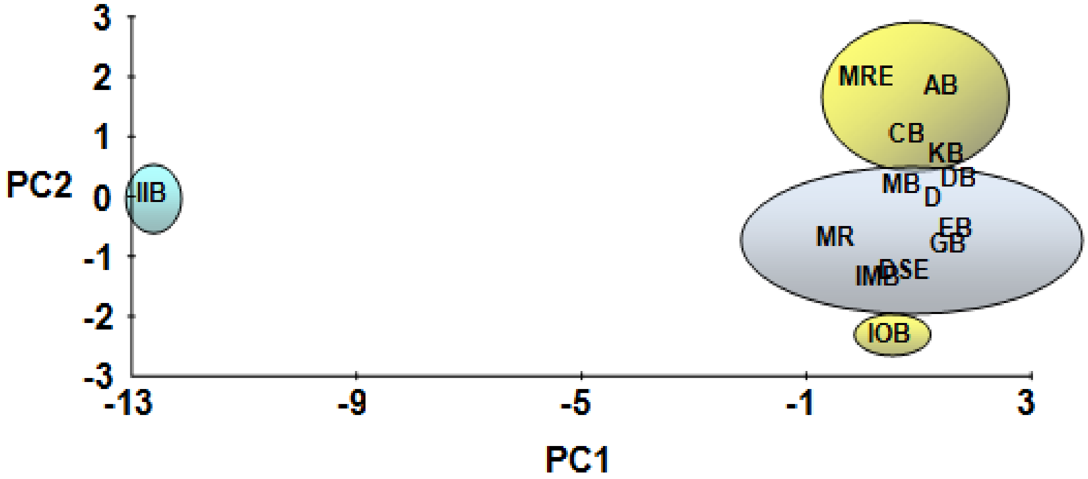


Figure 5.15 Principal component analysis loading plots for sediment samples collected in the different sites of the Eastern Aegean coasts for polycyclic aromatic hydrocarbons.

5.5 Assessment of Sediment Quality Using Biological Thresholds

As shown in Table 5.6, two widely used sediment quality guidelines, i.e. the effects range-low value (ERL) and effects range-median value (ERM) guidelines (Long, Field, & MacDonald, 1998; Long, MacDonald, Smith, & Calder, 1995) as well as the threshold effects level (TEL) and probable effects level (PEL) guidelines (CCME, 2002) were applied to evaluate the possible ecotoxicological risks of PAHs in the study area. The measured concentrations of PAHs were compared with the ERL, ERM, TEL and PEL values.

Table 5.6 Standard pollution criteria of PAH components for sediment matrix (ng g^{-1})

Compound	ERL	ERM	TEL	PEL	*This study*	
					Average	Maximum
Naphthalene	160	2100	34.6	391	18.0	49.8
Fluorene	19	540	21.2	144	19.1	27.6
Phenanthrene	240	1500	86.7	544	64.4	223.0
Anthracene	85.3	1100	46.9	245	13.7	23.4
Fluoranthene	600	5100	113	1494	83.6	356.0
Pyrene	665	2600	153	1398	83.6	379.0
Benzo[a]anthracene	261	1600	74.8	693	32.7	107.0
Chrysene	384	2800	108	846	53.6	260.0
Benzo[b]fluoranthene	NA[a]	NA	NA	NA	30.8	105.0
Benzo[k]fluoranthene	NA	NA	NA	NA	30.7	63.1
Benzo[a]pyrene	430	1600	88.8	763	25.2	47.3
Indeno[1,2,3-*cd*]pyrene	NA	NA	NA	NA	35.1	81.4
Benzo[g,h,i]perylene	NA	NA	NA	NA	38.2	64.3
Total	3612	18940	727	6518	529	1787

[a] NA, not available

Results showed that the concentration levels of naphthalene, fluorene, phenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene were higher than TEL values at Izmir Inner Bay. Meanwhile, fluorene also exceeded the ERL value at the same site, but all these compounds were significantly lower than the PEL and ERM values. These findings indicated that the sediments from the entire sampling sites except Izmir Inner Bay should have no potential biological impact.

5.6 Organochlorine pesticides in the sediments from the Aegean coast

5.6.1 Contamination profiles of OCPs in sediment

Table 5.7 illustrates the concentration ranges and mean values of OCP compositions with standard deviations in the surface sediments from the Eastern Aegean coasts. Compounds identified included hexachlorocyclohexane (γ HCH), cyclodienes (aldrin, dieldrin, endrin, heptachlor), HCB, dichlorodiphenyltrichloroethane and its degradates (*p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT). Environmental levels were generally low for all compounds by global standards (Fowler, 1990), including the relatively higher values for chlorinated hydrocarbons found areas from the inner part of Izmir and Candarli Bay. The concentrations of ΣOCPs were in the range of bdl-17.8 ng g^{-1} dry wt^{-1} with an average value of 3.20 ng g^{-1} dry wt^{-1}. Distribution of total OCPs in the sediments from the Eastern Aegean coast were shown in Figure 5.16

The results indicated that the DDTs were the predominant contaminant in sediments of the Eastern Aegean coasts. *p,p'*-DDE was the most often found OCP compound at all stations except Dardanelles Strait Entrance, followed by *p,p'*-DDD at 11 out of 14 sampling statitons, *p,p'*-DDT and HCB at 7 out of 14 sampling stations. The concentrations ranged between bdl-14.0 for *p,p'*-DDE, bdl-3.45 for *p,p'*-DDD, bdl-0.95 for *p,p'*-DDT, bdl-0.89 for HCB, bdl-0.78 for Dieldrin and bdl-0.88 ng g^{-1} dry wt^{-1} for Heptachlor. The mean concentrations were 2.10 for *p,p'*-DDE, 0.64 for *p,p'*-DDD, 0.14 for *p,p'*-DDT, 0.15 for HCB, 0.06 for Dieldrin and 0.10 ng g^{-1} dry wt^{-1} for Heptachlor.

Concentrations of the total DDT (the sum of 3 isomers of DDT) ranged from bdl to 17.3 ng g^{-1} dry wt^{-1} with a mean value of 2.87 ng g^{-1} dry wt^{-1} (Table 5.8).

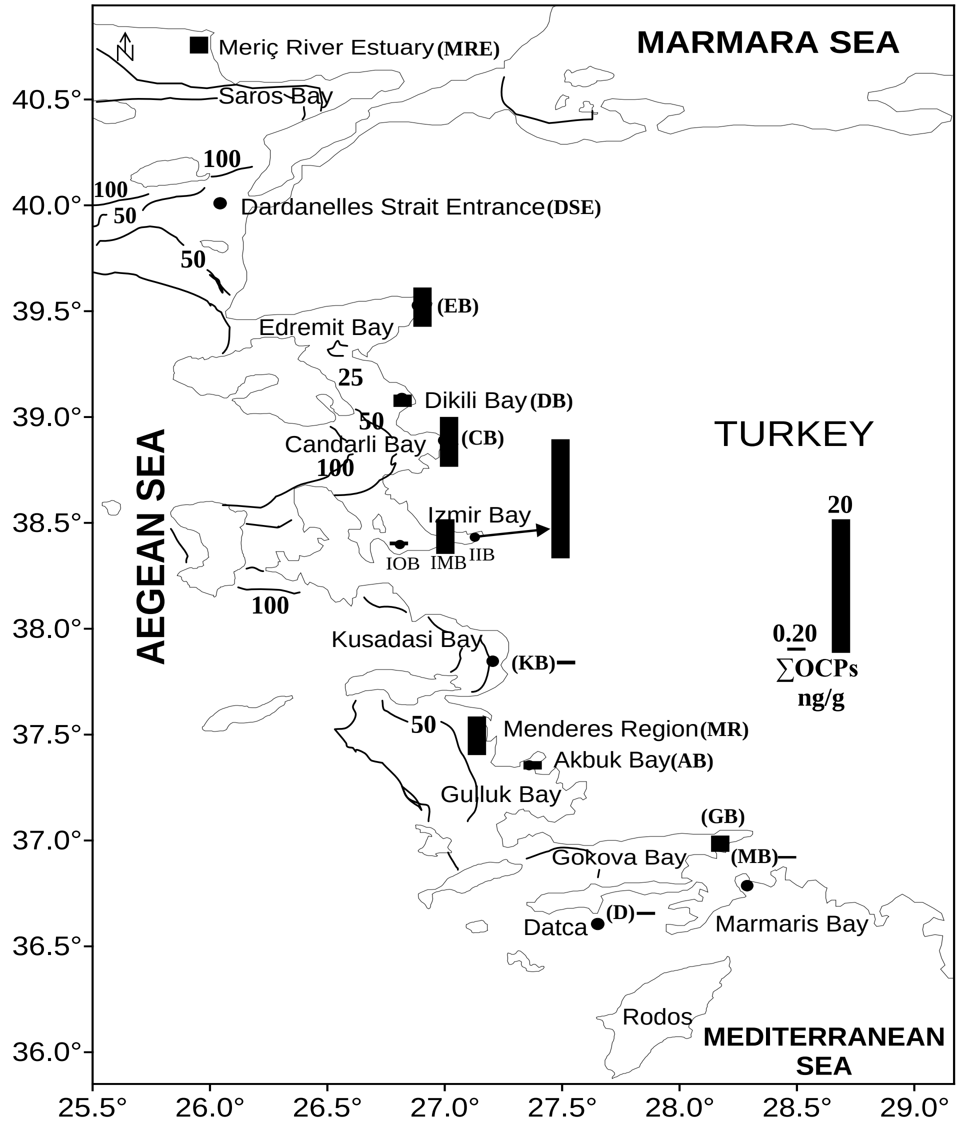


Figure 5.16 Distribution of total OCP concentrations along the Eastern Aegean coasts.

Table 5.7 The range and mean±standard deviation of halogenated hydrocarbons along the Eastern Aegean coasts in 2008 (ng g^{-1} dry weight)

Location	***p,p'*-DDE**	***p,p'*-DDD**	***p,p'*-DDT**	**HCB**	**γ-HCH**	**Heptachlor**	**Aldrin**	**Dieldrin**	**Endrin**	**Arochlor 1254**	**Arochlor 1260**
MRE	0.92-1.17 0.68±0.44	0.56-0.69 0.62±0.06	0.15-0.18 0.16±0.01	bdl	0.03-0.06 0.04±0.01	0.70-0.88 0.78±0.09	bdl	0.03-0.05 0.04±0.01	bdl	bdl	bdl
DSE	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
EB	2.64-2.81 2.72±0.09	2.14-2.30 2.23±0.08	bdl	0.14-0.22 0.18±0.04	bdl	0.45-0.61 0.54±0.08	bdl	0.02-0.03 0.02±0.01	bdl	bdl	bdl
DB	1.06-1.20 1.13±0.07	0.22-0.32 0.26±0.05	0.10-0.22 0.167±0.06	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
CB	4.13-4.86 4.48±0.37	1.33-1.54 1.44±0.11	0.33-0.36 0.34±0.09	0.71-0.89 0.78±0.10	bdl	bdl	0.20-0.26 0.23±0.03	bdl	bdl	11.12-13.51 12.49±1.23	8.85-10.51 9.56±0.86
IOB	0.18-0.20 0.19±0.01	0.10-0.15 0.13±0.03	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
IMB	0.20-0.33 0.28±0.07	0.20-0.22 0.21±0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
IIB	12.23-13.96 13.09±0.87	3.19-3.45 3.31±0.13	0.77-0.95 0.86±0.09	0.30-0.52 0.42±0.11	bdl	bdl	bdl	0.12-0.18 0.14±0.03	bdl	11.92-13.16 12.38±0.68	12.27-15.48 13.69±1.63
KB	0.07-0.08 0.07±0.01	bdl	bdl	0.14-0.23 0.18±0.05	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MR	4.03-5.21 4.48±0.64	0.48-0.55 0.52±0.04	0.22-0.27 0.24±0.03	0.37-0.40 0.39±0.02	bdl	bdl	bdl	bdl	bdl	bdl	bdl
AB	0.73-1.16 0.90±0.13	0.11-0.13 0.12±0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
GB	0.88-1.12 0.99±0.12	0.14-0.16 0.15±0.01	0.10-0.14 0.12±0.02	0.07-0.10 0.08±0.01	bdl	0.11-0.13 0.12±0.01	bdl	0.62-0.78 0.69±0.08	bdl	bdl	bdl
D	0.12-0.14 0.13±0.01	0.027-0.028 0.028±0.00	0.02-0.03 0.03±0.01	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MB	0.08-0.12 0.09±0.02	bdl	bdl	0.03-0.06 0.04±0.02	bdl	bdl	bdl	bdl	bdl	bdl	bdl

bdl: below detection limit

Table 5.8 Total concentration of DDT, Cyclodienes, OCPs, Arochlors and the selected ratios of chlorinated pesticides in the Eastern Aegean coasts

Compounds/ Locations	MRE	DSE	EB	DB	CB	IOB	IMB	IIB	KB	MR	AB	GB	D	MB
ΣOCPs (ng g^{-1})	2.32	bdl	5.69	1.56	7.27	0.32	0.49	17.8	0.25	5.63	1.02	2.15	0.19	0.13
ΣDDTs (ng g^{-1})	1.46	bdl	4.95	1.56	6.26	0.32	0.49	17.26	0.07	5.24	1.02	1.26	0.19	0.09
ΣCyclodienes (ng g^{-1})	0.82	bdl	0.56	bdl	0.23	Bdl	bdl	0.14	bdl	bdl	bdl	0.81	bdl	bdl
ΣArochlors* (ng g^{-1})	bdl	bdl	bdl	bdl	22.05	Bdl	bdl	26.07	bdl	bdl	bdl	bdl	bdl	bdl
EOM (µg g^{-1})	2880	100	2760	4420	1860	2490	2420	6740	1200	2300	100	2220	100	2600
TOC (%)	2.1	1.2	1.8	2.4	2.2	2.0	0.8	3.3	1.2	1.4	1.9	1.1	1.1	1.0
DDD/DDE	0.91	-	0.82	0.23	0.32	0.68	0.75	0.25	-	0.12	0.13	0.15	0.23	-
(DDE+DDD)/ΣDDT	0.89	-	1.0	0.89	0.95	1.0	1.0	0.95	1.0	0.95	1.0	0.90	0.84	1.0
DDT/DDE	0.24	-	-	0.15	0.08	-	-	0.07	-	0.05	-	0.12	0.23	-

* ΣArochlors: Arochlor 1254+Arochlor 1260

Highest ∑DDTs levels occurred at Izmir Inner Bay, followed by Candarlı Bay, Menderes Region, Edremit Bay while low concentrations were observed at Kusadasi Bay, Marmaris Bay and Datca. ∑DDTs were only observed below detection limit at Dardannels Strait entrance.

Panagiotopoulou, Tsipi, Hiskia, & Scoullos, (1996), Tolosa, Bayona, & Albaige´s, (1995), Fillmann et al., (2002), Picer, (2000), De Mora, Villeneuve, Sheikholeslami, Cattini, & Tolosa, (2004), IFREMER (1998), Albanis, Danis, & Hela, (1995a), Camusso, Golossi, & Vignati, (2002) reported a similar concentration level of DDT (as ng g^{-1} dry wt^{-1}) in samples collected from Gulf of Elefsis, Greece (2.64-15); the Northwest Mediterranean (3.5-12); Russian Federation coast, Black Sea (3.3-12); Adriatic Sea (0.2-35); Caspian Sea, Azerbaijan (0.56-13); Rhone Delta, France (5-15); Northern Estuaries, Greece (0.3-60); Po River, Italy (3.9-19).

The levels of organochlorinated pesticides and polychlorinated biphenyls (PCBs) in marine surface sediments and sediment cores of different areas in the world were given in Table 5.9. Such concentrations from the Eastern Aegean were lower than those in samples collected from Northwest Mediterranean and Mediterranean Sea (Tolosa et al., 1995), Black Sea coast of Samsun, Turkey (Bakan & Ariman, 2004), from Egypt (Abdallah, 1992; Abdallah & Abbas, 1994), from Alexandria Harbour, Egypt (Barakat, Kim, Qian, & Wade, 2002) and from Danube and Romania coastline, Black Sea (Fillman et al., 2002).

However, the contamination levels of ∑DDT were higher than those in the marine surface sediments from Caspian Sea (De Mora et al., 2004) and from the Persian/Arabian Gulf and the Gulf of Oman (De Mora, Fowler, Tolosa, Villeneuve, & Cattini, 2005). Fowler, (1990) also reported that DDT concentrations in near-shore surface sediments worldwide ranged between <0.1 and 44 ng g^{-1} dry wt^{-1}. This means that the contamination of DDTs in sediments from the Eastern Aegean coasts is low as compared to the other areas.

Table 5.9 Chlorinated organic pesticides and polychlorinated biphenyls (PCBs) pollution levels in marine surface sediments and sediment cores of different areas in the world as ng g^{-1} dry weight

Location	ΣDDTs	HCB	ΣPCBs	References
Gulf of Elefsis, Greece	2.64-15.32		7.68-95 (Σ^{7}PCBs)	Panagiotopoulou et al., 1996
Gulf of South Euvoikos, Greece	-		10-62 (Σ^{12}PCBs)	Haldezos, Scoullos, & Dassenakis, 2002
French and Monaco coasts			29-181 (Σ^{20}PCBs)	Piérad, Budzinski, & Carrigues, 1996
Northwest Mediterranean	1.4-675		14-228.5 (Σ^{12}PCBs)	Tolosa et al., 1995
Rhone prodelta, Mediterranean Sea	62-675	11-39	-	Tolosa et al., (1995)
Deep basin of NW Mediterranean Sea	1.4-5.5	0.05-0.5	1.1-2.5 (Σ^{9}PCBs)	Tolosa et al., (1995)
Bosphorus, Black Sea, Turkey	0.2-7.2		0.4-44	Fillmann et al. (2002)
Odessa, Black Sea, Ukrania	35-65		5.7-6.8	Fillmann et al. (2002)
Coastline, Black Sea, Ukrania	0.06-0.6		ND-0.4 (Σ^{13}PCBs)	Fillmann et al. (2002)
Danube Coastline, Black Sea, Ukrania	9.2-43		1.4-2.7	Fillmann et al. (2002)
Romania Coastline, Black Sea	0.6-72	5.3-23	0.1-24	Fillmann et al. (2002)
Yeşilırmak river, Turkey (wet wt.)	7		NA	Bakan & Ariman (2004)
Mert Stream, Turkey (wet wt.)	71		NA	Bakan & Ariman (2004)
Black Sea coast of Samsun (wet wt.)	18-55		NA	Bakan & Ariman (2004)
Adriatic Sea	0.2-35		6-2203	Picer, (2000)
Caspian Sea, Azerbaijan	0.56-13.4	0.04-0.6	0.3-2.8 (Σ^{28}PCBs)	De Mora et al., (2004)
Caspian Sea, Russia	0.01-1.9	0.01-0.07	1.3-6.4 (Σ^{28}PCBs)	De Mora et al., (2004)
Caspian Sea, Iran	0.06-3.9	0.01-0.2	0.1-0.8 (Σ^{28}PCBs)	De Mora et al., (2004)
Caspian Sea, Kazakhstan	0.01-1.9	0.01-0.04	0.03-0.6 (Σ^{28}PCBs)	De Mora et al., (2004)
Abu-Quir Bay, Egypt	44-223		53-231	Abdallah, (1992); Abdallah & Abbas, (1994)
Alexandria Harbour, Egypt	<0.25-885		0.9-1211	Barakat et al., 2002
World coastal sediments	0.1-44		0.2-400	Fowler, (1990)
Oman	0.0007-0.0852	0.0006-0.010		De Mora et al., (2005)
UAE	n.d.-0.0519	0.0009-0.0073		De Mora et al., (2005)
Rhone Delta, France	5-15			IFREMER, 1998
Northern Estuaries, Greece	0.3-60			Albanis et al., 1995a
Danube, Yugoslavia	3.20		0-774 (Σ^{7}PCBs)	UNEP, 2002
Po River, Italy	3.9-18.7		4.5-76.1	Camusso et al., 2002
Gediz River, Turkey	0.09-5.53			Filiz & Kucuksezgin, 2008
Bakırçay River, Turkey	0.56-5.37			Filiz & Kucuksezgin, 2008
Eastern Aegean Sea, Turkish coastline	nd-17.3	nd-0.78	nd-26.1	*This Study*

5.6.2 Characteristics of OCP Contamination in Sediments

The relative concentration of the parent DDT compound and its biological metabolites, DDD and DDE, can be used as indicative indices for assessing the possible pollution sources. Since DDT can be biodegraded under aerobic condition to DDE and under anaerobic condition to DDD, ratio of (DDE+DDD)/ΣDDT> 0.5 can be thought to be subjected to a long-term weathering (Hites & Day, 1992; Hong, Chen, Xu, Wang, & Zhang, 1999; Zhang, Min, Mai, Sheng Gy, & Wang, 1999).

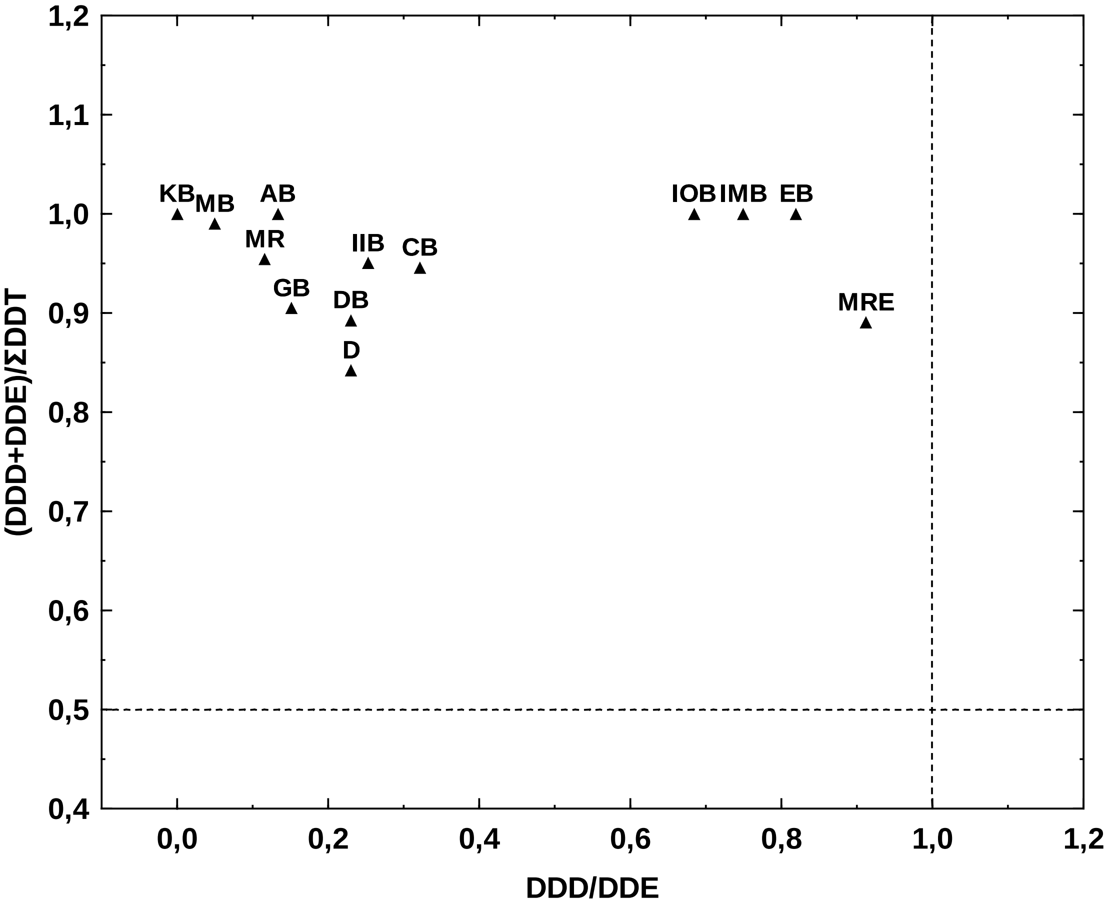


Figure 5.17 Relationship between (DDD+DDE)/ΣDDT and DDD/DDE in the sediments from the Eastern Aegean coasts.

Figure 5.17 illustrates the relationship between (DDE+DDD)/ΣDDT and DDD/DDE in the surface sediments collected from the Eastern Aegean coasts. Ratios of (DDE+DDD)/ΣDDT were in the range of 0.84-1.0 with entire values being >0.5 (Table 5.8). This infers that the degraded metabolites formed a significant proportion of total DDT compounds. Also, whole values of DDD/DDE ratio ranged between 0.12-0.91 and were lower than unity, indicating that the sediments was dominated by *p,p'*-DDE, the product of aerobic degradation of *p,p'*-DDT. This result showed that the sediments collected from the Eastern Aegean Sea were mainly under oxic conditions. Also, the results obtained from the indices clearly indicate that DDTs in the sediments from the Eastern Aegean coasts may be derived from the aged and weathered agricultural soils and transported by surface run-off from the rivers. Oxic conditions were particularly confirmed by the higher dissolved oxygen concentrations in the inner part of Izmir Bay (Figure 5.18) during different seasons after 2002. It was due to the fact that in early 2000, a wastewater treatment plant (WTP) began operation to treat domestic and industrial wastes in the Izmir Metropolitan Municipality.

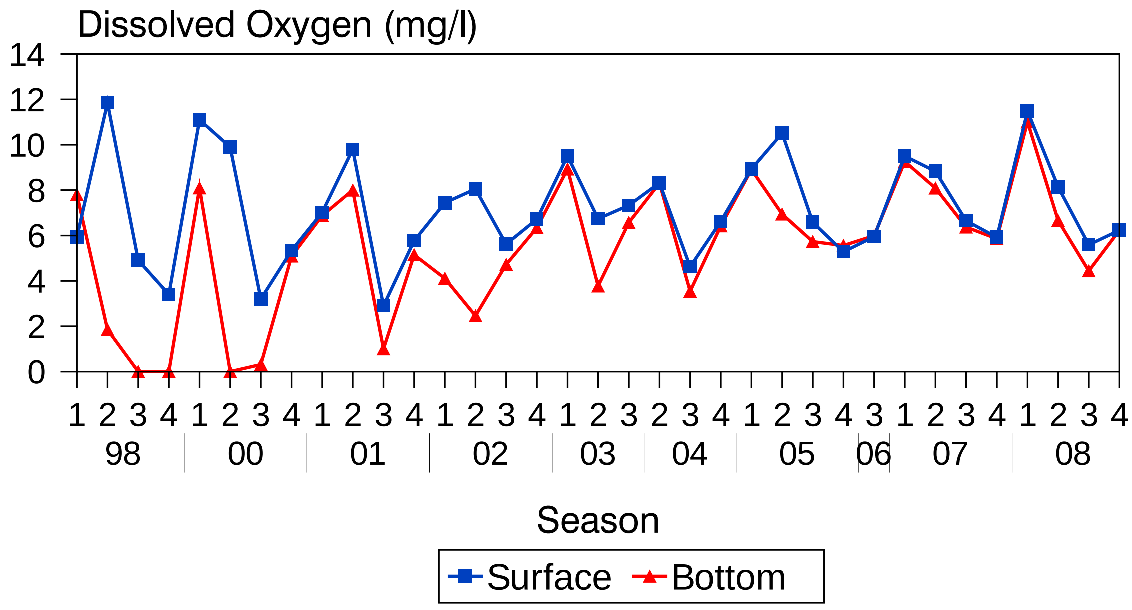


Figure 5.18 Dissolved oxygen concentrations in the Izmir Inner Bay (1-Winter, 2-Spring, 3-Summer, 4-Fall).

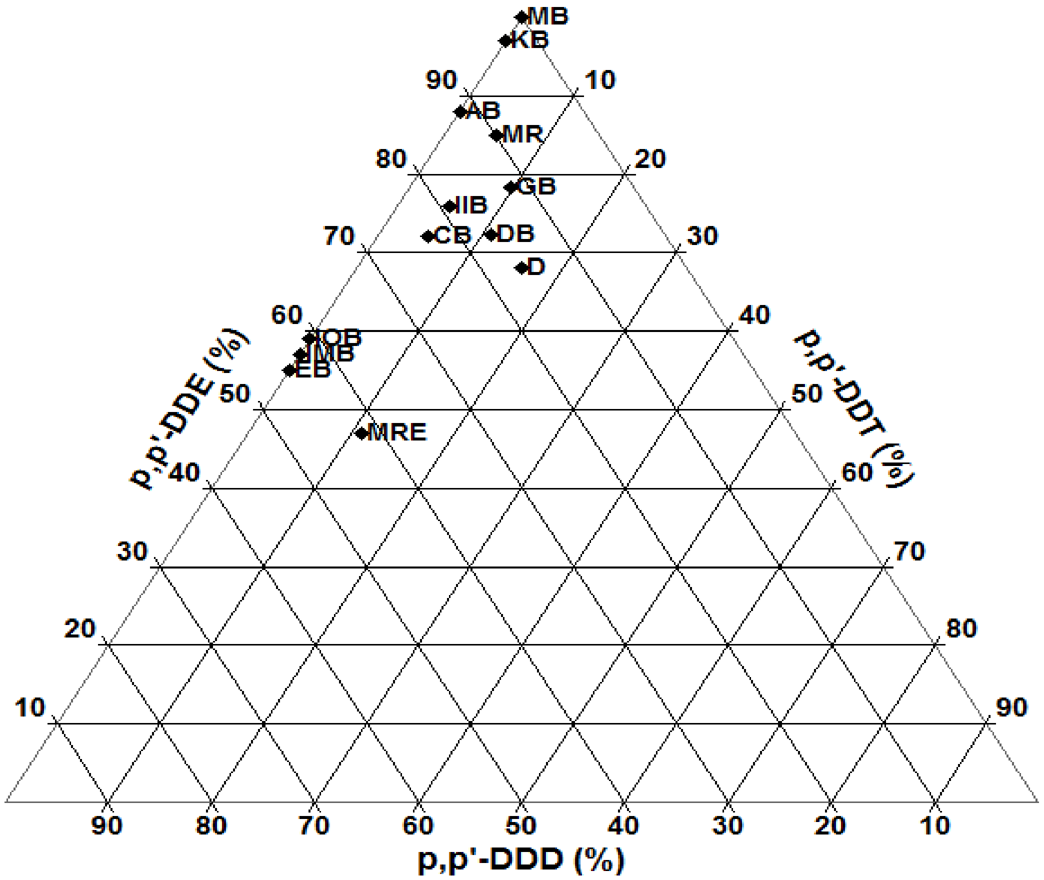


Figure 5.19 Percentage of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD in the Eastern Aegean Sea sediments.

While it would be comforting to ascribe the high content of ΣDDTs recorded here in sediments to historic usage, relatively high proportions of *p,p'*-DDE compared to *p,p'*-DDD and *p,p'*-DDT were evident at all locations (Figure 5.19). This ternary diagram, showing the relative percentages of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD, illustrates that *p,p'*-DDT doesn't even exceed 16% of the ΣDDTs at all stations. Given the relatively slow degradation rate of DDT in the environment (Woodwell, Craig, & Horton, 1971), such findings indicate early DDT influxes and, by implication, non-existing DDT use throughout the region. The ratio of *p,p'*-DDT/*p,p'*-DDE provides a useful index to assess whether the DDTs at a given site is fresh or aged, a value <0.33 generally indicative of an aged input (Stranberg et al., 1998). As shown in Table 5.8, aged mixture of DDT was evident through the entire of the Eastern Aegean coasts. Aged DDT was observed in all sampling stations in the western part of the Turkish coastal zone. In summary, DDT contamination of the Eastern Aegean Sea is not highlighted as a contemporary and ubiquitous problem in the Eastern Aegean Sea.

The highest levels of HCB were measured at Candarli Bay, similar levels were also found at Edremit Bay, Kusadasi Bay, Izmir Inner Bay and Menderes Region, while low concentrations were observed at Gokova Bay and Marmaris Bay. The concentrations of HCB from the Eastern Aegean were higher than those of Bahrain (0.005-0.027 ng g^{-1}), Oman (0.0006-0.010 ng g^{-1}), Qatar (0.0010-0.0054 ng g^{-1}), UAE (0.0009-0.0073 ng g^{-1}) (De Mora et al., 2005), Caspian Sea, Russia (0.01-0.07 ng g^{-1}), Caspian Sea, Iran (0.01-0.2 ng g^{-1}), Caspian Sea, Kazakhstan (0.01-0.04 ng g^{-1}) (De Mora et al., 2004), Deep basin of NW Mediterranean Sea (0.05-0.5 ng g^{-1}) (Tolosa et al., 1995) but were lower than those of Romania Coastline, Black Sea (5.3-23 ng g^{-1}) (Fillmann et al., 2002), Gulf of Lions, Northwest Mediterranean (0.2-1.5 ng g^{-1}), Ebro Prodelta, Northwest Mediterranean (0.1-18.8 ng g^{-1}), Rhone prodelta, Mediterranean Sea (11-39 ng g^{-1}), Offshore Barcelona, Mediterranean Sea (0.4-2.9 ng g^{-1}) (Tolosa et al., 1995).

The concentrations of Σcyclodienes (including heptachlor, aldrin, dieldrin, endrin) in the sediments from 14 sampling sites were bdl-0.82 ng g^{-1} dry wt^{-1}. The mean concentrations of heptachlor in sediments ranged from 0.12 ng g^{-1} dry wt^{-1} at Gökova Bay to 0.78 ng g^{-1} dry wt^{-1} at Meric River Estuary. Maximum dieldrin level was found at Gokova Bay (0.69 ng g^{-1}). Concentration levels of dieldrin found at Izmir Inner Bay were close to those found at Meric River Estuary and Edremit Bay. Endrin was observed below detection limits at all sampling locations (Table 5.7).

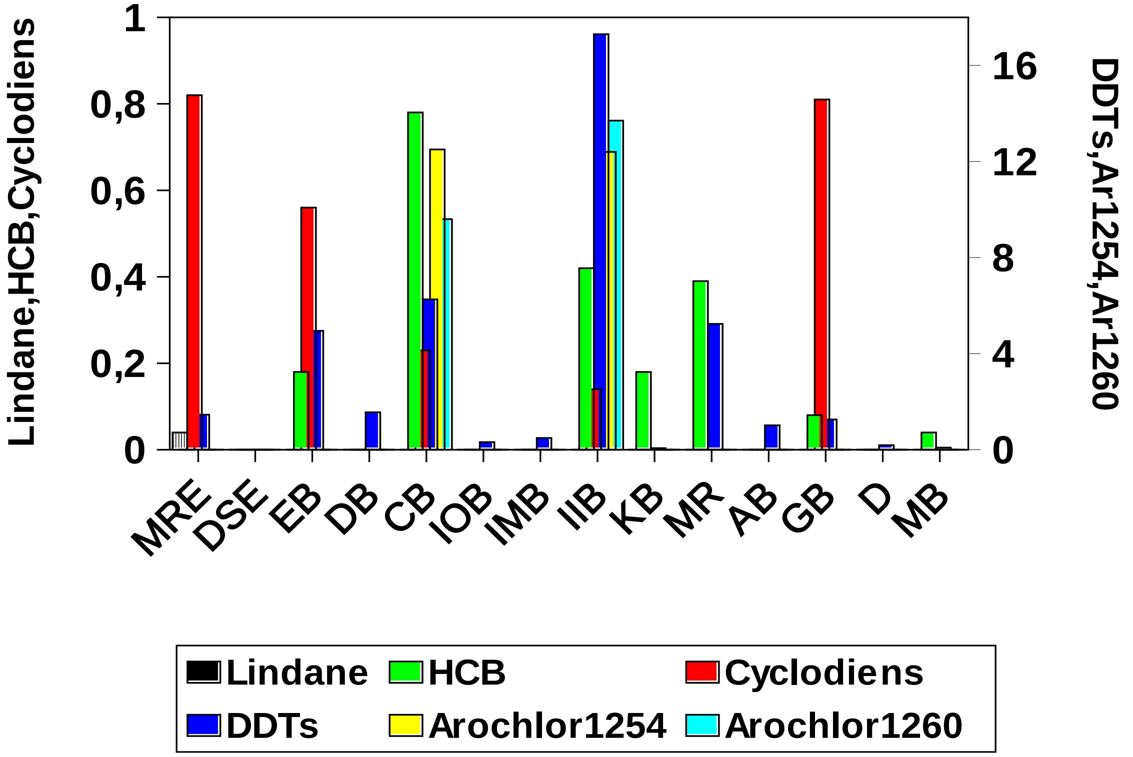


Figure 5.20 the total concentration profiles of OCPs (as ng g^{-1} dry weight) in the sediments of the Eastern Aegean coasts.

It can be seen from Figure 5.20 that the highest concentrations of DDTs in sediment samples were found at Izmir Inner Bay (17.3 ng g^{-1}), Candarli Bay (6.3 ng g^{-1}), Menderes Region (5.24 ng g^{-1}), Edremit Bay (4.95 ng g^{-1}), Meric River Estuary (1.46 ng g^{-1}) and Gokova Bay (1.26 ng g^{-1}). The high concentrations at these sites might be associated with the input of pollutants from agricultural activities.

Arochlor 1254 and 1260 were present in noticeably higher concentrations at Candarli and Izmir Inner Bay than in sediments along the Eastern Aegean coasts. Arochlors are used as industrial chemicals and their probable source is industrial waste. Arochlor 1254 and 1260 in the sediments ranged from 11.1-13.5 ng g^{-1} dry wt^{-1} and 8.9-15.5 ng g^{-1} dry wt^{-1}, respectively. The highest concentrations of ΣPCBs were found in samples collected from the inner part of Izmir Bay.

Table 5.11 Pearson's correlation coefficients for relationship between organochlorine compounds and organic carbon in the Eastern Aegean coasts (Marked correlations are significant at $p<0.05$)

	Lindane	HCB	Heptachlor	Aldrin	Dieldrin	DDE	DDD	DDT	TOC
Lindane	1.00								
HCB	-0.18	1.00							
Heptachlor	**0.80**	-0.14	1.00						
Aldrin	-0.08	**0.78**	-0.12	1.00					
Dieldrin	-0.04	-0.03	0.06	-0.10	1.00				
ppDDE	-0.11	**0.66**	-0.08	0.20	0.09	1.00			
ppDDD	-0.01	**0.59**	0.25	0.23	0.03	**0.88**	1.00		
ppDDT	0.03	**0.63**	-0.08	0.25	0.16	**0.95**	**0.78**	1.00	
TOC	0.18	0.40	0.15	0.22	-0.09	**0.73**	**0.72**	**0.76**	1.00

5.6.3 Data Analysis

Matrices of Pearson's correlation coefficients were calculated for pairs of organochlorine compounds (Table 5.11). Significant correlations were found between *p,p'*-DDT and *p,p'*-DDE (R=0.95, $p<0.05$), *p,p'*-DDD and *p,p'*-DDE (R=0.88, $p<0.05$), heptachlor and lindane (R=0.80, $p<0.05$), *p,p'*-DDT and *p,p'*-DDD (R=0.78, $p<0.05$), aldrin and HCB (R=0.78, $p<0.05$), TOC and *p,p'*-DDT (R=0.76, $p<0.05$), TOC and *p,p'*-DDE (R=0.73, $p<0.05$), TOC and *p,p'*-DDD (R=0.72, $p<0.05$), *p,p'*-DDE and HCB (R=0.66, $p<0.05$), *p,p'*-DDT and HCB (R=0.63, $p<0.05$), *p,p'*-DDD and HCB (R=0.59, $p<0.05$) in the Eastern Aegean coasts. Positive high correlations were found between DDT metabolites and organic carbon while low negative correlations were detected between lindane and *p,p'*-DDE (R=-0.11, $p<0.05$), HCB and heptachlor (R=-0.14, $p<0.05$), heptachlor and aldrin (R=-0.12, $p<0.05$) in the Eastern Aegean coasts.

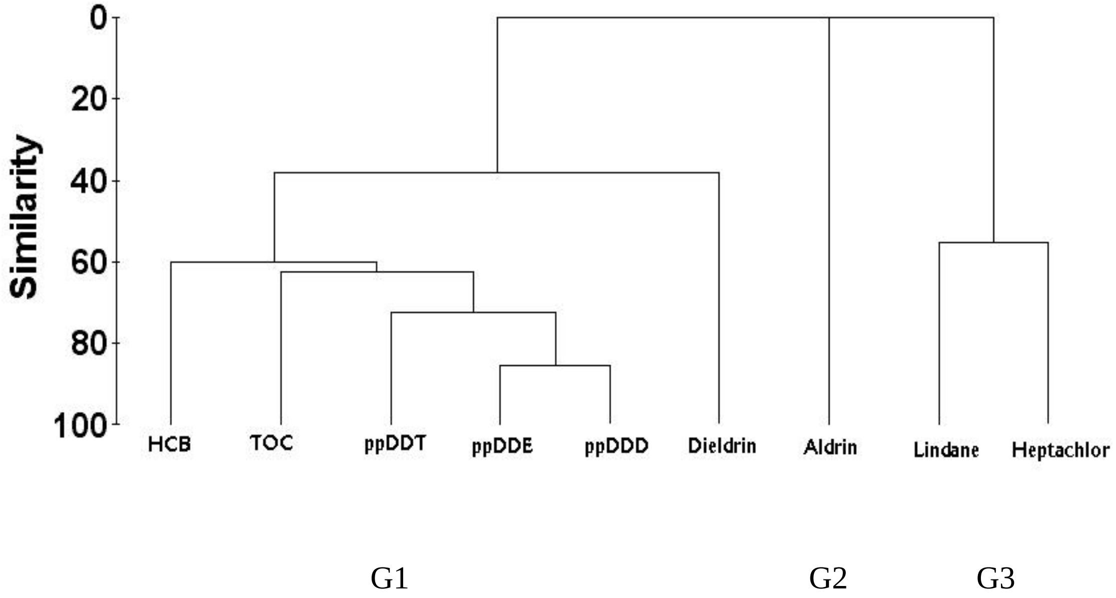


Figure 5.21 Hierarchical dendogram for organochlorinated pesticides and total organic carbon in sampling sites from the Eastern Aegean coasts.

Cluster analysis was performed to identify the complete linkage groups of individual organochlorinated pesticides and total organic carbon in the sediments from the Eastern Aegean coasts. The data set was standardized and normalized using log (x+1) transformation. Three major clusters of compounds with sub-groups were identified in sediment samples. The first group was comprised of two sub-groups; the first group contained HCB, TOC, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD and the second group indicated Dieldrin. The second major group included Aldrin while the third group contained Lindane and Heptachlor (Figure 5.21).

The cluster analysis was engaged according to the group average between groups method on the transformated log (x+1) organochlorinated compounds and total organic carbon data from the different sites of the Eastern Aegean coasts. Two big clusters with sub groups were identified; the first major group (G1) represented polluted sites (Izmir Inner Bay, Edremit Bay, Candarli Bay, Menderes Region); the second major group with sub-groups (G2) contained unpolluted sites (Izmir Middle Bay, Datca, Marmaris Bay, Dardanelles Strait Entrance, Kusadasi Bay, Gokova Bay, Meric River Estuary, Izmir Outer Bay, Dikili Bay and Akbuk Bay) from the Eastern Aegean coasts (Figure 5.22).

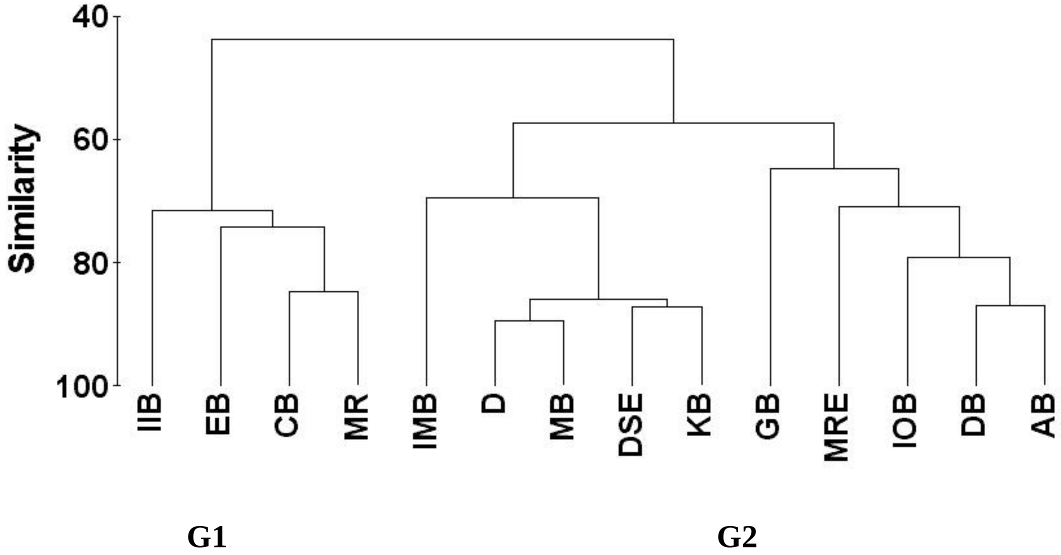


Figure 5.22 Hierarchical dendogram for sampling sites for different organochlorinated pesticides from the Eastern Aegean coasts.

In this study, principal component analysis (PCA) was deployed in order to analyze the data. The first step in the multivariate statistical analysis was application of PCA with the aim of grouping the individual organochlorinated compounds and TOC. The PCA results were generally similar to those of the cluster analysis discussed in the previous paragraph. The first two principal components explained 98.2 % of the total variability in the sediments. These two principal components were highly weighted due to the contributions of organochlorinated pesticides and TOC. After auto scaling, the two significant components were identified giving account for 89.5 % and 8.7 % of the total variation, respectively.

The horizontal axis PC1 correlated with *p,p'*-DDE, *p,p'*-DDD and TOC in the negative part and *p,p'*-DDT in the positive part, showing that the contamination of the Eastern Aegean coasts is a mixture of *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT. Furthermore, as shown in Figure 5.19, TOC gave a high negative loading on PC1, and there was a significant correlation between these organic compounds (*p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT) and TOC (Table 5.11).

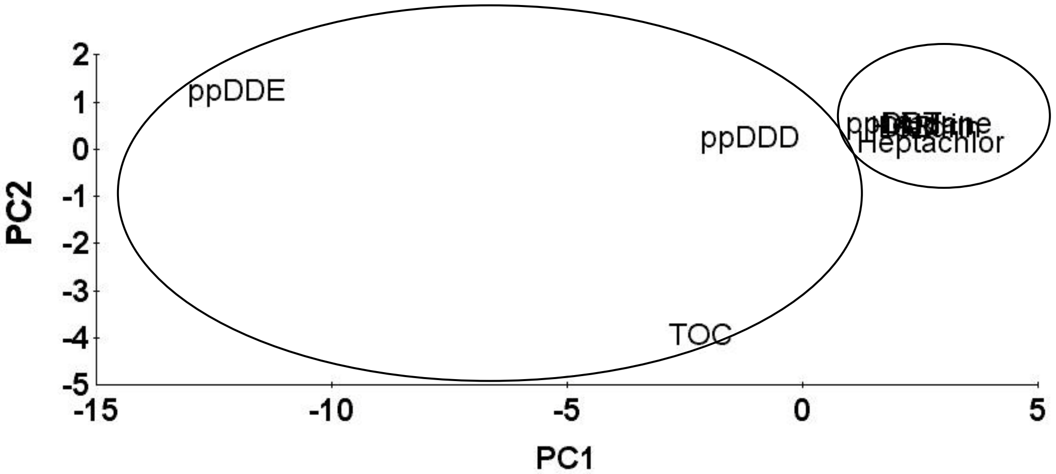


Figure 5.23 Principal component analysis loading plots for sediment samples collected in sampling sites of the Eastern Aegean coasts for organochlorinated compounds and TOC.

The presence of *p,p'*-DDD and *p,p'*-DDT residues in the same group of PC1 could suggest the occurrence status of these pesticides in the coastal areas. The sedimentary condition in these coastal areas is oxic due to the opened setting. The historical/fresh inputs of DDT in these areas could be more easily degraded into DDE under an oxic condition, inducing a common appearance of DDT and DDE in PC1. The vertical axis PC2 represented lindane, HCB, heptachlor, aldrin and dieldrin in the positive part, indicating the same origin of these compounds (Figure 5.23).

The score plot of first two components allows for the characterization of the sampling stations according to the first and second component for organochlorinated compounds and TOC. The three principal components explained 80.6 % of the total variance with the values for PC1, PC2 and PC3 of 45.0 %, 21.9 % and 13.7%, respectively. Stations Izmir Inner Bay, Candarli Bay, Edremit Bay and Menderes Region sediments were well differentiated by the higher scores on the first component in the negative part and exhibited high pollution extent (Figure 5.24).

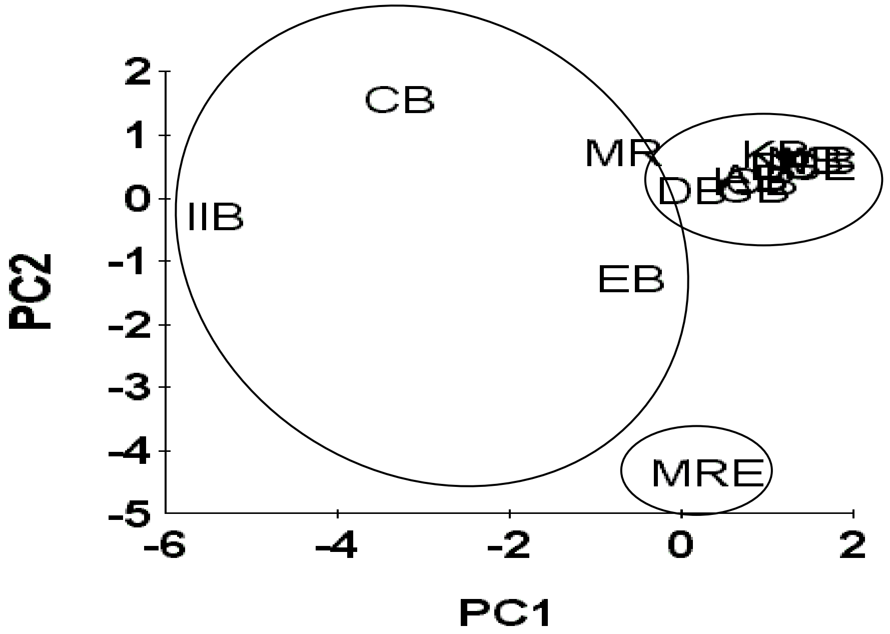


Figure 5.24 Principal component analysis loading plots for sediment samples collected in the different sites of the Eastern Aegean coasts.

Sample from Meric River Estuary was clearly separated from other stations in the negative part of the second component. PC3 represented Dardanelles Strait Entrance, Kusadasi Bay, Marmaris Bay in the negative and Dikili Bay, Akbuk Bay, Gokova Bay, Datca, Izmir Outer Bay, Izmir Middle Bay in the positive part (Figure 5.24).

5.6.4 Potential biological effects of OCPs

As shown in Table 5.12, two widely used sediment quality guidelines, i.e. the effects range-low value (ERL) and effects range-median value (ERM) guidelines (Long et al., 1998; Long et al., 1995), as well as the threshold effects level (TEL) and probable effects level (PEL) guidelines (CCME, 2002) were applied to evaluate the possible ecotoxicological risks of OCPs in the study area.

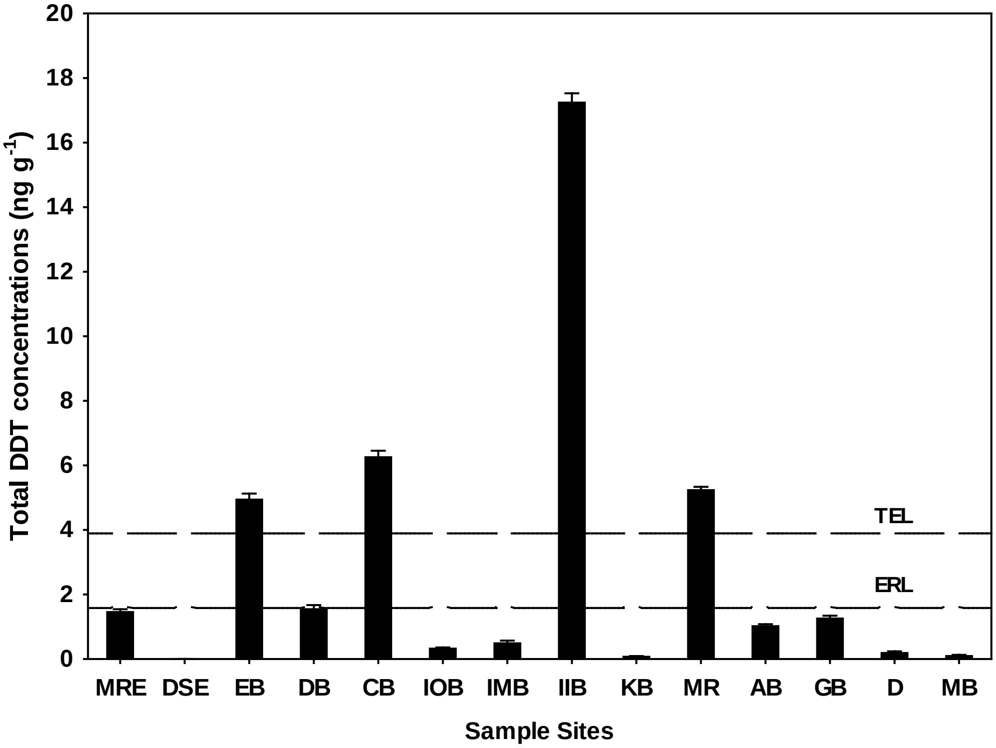


Figure 5. 25 Concentrations of ΣDDT in the sediments from the Eastern Aegean coasts. ERL: the effect range low value (Long et al., 1995); TEL: Canadian interim sediment quality guideline for DDTs in marine sediment, threshold effect level (CCME, 1999).

Concentration levels of *p p'*-DDE and *p,p'*-DDD were higher than ERL values at 4 sites (Edremit Bay, Candarli Bay, Izmir Inner Bay and Menderes Region) and 2 sites (Edremit Bay and Izmir Inner Bay), respectively (Figure 5.25). Meanwhile, these compounds also exceeded the TEL value at the same sites, but were significantly lower than the PEL and ERM values. The level of heptachlor was over the ERL value at 2 sites located in Meric River Estuary and Edremit Bay, whereas they were below the ERM, TEL and PEL values. This suggested that the concentration levels of *p,p'*-DDE, *p,p'*-DDD and heptachlor at most sites other than Edremit Bay, Candarli Bay, Izmir Inner Bay, Menderes Region and Meric River Estuary were lower than the values that may cause adverse biological risk.

Table 5.12 Assessments of potential biological risks of selected OCPs in the surface sediments of the Eastern Aegean coasts using two sediment quality guidelines (SQG).

Chemical	Range (ng g^{-1})	ER-L[a]	Above ER-L (%)[e]	ER-M[b]	Above ER-M (%)[e]	TEL[c]	Above TEL (%)[e]	PEL[d]	Above PEL (%)[e]
p,p'-DDT	NA-0.86	1.0	0	7	0	1.19	0	4.77	0
p,p'-DDE	NA-13.1	2.2	31	27	0	2.07	31	374	0
p,p'-DDD	NA-3.31	2.0	18	20	0	1.22	27	7.81	0
DDTs	NA-17.3	1.58	31	46.1	0	3.89	31	51.7	0
Dieldrin	NA-0.69			NA	-	0.71	0	4.30	0
γ-HCH	0.04	NA	-	NA	-	0.32	0	0.99	0
Heptachlor	NA-0.78	0.50	67	6	0	2.26	0	4.79	0
PCBs[f]	NA-26.1	22.7	50	180	0	21.5	100	189	0

[a] Effect range-low value.

[b] Effect range-median value.

[c] Threshold effect level.

[d] Probable effect level.

[e] Percentage of samples above the corresponding levels.

[f] Sum of Arochlor1254 and Arochlor1260

NA: Not available

For DDTs, although not exceed than ERM and PEL values, 31% of total sites in the study area (mostly observed in the Izmir Inner Bay, Edremit Bay, Candarli Bay and Menderes Region) were higher than ERL and TEL values (Figure 5. 25), suggesting that the exposure of DDTs may cause ecological risk on the neighboring benthic organisms. Therefore, DDTs could be the one-main species of OCPs with more ecotoxicological concern in the Eastern Aegean coasts, especially in the Izmir Inner Bay and coastal regions of the study area, while other OCPs in surface sediments would be less possible to cause adverse biological effect.

5.6.5 Ecotoxicological concerns for PCBs

Sediment-bound PCBs can affect benthic organisms. To evaluate the ecotoxicological aspect of sediment contamination, some published sediment quality guidelines were applied in this study. Although the guidelines are limited in some cases, they provide useful indicators of the effects of PCB contamination in the absence of environmental assessment criteria for PCBs in Turkey.

The effect range low value (ERL, 22.7 ng g^{-1} dry weight) suggests that PCBs can exert toxic biological effects on aquatic organisms, while the effect range median value (ERM, 180 ng g^{-1} dry weight) indicates the high possibility of PCBs posing detrimental biological effects on aquatic organisms (Long et al., 1995). Based on Canadian quality guidelines for PCBs in marine sediment, PCB concentrations at the probable effect level (PEL, 189 ng g^{-1} dry weight) frequently cause adverse effects on aquatic biota, whereas at concentrations corresponding to the threshold effect level (TEL, 34.1 ng g^{-1} dry weight), the effects are negligible (CCME, 1999). PCBs were only measured at Candarli Bay and Izmir Inner Bay sites. The total PCB concentrations of the samples collected for this study did not exceed the ERM or PEL values, with the exception of sites Candarli Bay and Izmir Inner Bay, which showed concentrations above the ERL and TEL values (Table 5. 12). Thus, the sediments at sites Candarli Bay and Izmir Inner Bay have a potential biological impact, but should cause no impairment.

CHAPTER SIX
CONCLUSIONS

The present work represents the first detailed study of the distribution and origin of petroleum hydrocarbons in sediments from the Eastern Aegean Sea, an area economically important for the western part of Turkey due to maritime, industrial and tourism activities. This investigation showed that sedimentary hydrocarbons in the Eastern Aegean coasts consist in a mixture of compounds from natural and anthropogenic sources. Natural hydrocarbons are mainly from planktonic inputs derived from eutrophication with the development of blooms, which is a normal process in the estuary such as Izmir Inner Bay, Gediz, Kucuk Menderes and Buyuk Menderes River estuary. Natural PAHs from *in situ* biological activity were only important at a few sites (Dikili, Kusadasi, Akbuk, Edremit and Gokova Bays) influenced by the terrestrial higher plants. The Pri/Phy was greater than 1 in all samples except Dardanelles Strait Entrance and Izmir Inner Bay; this ratio showed slightly fluctuating values ranging from 1.02 to 1.61, indicating mainly a biogenic source. Since the Pri/Phy was smaller than 1 in Dardanelles Strait Entrance and Izmir Inner Bay stations, they indicated reducing conditions.

Analysis of 14 surface sediment samples from the Eastern Aegean coasts showed that the levels for 20 PAHs ranged from 73.5-2169.8 ng g^{-1} dry weight, with the mean value of 323.7 ng g^{-1} dry weight. PAHs ranged from a relatively low to a moderate PAHs pollution compared to other urbanized coastal areas worldwide. With respect to PAHs in the Eastern Aegean Sea, they tend to be derived predominantly from pyrolytic sources, contributing 19.4 to 85% of the total PAHs. Considering some concentration ratios between the different PAHs it was possible to indicate pyrolysis processes as the most probable source of contamination. Four- to five-ring PAHs were predominant in sediments. High concentrations of perylene were recorded in most of the samples. The diagenetic origin of this compound was most notable in samples taken from Edremit, Dikili, Kusadasi, Akbuk and Gokova bay stations. The sediments of Izmir Inner Bay, Dardanelles Strait Entrance and Candarli Bay presented pyrolytic inputs.

Results showed that some of the concentration levels of PAHs (naphthalene, fluorene, phenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene) were higher than TEL values at Izmir Inner Bay. Meanwhile, fluorene also exceeded the ERL value at the same site, but all these compounds were significantly lower than the PEL and ERM values. These findings indicated that the sediments from the entire sampling sites except Izmir Inner Bay should have no potential biological impact.

This study first documented the composition and distribution of OCPs in sediments collected from the Eastern Aegean Sea. Environmental levels were generally low for all compounds by global standards, including the relatively higher values for chlorinated hydrocarbons found areas from the inner part of Izmir and Candarli Bay. The concentrations of ΣOCPs were in the range of bdl-17.8 ng g^{-1} dry weight with an average value of 3.20 ng g^{-1} dry weight. The results indicated that the DDTs were the predominant contaminant in sediments of the Eastern Aegean coasts. *p,p'*-DDE was the most often found OCP compound at all stations except Dardanelles Strait Entrance. PCBs were only measured at Candarli Bay and Izmir Inner Bay sites. Highest concentrations of ΣPCBs were found in samples collected from the inner part of Izmir Bay. Positive high correlations were detected between DDT metabolites and organic carbon in sediments.

DDD/DDE ratio were lower than unity, indicating that the sediments was dominated by *p,p'*-DDE, the product of aerobic degradation of *p,p'*-DDT. This result showed that the sediments collected from the Eastern Aegean Sea were mainly under oxic conditions. The OCP contamination was mainly from the aged and weathered agricultural soils in all sampling stations in the western part of the Turkish coastal zone. In summary, DDT contamination was not highlighted as a contemporary and ubiquitous problem in the Eastern Aegean Sea.

Based on the sediment quality guidelines, DDTs and heptachlor would be more concerned for the ecotoxicological risk in the Eastern Aegean coasts. The total PCB concentrations of the samples collected for this study did not exceed the ERM or PEL values, with the exception of sites Candarli Bay and Izmir Inner Bay, which showed concentrations above the ERL and TEL values. Thus, the sediments at sites Candarli Bay and Izmir Inner Bay could potentially cause acute biological impairment.

The results of this work provide an insight related to input of organic pollutants from natural and anthropogenic sources to the Eastern Aegean Sea. Data on the petroleum hydrocarbons and the organochlorine pesticides found in this study can be used as baseline reference concentration for future aliphatic and polycyclic aromatic hydrocarbons and organochlorinated pesticides monitoring programs.

REFERENCES

Abdallah, A. M. (1992). Determination of DDTs and PCBs residues in Abu-Quir and El-Max Bays, Alexandria, Egypt. *Toxicological and Environmental Chemistry, 36*, 89-97.

Abdallah, A. M., & Abbas, M. M. (1994). Residue level of organochlorine pollutants in the Alexandria Region, Egypt. *Toxicological and Environmental Chemistry, 41*, 39-247.

Aboul-Kassim, T. A. T., & Simoneit, B. R. T. (1995). Petroleum hydrocarbon fingerprinting and sediment transport assessed by molecular biomarker and multivariate statistical analyses in the Eastern harbor of Alexandria, Egypt. *Marine Pollution Bulletin, 30*, 63-73.

Albanis, T. A., Danis, T. G., & Hela, D. G. (1995a). Transportation of pesticides in estuaries of Louros and Arachthos rivers (Amvrakikos Gulf, N.W.Greece). *The Science of the Total Environment, 171*, 85-93.

Allen-gil, S. M., Gubalas, G. P., Wilson, R. E, Landers, D. H., Wade, T. L., & Sericano, J. L. (1998). Organochlorine pesticides and polychlorinated biphenyls (PCBs) in sediments and biota from four US Arctic Lakes. *Archives of Environmental Contamination and Toxicology, 33,* 378-87.

Arias, A. H., Spetter, C. V., Freije, R. H., & Marcovecchio, J. E. (2009). Polycyclic aromatic hydrocarbons in water, mussels (Brachidontes sp., Tagelus sp.) and fish (Odontesthes sp.) from Bahía Blanca Estuary, Argentina. *Estuarine, Coastal and Shelf Science, 85*, 67-81.

Bakan, G., & Ariman, S. (2004). Persistent organochlorine residues in sediments along the coast of mid-Black Sea region of Turkey *Marine Pollution Bulletin, 48,* 1031-1039

Balopoulos, E. Th., Theocharis, A., Kontoyiannis, H., Varnavas, S., Voutsinou-Taliadoruri, F., Iona, A., Souvermezoglu, A., Ignatiades, L., Gotsis-Skretas, O., & Pavlidou, A. (1999). Major advances in the oceanography of the southern Aegean Sea-Cretan straits system (Eastern Mediterranean). *Progress in Oceanography, 44*, 109-130.

Barakat, A. O., Kim, M., Qian, Y., & Wade, T. L. (2002). Organochlorine pesticides and PCB residues in sediments of Alexandria Harbour, Egypt. *Marine Pollution Bulletin, 44,* 1421-1434.

Baumard, P., Budzinski, H., & Garrigues, P., (1998). Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean Sea. *Environmental Toxicology and Chemistry, 17*, 765-776.

Baumard, P., Budzinski, H., Mchin, Q., Garrigues, P., Burgeot, T., & Bellocq, J. (1998a). Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuarine, Coastal and Shelf Science, 47*, 77-90.

Baumard, P., Budzinski, H., & Garrigues, P. (1998b). PAHs in Arcachon Bay, France: origin and biomonitoring with caged organisms. *Marine Pollution Bulletin, 36,* 577-586.

Benlahcen, K. T., Chaoui, A., Budzinski, H., Bellocq, J., & Garrigues, P. H. (1997). Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments. *Marine Pollution Bulletin, 34*, 298-305.

Bildeman, T. F., & Olney, C. E. (1974). Chlorinated hydrocarbons in the Sargano Sea atmosphere and surface water. *Science*, *183*, 516-8.

Botello, A. V., Gonzalez, C., & Diaz, G. (1991). Pollution by petroleum-hydrocarbons in sediments from continental-shelf of Tabasco State, Mexico. *Bulletin of Environmental Contamination and Toxicology, 47*, 565-571.

Bouloubassi, I., & Saliot, A. (1993). Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH). *Oceanologica Acta, 16*, 145-161.

Breivik, K., Alcock, R., Li, Y., Bailey, R. E., Fiedler, H., & Pacyna, J. M. (2004). Primary sources of selected POPs: regional and global scale emission inventories. *Environmental Pollution, 128,* 3-16.

Budzinski, I., Bellocq, J., Pierard, C., & Garrigues, P. (1997). Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry, 58 (1-2),* 85-97.

Burt, J. S., & Ebell, G. F. (1995). Organic pollutants in mussels and sediments of the coastal waters off Perth, Western Australia. *Marine Pollution Bulletin 30,* 723-732.

Camusso, M., Golossi, S., & Vignati, D. (2002). Assessment of river Po sediment quality by micropollutant analysis. *Water Research, 36*, 2491-2504.

Castilho, J. A. A., Fenzl, N., Guillen, S. M., & Nascimento, F. S. (2000).Organochlorine and organophosphorus pesticide residues in the Atoya riverbasin, Chinandega, Nicaragua. *Environmental Pollution, 110,* 523-53.

CCME (Canadian Council of Ministers of the Environment), (1999). Canadian Council of Ministers of the Environment Canadian sediment quality guidelines for the protection of aquatic life: polychlorinated biphenyls (PCBs). In: Canadian Environmental Quality Guidelines, Canadian Council of Ministers of the Environment: Winnipeg, Manitoba.

CCME (Canadian Council of Ministers of the Environment) (2002). Canadian sediment quality guidelines for the protection of aquatic life. Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment, Winnipeg, MB.

Ciaccio, L. L. (Ed.). (1972). *Water and Water Pollution Handbook*. New York.

Clark, R. B. (1997). *Marine Pollution* (4th ed.). Oxford: Clarendan Press.

Colombo, J. G., Khali, M. F., Horth, A. C., & Catoggio, J. A. (1990). Distribution of chlorinated pesticides and individual polychlorinated biphenyls in biotic and abiotic compartments of the Rio de La Plate. *Environmental Science & Technology, 24*, 498-505.

Cripps, G.C. (1990). Hydrocarbons in the seawater and pelagic organisms of the Southern Ocean. *Polar Biology, 10,* 393-402.

Cripps, G. C., & PRIDDLE, J. (1991). Hydrocarbons in the Antarctic marine environment. *Antarctic Science, 3,* 233-250.

Cripps, G. C. (1994). Hydrocarbons in the Antarctic marine environment: monitoring and background. *International Journal of Environmental Analytical Chemistry, 55*, 3-13.

Dalman, Ö., Demirak, A., & Balcı, A. (2006). Determination of heavy metals (Cd, Pb) and trace elements (Cu, Zn) in sediments and fish of the SouthEastern Aegean Sea (Turkey) by atomic absorption spectrometry. *Food Chemistry, 95 (1)*, 157-162.

Darilmaz, E., & Kucuksezgin, F. (2007). Distribution and origin of hydrocarbons in surficial sediments from the Eastern Aegean Sea (Izmir Bay). *Marine Pollution Bulletin, 54*, 1813-1838.

Dave, P. P. India: a generics giant. *Farm chemicals international*, November 10, p. 36-7.

De Mora, S., Villeneuve, J. P., Sheikholeslami, M. R., Cattini, C., & Tolosa, I. (2004). Organochlorinated compounds in Caspian Sea sediments. *Marine Pollution Bulletin, 48,* 30-43.

De Mora, S., Fowler, S. W., Tolosa, I., Villeneuve, J. P., & Cattini, C. (2005). Chlorinated hydrocarbons in marine biota and coastal sediments from the Gulf and Gulf of Oman. *Marine Pollution Bulletin, 50,* 835-849.

Demirkurt, E., Uysal, H., & Parlak, H. (1990). The levels of heavy metals accumulationin some benthic organisms living in Izmir Bay. *Rapport du Congrès de la Commission Internationale pour l'Exploration Scientifique de la Mer Méditerranée, 32*, 170.

Didyk, B. M., Simoneit, B. R. T., Brassell, S. C., & Eglinton, G. (1978). Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature*, *272*, 216-222.

Diez, S., Jover, E., Bayona, J. M., & Albaiges, J. (2007). Prestige oil spill. III. Fate of a heavy oil in the marine environment. *Environmental Science & Technology, 41*, 3075-3082.

Doong, R. A., Peng, C. K., Sun, Y. C., & Liao, P. L. (2002).Composition and distribution of organochlorine pesticide residues in surfacesediments from the Wu-Shi River estuary, Taiwan. *Marine Pollution Bulletin*, *45*, 246-253.

Doong, R. A., & Lin, Y. T. (2004). Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan. *Water Research, 38*, 1733-1744.

Equipe Cousteau. (1993). Concentration of chemical pollutants in sediments and mussels along Danube. In: The Danube... for whom and for what? *Equipe Cousteau's Final Report, Paris*, pp. 104-126.

Er-Raioui, H., Bouzid, S., Marhraoui, M., & Saliot, A. (2009). Hydrocarbon pollution of the Mediterranean coastline of Morocco. *Ocean & Coastal Management*, *52*, 124-129.

Ezra, S., Feinstein, S., Pelly, I., Bauman, D., & Miloslavsky, I. (2000). Weathering of fuel oil spill on the east Mediterranean coast, Ashdod. Israel. *Organic Geochemistry, 31*, 1733-1741.

Fang, M. D., Lee, C. L., & Yu, C. S. (2003). Distribution and source recognition of polycyclic aromatic hydrocarbons in sediments of Hsin-ta Harbour and adjacent coastal areas, Taiwan. *Marine Pollution Bulletin, 46*, 941-953.

Farm Chemicals Handbook. (1993). Pesticide dictionary. Willoughby, OH: Meister Publishing Company, C204.

Farrington, J. W., & Tripp, B. W. (1977). Hydrocarbons in western North Atlantic surface sediments. *Geochimica et Cosmochimica Acta, 41*, 1627-1641.

Filiz, N., & Kucuksezgin, F. (2008). Composition and distribution of organochlorine pesticide residues in surface sediments from Gediz and Bakırçay Rivers (Eastern Aegean). *Fresenius Environmental Bulletin, 17(6),* 744-754.

Fillmann, G., Readman, J. W., Tolosa, I., Bartocci, J., Villeneuve, J. P., Cattini, C., & Mee, L. D. (2002). Persistent organochlorine residues in sediments from Black Sea. *Marine Pollution Bulletin, 44*, 122-133.

Fowler, S. W., Readman, J. W., Oregioni, B., Villeneuve, J. P., & Mckay, K. (1993). Petroleum hydrocarbons and trace metals in nearshore Gulf sediments and biota before and after the 1991 war: an assessment of temporal and spatial trends. *Marine Pollution Bulletin, 27*, 171-182.

Fowler, S. W. (1990). Critical review of selected heavy metal and chlorinated hydrocarbon concentrations in the marine environment. *Marine Environmental Research, 29*, 1-64.

Friligos, N. (1986a). Distribution of nutrients in the Ionian Sea. *Rapport du Congrès de la Commission Internationale pour l'Exploration Scientifique de la Mer Méditerranée, 30(2)*, 35.

Gogou, A., Apostolaki, M., & Stephanou, E. G. (1998). Determination of organic molecular markers in marine aerosols and sediments: one-step flash chromatography compound class fractionation and capillary gas chromatographic analysis. *Journal of Chromatography A, 799*, 215-231.

Gogou, A., Bouloubassi, I., & Stephanou, E. G. (2000). Marine organic geochemistry of the Eastern Mediterranean: 1. Aliphatic and polyaromatic hydrocarbons in Cretan Sea surficial sediments. *Marine Chemistry, 68,* 265-282.

Guo, W., He, M., Yang, Z., Lin, C., Quan, X., & Wang, H. (2007). Distribution of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River watershed, China. *Chemosphere, 68 (1),* 93-104.

Guzzella, L., & De Paolis, A. (1994). Polycyclic aromatic hydrocarbons in sediments of the Adriatic sea. *Marine Pollution Bulletin, 28,* 159-165.

Hach Publication 3061, (1988). Procedures for Water and Waste Water Analysis.

Hakanson, L. & Jansson, M. (1983). Principles of Lake Sedimentology. *Springer-Verlag*.

Haldezos, C., Scoullos, M., & Dassenakis, M. (2002). Levels of Seven PCBs Congeners in the coastal Marine Environment of South Euvoikos Gulf, Greece. *In: Environmental Science and Pollution Research*, 8th FECS Conference on Chemistry and the Environment: Chemistry for a Sustaining World, Athens, Greece, 188-190.

Harvey, L. T. (1992). *A guide to agricultural spray surfactants used in the UnitedStates*.

Hill, M. K. (1997). *Understanding Environmental Pollution*, Cambridge University Press, USA.

Hites R. K., & Day H. R. (1992). Unusual persistence of DDT in some western USA soil. *Bulletin of Environmental Contamination and Toxicology, 48*, 259-64.

Hong, H., Chen, W., Xu, L., Wang, Z., & Zhang, L. (1999). Distribution and fate of organochlorine pollutants in the Pearl River Estuary. *Marine Pollution Bulletin, 39*, 376-82.

Hu, L., Guo, Z., Feng, J., Yang, Z., & Fang, M. (2009). Distributions and sources of bulk organic matter and aliphatic hydrocarbons in surface sediments of the Bohai Sea, China. *Marine Chemistry, 113,* 197-211.

IFREMER (1998). *Reseau National d'Observation de la Qualite du Milieu Marin(RNO)* from http://www.ifremer.fr

IOC, (1993). Chlorinated Biphenyls in Open Ocean Waters; Sampling,Extraction, Clean-up and Instrumental Determination, Manualand Guides No. 27. Paris, *Intergovernmental Oceanographic Commission,* UNESCO, p. 36.

Iwata, H., Tanabe, S., Aramoto, M., Sakai, N., & Tatsukawa, R. (1994). Persistentorganochlorine residues in sediments from the Chukechi Sea, BeringSea and Gulf of Alaska. *Marine Pollution Bulletin, 28*, 746-53.

Jones, K. C., & de Voogt, P. (1999). Persistent organic pollutants (POPs): state of the science. *Environmental Pollution, 26(10)*, 2012-7.

Karickhoff, S. W. (1984). 'Organic pollutant sorption in aquatic systems', *J. Hydraul Eng. 110,* 707-735.

Kennish, M. J. (1997). *Practical handbook of estuarine and marine pollution*. BocaRaton, FL7 CRC Press;.

Kucuksezgin, F., Balcı, A., Kontas, A. & Altay, O. (1995). Distribution of nutrients and Chlorophyll a in the Aegean Sea. *Oceanologica Acta, 18(3),* 343-352.

Kucuksezgin, F., Çağlar, B., & Uslu, O. (1999). Polycyclic Aromatic Hydrocarbons in Red Mullet (Mullus barbatus) and Sediments from the Eastern Aegean Sea. *Toxicological and Environmental Chemistry, 73,* 247-256.

Kucuksezgin, F., Uluturhan, E., Kontas, A., & Altay, O. (2002). Trace metal concentrations in edible fishes from Izmir Bay, Eastern Aegean. *Marine Pollution Bulletin, 44,* 827-832.

Kucuksezgin, F., Kontas, A., Altay, O., Uluturhan, E., & Darilmaz, E. (2006). Assesment of marine pollution in Izmir Bay:Nutrient, heavy metal and total hydrocarbon concentrations. *Environment International, 32,* 41-51.

Kutz, F., Wood, P., & Bottimore, D. (1991). Organochlorine pesticides and polychlorinated biphenyls in human adipose tissue. *Reviews of Environmental Contamination & Toxicology, 120,* 1-82.

La Flamme, R. E., & Hites, R. A. (1978). The global distribution of polyclycic aromatic hydrocarbons in recent sediments. *Geochimica et Cosmochimica Acta, 42,* 289-303.

Lee, C. L., Hsieh, M. T., & Fang, M. D. (2005). Aliphatic and Polycyclic Aromatic Hydrocarbons in Sediments of Kaohsiung Harbour and Adjacent Coast, Taiwan. *Environmental Monitoring and Assessment, 100,* 217-234.

Le Dréau, Y., Jacquot, F., Doumenq, P., Guiliano, M., Bertrand, J.C., & Mille, G. (1997). Hydrocarbon balance of a site which had been highly and chronically contaminated by petroleum wastes of a refinery (from 1956 to 1992). *Marine Pollution Bulletin, 34,* 456-468.

Lenihan, H. S., Oliver, J. S., Oakden, J. M., & Stephenson, M. D. (1990). Intense and localized benthic marine pollution around McMurdostation, Antarctica. *Marine Pollution Bulletin, 21,* 422-430.

Li, Y. F. (1999). Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1994 to 1997. *Science of the Total Environment, 232,* 121-58.

Liu, W. X., Chen, J. L., Lin, X. M., & Tao, S. (2007). Spatial distribution and species composition of PAHs in surface sediments from the Bohai Sea. *Marine Pollution Bulletin, 54 (1),* 113-116.

Long, E. R., MacDonald, D. D., Smith, S. L., & Calder, F. D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuary sediments. *Environmental Management, 19*, 81-97.

Long, E. R., Field, L. J., & MacDonald, D. D. (1998). Predicting toxicity in marine sediments with numeral sediment quality guidelines. *Environmental Toxicology and Chemistry, 17*, 714-727.

Magi, E., Bianco, R., Ianni, C., & Di Carro, M. (2002). Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea. *Environmental Pollution, 119*, 91-98.

Maioli, O. L. G., Rodrigues, K. C., Knoppers, B. A., & Azevedo, D. A. (2010). Pollution source evaluation using petroleum and aliphatic hydrocarbons in surface sediments from two Brazilian estuarine systems. *Organic Geochemistry, 41(9),* 966-970.

McElroy, A. E., Farrington, J. W., & Teal, J. M. (1989). Bioavailability of polycyclic aromatic hydrocarbons in the aquatic environment. *In: Vanarasi* U (ed) CRC, Boca Raton, pp 1-40.

MEDPOL. (1997). Long term programme for pollution and research in the Mediterranean Sea “Aegean Part” *Medpol-phase II. Final report*.

Metcalf, R. L. (1995). Insect Control Technology. In: Kroschwitz J, Howe-Grant M, eds. Kirk-Othmer encyclopedia of chemical technology. Volume 14. New York, NY: John Wiley and Sons, Inc., 524-602.

Mostafa, A. R., Wade, T. L., Sweet, S. T., Al-Alimi, A. K. A., & Barakat, A. O. (2009). Distribution and characteristics of polycyclic aromatic hydrocarbons

(PAHs) in sediments of Hadhramout coastal area, Gulf of Aden, Yemen. *Journal of Marine Systems, 78,* 1-8.

Mörner, J. (1996). Alternatives to POP pesticides for the protection of plants and building constructions. In: Alternatives to persistent organic pollutants. The Swedish input to the IFCS Expert Meeting on persistent organic pollutants (Manila, 17-19 June 1996). *Report from the Swedish National Chemicals Inspectorate 4/96*. 79-116.

Nhan, D. D., Carvalho, F. P., Am, N. M., Tuan, N. Q., Yen, N. T. H., Villeneuve, J. P., & Cattini, C. (2001). Chlorinated pesticides and PCBs in sediments and molluscsfrom freshwater canals in the Hanoi region. *Environmental Pollution, 112*, 311-320.

Nishigima, F. N.,Weber, R. R., & Bícego, M. C. (2001). Aliphatic and aromatic hydrocarbons in sediments of Santos and Cananéia, SP, Brazil. *Marine Pollution Bulletin*, *42*, 1064-1072.

NRC (National Research Council). (1985). Oil in the sea, inputs, fates and effects. Washington, DC: *National Academy Press*, 602 pp.

Oğuz, T., & Tuğrul, S. (1998). Türkiye Denizlerinin ve Çevre Alanlarının Jeolojisi. Görür, N. Editor). *Denizlerimizin Genel Oşinografik Özelliklerine Toplu Bir Bakış*, 1-19.

Page, D. S., Boehm, P. D., Douglas, G. S., Bence, A. E., Burns, W. A., & Mankiewicz, P. J. (1999). Pyrogenic polycyclic aromatic hydrocarbons in sediments record past human activity: a case study in Prince William Sound. Alaska. *Marine Pollution Bulletin, 38*, 247-260.

Panagiotopoulou, V. Y., Tsipi, T., Hiskia, A., & Scoullos, M. (1996). Levels of organochlorine pesticides and PCB congeners in the gulf of Elefsis. *Fresenius Environmental Bulletin*, *5*, 545-550.

Parlak, H., & Demirkurt, E. (1990). Levels of heavy metals in two demersal fishes, Arnoglossus laterna (RISSO, 1810) and Buglossidium luteum (WALBAUM, 1972) in Izmir Bay. *Rapport du Congrès de la Commission Internationale pour l'Exploration Scientifique de la Mer Méditerranée, 32 (1),* 274.

Picer, M. (2000). DDTs and PCBs in the Adriatic Sea. *Croatica Chemica Acta, 73,* 123.

Pie´rad, C., Budzinski, H., & Carrigues, P. (1996). Grain size distribution of polychlorobiphenyls in coastal sediments. *Environmental Science and Technology, 30,* 2776-2783.

Pruell, R. J., & Quinn, J. G. (1985). Geochemistry of organic contaminants in Narragansett Bay sediments. *Estuarine, Coastal and Shelf Science, 21,* 295-312.

Readman, J. W., Preston, M. R., & Mantoura, R. F. C. (1986a). An integrated technique to quantify sewage, oil and PAH pollution in estuarine and coastal environments. *Marine Pollution Bulletin, 17,* 298-308.

Readman, J. W., Bartocci, J., Tolosa, I., Fowler, S. W., Oregioni, B., & Abdulraheem, M. Y. (1996). Recovery of the coastal marine environment in the Gulf following 1991 the war related oil spills. *Marine Pollution Bulletin, 32,* 493-498.

Readman, J. W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J. P., Catinni, C., & Mee, J. W. (2002). Petroleum and PAH contamination of the Black Sea. *Marine Pollution Bulletin, 44,* 48-62.

Reinhardt, S. B. & Van Vleet, E. S. (1986). Lipid composition of twentytwo species of Antarctic mid-water zooplankton and fish. *Marine Biology, 91,* 149-159.

Rocher, V., Azimi, S., Moilleron, R., & Chebbo, G. (2004). Hydrocarbons and heavy metals in the different sewer deposits in the Le Marais' catchment (Paris, France): stocks, distributions and origins. *Science of the Total Environment, 323,* 107-22.

Safe, S. H. (1993). Toxic aromatics. In: Kroschwitz JI, Howe-Grant M, eds. *Kirk Othmer's encyclopedia of chemical technology*. New York, NY: John Wiley & Sons, 127-139.

Saliot, A. (1981). Natural hydrocarbons in sea water. In: Duursma, E.K., Dawson, R. (Eds.), Marine Organic Chemistry. Evolution, Composition, Interactions and Chemistry of Organic Matter in Seawater. *Elsevier Oceanography Series, Amsterdam*, pp. 327-374.

Sarı, E., & Çağatay, M. N. (2001). Distributions of heavy metals in the surface sediments of the Gulf of Saros, NE Aegean Sea. *Environment International, 26 (3)*, 169-173.

Shepard, F. P. (1954). Nomenclature based on sand–silt–clay ratios. *Journal of Sedimentary Petrology, 24 (3)*, 151-158.

Sicre, M. A., Marty, J. C., Saliot, A., Aparicio, X., Grimalt, J., & Albaiges, J. (1987). Aliphatic and aromatic hydrocarbons in the Mediterranean aerosol. *International Journal of Environmental Analytical Chemistry, 29*, 73-94.

Soclo, H. (1986). Etude de la Distribution des Hydrocarbures Aromatiques Polycycliques dans les Se´diments Morins Re´cents, Identification des Sources *Ph.D. Thesis*, University Bordeaux I, Bordeaux, France.

Soclo, H. H., Garrigues, P., & Ewald, M. (2000). Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Marine Pollution Bulletin, 40,* 387-96.

Sprovieri, M., Feo, M. L., Prevedello, L., Manta, D. S., Sammartino, P., Tamburrino, S., & Marsella, E. (2007). Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere, 67 (5),* 998-1009

Steinhauer, M. S., & Boehm, P. D. (1992). The composition and distribution of saturated and aromatic hydrocarbons in nearshore sediments, river sediments, and coastal peat of Alaskan Beaufort Sea: implications for detecting anthropogenic hydrocarbon inputs. *Marine Environmental Research, 33*, 223-53.

Stranberg, B., Van Bavel, B., Bergqvist, P. A., Broman, D., Ishaq, R., Näf, C., Pettersen, H., & Rappe, C. (1998). Occurrence, sedimentation, and spatial variations of organochlorine contaminants in settling particulate matter and sediments in the Northern part of the Baltic Sea. *Environmental Science and Technology, 32,* 1754-1759.

Swackhamer, D., & Hites, R. A. (1988). Occurrence and bioaccumulation of organochlorine compounds in fish from Siskiwit Lake, Isle Royale, LakeSuperior. *Environmental Science & Technology, 22,* 543-8.

Tam, N. F. Y., Ke, L., Wang, X. H., & Wong, Y. S. (2001). Contamination of polycyclic aromatic hydrocarbons in surface sediment of mangrove swamps. *Environmental Pollution, 114,* 225-263.

Tanabe, S., Tatbukawa, R., Kawano, M., & Hidaka, H. (1982). Global distribution andatmospheric transport of chlorinated hydrocarbons: HCH (BHC)isomers and DDT compounds in the Western Pacific, Eastern India and Antarctic Oceans. *The Oceanographic Society of Japan, 38,* 137-48.

Tanabe, S., Iwata, H., & Tatsukawa, R. (1994). Global contamination by persistentorganochlorines and their ecotoxicological impact on marine mammals. *Science of the Total Environment, 154,* 163-77.

TCV (Environment Foundation of Turkey), (1998). *Environmental Problems of Turkey '99,* p. 464 (In Turkish).

Tolosa, I., Bayona, J. M., & Albaige´s, J. (1995). Spatial and temporal distribution, fluxes, and budgets of organochlorinated compounds in northwest mediterranean sediments. *Environmental Science and Technology, 29,* 2519-2527.

Tolosa, I., de Mora, S., Sheikholeslami, M. R., Villeneuve, J. P., Bartocci, J., & Cattini, C. (2004). Aliphatic and aromatic hydrocarbons in coastal Caspian Sea sediments. *Marine Pollution Bulletin, 48*, 44-60.

Tolosa, I., de Mora, S., Fowler, S. W., Villeneuve, J. P., Bartocci, J., & Cattini, C. (2005). Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf and the Gulf of Oman. *Marine Pollution Bulletin, 50 (12)*, 1619-1633.

Tolosa, I., Mesa-Albernas, M., & Alonso-Hernandez, C. M. (2009). Inputs and sources of hydrocarbons in sediments from Cienfuegos bay, Cuba. *Marine Pollution Bulletin, 58*, 1624-1634.

Tolun, L. G., Okay, O. S., Grains, A. F., Tolay, M., Tüfekci, H., & Kiratli, N. (2001). The pollution status and the toxicity of surface sediments in Izmit Bay (Marmara Sea), Turkey. *Environmental International, 26*, 163-168.

Uckac, S. (2004). Determination of Pysical Pocesses in the Agean Sea: Dokuz Eylül University, *PhD thesis*.

United Nations Economic Commission for Europe, (1998). Timber Committee - Meetings and Documentation.

United Nations Environment Programme, (1991). Determinations of petroleum hydrocarbons in sediments. *Reference Methods For Marine Pollution Studies*, No. 20. Monaco Cedex: IAEA, 97 pp.

United Nations Environment Programme, (2001). The Stockholm Convention on persistent organic pollutants. *United Nations Environmental Programme*;. [Internet: http://www.chem.unep.ch/sc/default.htm].

United Nations Environment Programme, (1996). *MAP Technical Reports Series*, 106, 457 p.

United Nations Environment Programme/Intergovernmental Oceanographic Commission/International Atomic Energy Agency, (1992). Determination of petroleum hydrocarbons in sediments. *Reference Methods For Marine Pollution Studies,* No. 20, UNEP, Nairobi, Kenya, 75pp.

United Nations Environment Programme/Food and Agriculture Organization/International Atomic Energy Agency/Intergovernmental Oceanographic Commission, (1991). Sampling of selected marine organisms and sample preparation for the analysis of chlorinated hydrocarbons. *Reference Methods for Marine Pollution Studies*, Ref. No.12, Revision 2. Nairobi: United Nations Environment Program 17.

United Nations Environment Programme/Intergovernmental Oceanographic Commission/International Atomic Energy Agency, (1988). Determination of DDTs and PCBs bycapillary gas chromatography and electron capture detection(ECD). *Reference Methods for Marine Pollution Studies*, No. 40.

United Nations Environment Programme/Intergovernmental Oceanographic Commission/International Atomic Energy Agency, (1995). Reagent and laboratory-ware clean-upprocedures for low-level contaminant monitoring. *ReferenceMethods for Marine Pollution Studies*, No. 65.

United Nations Environment Programme/Intergovernmental Oceanographic Commission/International Atomic Energy Agency, (1996). Sample work-up for the analysis of selectedchlorinated hydrocarbons in the marine environment. *ReferenceMethods for Marine Pollution Studies*, No. 71.

United Nations Environment Programme. (2002). Regionally based assessment of persistent toxic substances. *Mediterranean Regional Report*.

Ünlü, S., & Alpar, B. (2006). Distribution and sources of hydrocarbons in surface sediments of Gemlik Bay (Marmara Sea, Turkey). *Chemosphere, 64(5),* 764-777.

Vallack, H. W., Bakker, D. J., Brandt, I., Brorstrom-Lunden, E., Brouwer, A., & Bull, R. (1998). Controlling persistent organic pollutants-what next? *Environmental Toxicology and Pharmacology, 6(3),* 143-75.

Vassilopoulou, V., & Georgakopoulous-Gregoriades, E. (1993). Factors influencing theuptake of organochlorines in red mullet (Mullus barbatus) from a gulf of central Greece. *Marine Pollution Bulletin, 26,* 285-7.

Venkatesan, M. I. (1988). Occurrence and possible sources of perylene in marine sediments: a review. *Marine Chemistry, 25,* 1-27.

Volkman, J. K., Holdsworth, D. G., Neill, G. P., & Bavor, Jr H. J. (1992). Identification ofnatural, anthropogenic and petroleum hydrocarbons in aquatic sediments. *Science of the Total Environment, 112,* 203-19.

Voutsinou, F., Varnavas, S., Nakopoulou, C., & Moriki, A. (1997). Dissolved Trace elements in south Aegean Seawater. *Marine Pollution Bulletin*, *34(10)*, 840-843.

Voutsinou, F., & Zeri, C. (2001). Seasonal variability of dissolved trace elements at two stations of the Aegean Sea. *Rapport du Congrès de la Commission Internationale pour l'Exploration Scientifique de la Mer Méditerranée, 36*, 172.

Wade, T. L., Atlas, E. L., Brooks, J. E., Garcia-Roero, B., & Defreitas, D. A. (1988). Gulf of Mexico status and trends programme: trace organic contaminationdistribution in sediments and oysters. *Estuaries, 11*, 1171-9.

Wade, T. L., Jackson, T. J., Sericano, J. L.,Wong, J. M., Brooks, J. M., Summers, J., & Macauley, J. M. (1995). Gulf coast sediments organic contaminant distribution: results from EPA EMAPNC program. Long Beach Convention Center. *Long Beach California*, *vol. 22-24*, p.1993.

Wakeham, S. G. (1996). Aliphatic and polycyclic hydrocarbons in Black Sea sediments. *Marine Chemistry, 53*, 187-205.

Wang, Z. D., Fingas, M., & Page, D. S. (1999). Oil spill identification. *Journal of Chromatography A, 843(1-2)*, 369-411.

Wang, X. C., Sun, S., Ma, H. Q., & Liu, Y. (2006). Sources and distribution of aliphatic and polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Marine Pollution Bulletin, 52*, 129-38.

Wania, F., & Mackay, D. (1993). Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. *Ambio, 22(1)*, 10-8.

Ware, G. W. (1986). Fundamentals of Pesticides, *A Self-Instruction Guide* (2nd ed.). Thomson Publications, USA.

Webster, L., Fryer, R. J., Dalgarno, E. J., Megginson, C., & Moffat, C. F. (2001). The polycyclic aromatic hydrocarbon and geochemical biomarker composition of sediments from voes and coastal areas in the Shetland and Orkney Islands. *Journal of Environmental Monitoring, 3*, 591-601.

Woodwell, G. M., Craig, P. O., & Horton, A. J. (1971). DDT in the biosphere: where does it go?, *Science, 174*, 1101-1107.

Wright, D. A. (2001). Petroleum Hydrocarbons. In: P.G.C. Campbell, R.M. Harrison, S.J. de Mora (Eds),. Cambridge University Press, Port Chester, NY, *Environmental Toxicology*, 381-384.

Wu, Y., Zhang, J., & Zhou, Q. (1999). Persistent organochlorine residues in sediments from Chinese river/estuary systems. *Environmental Pollution, 105*, 143-50.

Yaşar, D. (1994). Late glacial-holocene evolution of the Aegean Sea. Izmir: Dokuz Eylül University, *PhD thesis*.

Zeri, C., Voutsinou, F., Romanov, A. S., Ovsjany, E., & Moriki, A. (2000). A Comparative approach of dissolved trace element exchange in two interconnnected basins: Black Sea and Aegean Sea. *Marine Pollution Bulletin, 40(8)*, 666-673.

Zhang, G., Min, Y. S., Mai, B. X., Sheng Gy, Fu J. M., & Wang, Z. S. (1999). Time trend of BHCs and DDTs in a sedimentary core in Macao estuary, Southern China. *Marine Pollution Bulletin, 39(1-12)*, 326-30.