DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

LEVELS OF ORGANIC CONTAMINATION IN BLUE CRAB AND EDIBLE FISH FROM THE AEGEAN AND EASTERN MEDITERRANEAN COAST

by
Serkan TEKİN

September, 2015
İZMİR

LEVELS OF ORGANIC CONTAMINATION IN BLUE CRAB AND EDIBLE FISH FROM THE AEGEAN AND EASTERN MEDITERRANEAN COAST

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by

Serkan TEKİN

September, 2015
İZMİR

M.Sc THESIS EXAMINATION RESULT FORM

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LEVELS OF ORGANIC CONTAMINATION IN BLUE CRAB AND EDIBLE FISH FROM THE AEGEAN AND EASTERN MEDITERRANEAN COASTS

ABSTRACT

The thesis represents the first detailed study of the contamination levels of OCPs and PCBs in fish and crabs from the Aegean and Mediterranean coast of Turkey. Analysis of biota samples showed that the maximum concentration of ΣOCPs (33.2 ng g^{-1} dry weight (dw)) was found in gray mullet samples collected from Antalya due to dense agricultural activities in the surroundings of Beymelek Lagoon. The minimum consecentration of ΣOCPs (0.87 ng g^{-1} dw) was found in male blue crab samples collected from Göksu Delta in Mersin. The contamination levels of OCPs and PCBs in biota samples are low as compared to the different areas in the world. The contamination levels of ΣPCB and ΣDDT in sea food samples ranging from 43-226 and 0.6-20.2 ngg^{-1} dw respectively. Although the highest ΣDDTs concentration was found in gray mullet, lowest concentration was found in male blue crab samples in Mersin. DDD/DDE ratios in biota samples were lower than 1, due to aerobic conditions. The highest concentration of ΣPCBs (226 ng g^{-1} dw) was found in sea bream samples collected in Dalyan. The minimum concentration of ΣPCBs was found in sea bream samples in Antalya (43 ng g^{-1} dw). In this study, health risk assesments were analyzed about OCPs and PCBs due to consumed sea food. The estimated daily intake deriving from the estimated daily fish consumption in Turkey is very much below the Acceptable Daily Intake. This represents a good indication for Turkish fish consumers. Concentrations of ΣDDT and ΣPCB in sea food lower than the Maxiumum Residue Limit established by the U.S Food and Drug Administration. According to average PCBs levels in samples four fish meals (average fish meal size 0.227 kg) per month for sea bream and gray mullet based on the cancer health endpoint can safely be consumed. However eight crab meals per month can safely be consumed. Environmental Protection Agency recommends using the more conservative of the two limits, for PCBs, this is the consumption limit based on the cancer endpoint.

Keywords: Pesticide, blue crab, sea bream, gray mullet, Eastern Mediterranean, Aegean coast

EGE VE DOĞU AKDENİZ KIYILARINDAKİ MAVİ YENGEÇ VE YENEBİLİR BALIK TÜRLERİNDE PESTİSİT SEVİYELERİ

ÖZ

Bu tez, Akdeniz ve Ege kıyılarındaki balık ve mavi yengeçlerin OCP ve PCB kontaminasyon düzeylerini gösteren ilk detaylı çalışmayı sunmaktadır. Biyota örneklerinin analizi sonucu maksimum ΣOCP (33.2 ng g^{-1} kuru ağırlık) konsantrasyonu, tarımsal aktivitelerin yoğun olduğu Antalya Beymelek Lagünü çevresindeki toplanan kefal örneklerinde bulunmuştur. Minimum ΣOCP (0.87 ng g^{-1} kuru ağırlık) konsantrasyonu Mersin Göksu Deltasından toplanan erkek mavi yengeç örneklerinde bulunmuştur. Dünyadaki farklı bölgelerle kıyaslanan biyota örneklerinin OCP ve PCB kontaminasyonu daha azdır. Deniz ürünleri örneklerindeki ΣPCB ve ΣDDT kontaminasyon miktarları, yaş ağırlık üzerinden sırasıyla 43-226 ng g^{-1} ve 0.6-20.2 ng g^{-1}'dır. En yüksek ΣDDT derişimi kefalde bulunmasına rağmen, en düşük derişim Mersin'deki erkek mavi yengeç örneklerinde bulunmuştur. Aerobik koşullar nedeniyle, biyota örneklerindeki DDD/DDE oranı 1'den düşük çıkmıştır. En yüksek ΣPCB derişimi (226 ng g^{-1} kuru ağırlık) Dalyan'dan toplanan çipura örneklerinde bulunmuştur. Bu çalışmada, tüketilen deniz gıdalarının sağlık açısından riskleri OCP ve PCB'ler bakımından analiz edilmiştir. Türkiye'deki tahmini günlük balık tüketimi esas alınarak hesaplanan kirletici seviyeleri kabul edilebilir günlük alım miktarının çok altındadır. Bu sonuç, Türk balık tüketicileri için iyi bir bulgu sunmaktadır. Deniz ürünlerindeki ΣDDT ve ΣPCB derişimleri, Birleşmiş Milletler Gıda ve İlaç İdaresinin Maksimum Kalıntı Limitinin altında kalmaktadır. Kanser riskinin oluşmaması adına aylık dört porsiyon çipura ve kefal (ortalama balık büyüklüğü 0,227 kg) güvenle tüketilebilir. Aynı şekilde, ayda 8 porsiyon mavi yengeç de güvenle tüketilebilir. Çevre Koruma Ajansı PCB'ler için verilen bu iki limitten daha koruyucu olması bakımından kanser oluşmama riskine göre hesaplanan tüketim limitini kullanmayı tavsiye etmektedir.

Anahtar kelimeler: Pestisit, mavi yengeç, çipura, kefal, Ege Denizi kıyıları, Doğu Akdeniz

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CHAPTER ONE
INTRODUCTION

Organochlorinated pesticides (e.g., aldrin, DDTs, dieldrin, endrin, heptachlor, HCB, lindane) and polychlorinated biphenyls (PCBs) have been recognized as persistent organic compounds (POPs). As such, they have adverse effects on humans and on ecosystems, according to the Stockholm Convention of 2009 (Stockholm convention on persistent organic pollutants, 2009). The aquatic ecosystems have been contaminated by POPs and major transport pathways of POPs are river discharges, ocean currents, atmospheric deposition and aerosols. POPs are compounds that, to a varying degree, are long-lasting in the marine environment, have the ability to bioaccumulate in fatty tissues and potentially damage the marine resources (Albaigés, 2005).

Organochlorinated compounds have had widespread use. Both industrial and agricultural sources have contributed significant amounts to the environment through leakage, disposal and evaporation (Tolosa et al., 2010). Thus there has been extensive POPs due to their high toxicity, persistence, bioaccumulation, and biomagnification in the environment (Zhang et al., 2002; Wan et al., 2005). In the northern hemisphere environmental levels of POPs, pesticides and technical chemicals generally declined in the 1970s and levelled off in the 1980s because of bans in the industrialised world. However, substantial export of banned persistent pesticides to developing countries continued at least until 1999 (Smith, 2001).

Biota, that provides relevant information on impacts of pollutans, defines ecological status of aquatic systems. In addition, biota is considered to assess of anthropogenic impacts in coastal regions. Fish are the most suitable indicators for the burden of aquatic pollution monitoring since they concentrate pollutants in their tissues and enabling the assessment of transfer of pollutants through the trophic web (Fisk et al., 2001; Boon et al., 2002). Thus, bioaccumulation of pollutants can be considered as an index of environmental pollutants in the aquatic bodies.

Taking into account that the Mediterranean is oligotrophic and the areas of higher productivity are generally those around outfalls, the concurrence of higher levels of pollutants in these areas could have general and long-term consequences on the ecosystem (Albaigés, 2005). It is known that POPs as a potential threat for the Mediterranean, a fragile ecosystem.

Information on levels of POPs in the different biotic (e.g. bivalves, fish, marine mammals and sea birds) and abiotic compartments (e.g.air, seawater and sediments) in Turkey coasts are scarcely. This study investigated the levels of OCPs and PCBs in edible fish species and blue crabs from the Eastern Mediterranean coasts. The levels of heavy metals in commercial and edible fish species from the Turkey coasts have been widely investigated in order to check human health hazards (Küçüksezgin et al., 2002; Küçüksezgin et al., 2006). However, there were limited study about both PCB and pesticide residues in fish and blue crab for the study area (Çalışkan & Yerli, 1999).

The main objectives of this thesis are;

1. To investigate levels of OCPs, PCBs, in different biota samples; blue crab *(Callinectes sapidus)*, sea bream (*Sparus aurata)* and gray mullet,

2. To asses the contamination degree of different coastal areas in the Dalyan, Fethiye, Antalya (Beymelek L.), Adana (Karataş L.), Mersin (Taşucu), İskenderun,

3. To compare OCPs and PCBs concentrations in muscle tissue with different regions of the world,

4. To compare the levels of POPs with recommended limits of POPs concentrations in sea food, suggested by different authorities,

5. To analyze health risk assesments about OCPs and PCBs due to consumed sea food.

CHAPTER TWO
ORGANIC POLLUTANTS

2.1 The Current Status Of POPs Use

POPs are mainly aromatic compounds with extreme high toxicity and received high publicity for their toxic characteristics because they are:

- Highly toxic to humans and environment
- Persistent in the environment, resisting biodegradation
- Taken up and bioaccumulated in terrestrial and aquatic ecosystems and capable of long-range transboundary atmospheric transport and deposition.

The Stockholm Convention on POPs was adopted by 125 countries including Turkey, on 22 and 23 May 2001 with the objective of protecting human health and environment, focusing one liminating or reducing releases of 12 POPs, the "Dirty Dozen". These 12 chemicals include aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, and toxaphene used principally as pesticides, two industrial chemicals PCBs and hexachlorobenzene (HCB) used in industry but also produced unintentionally together with dioxins and furans.

At its fourth meeting held from 4 to 8 May 2009, the Conference of the Parties adopted amendments to the Stockholm Convention to list nine new POPs (e.g. lindane).

In Turkey, on 15 January 2004, the POPs project started and the main objective of this project was to prepare inventories by the responsible authorities that would agree upon the information and experience gathered national environmental priorities evolve. Turkey has prepared National Implementation Plan (NIP) in 2005 and ratification process is underway. According to the first evaluation, Turkey has 10,930 kg of DDT and 2,700 kg of HCB in stocks (Dağlı, 2008).

PCBs have been used as insulators in almost every transformer for years in Turkey. The numbers of transformers are about 250,000 in Turkey and only 10% of these were examined yet. According to preliminary studies, country has 1,972 capacitor and 254 transformers contain PCB. Some of these products and equipments are exported to European Countries for destruction and very little of these are being destructed by Turkish Waste Incinerator Company Izaydas. According to first PCB analysis results in waste soils and treatment plant sludges, PCB levels in soils and treatment sludges are lower than 0.01 ppm. The most important POPs (dioxins and furans) introduced to air are discharged from ferrous and nonferrous metal production, production of mineral products, waste incineration, and power generation plants (Dağlı, 2008).

2.2 Pesticides

Pesticides are natural or synthetic agents that are used to kill unwanted plant or animal pests. While the term pesticide is now often associated with synthetic chemical compounds, it was not until relatively recently that synthetic pesticides came into use (What are pesticides?, n.d).

2.3 Definition and Classification of Pesticides

Synthetic pesticides are classified based on various ways depending on the needs. However, there are three most popular ways of classifying pesticides ; based on the mode of action, the targeted pestspecies and the chemical composition of the pesticide (Drum, 1980).

According to chemical classification, pesticides are classified into four main groups namely; organochlorines, organophosphorous, carbamates and pyrethrin and pyrethroids (Buchel, 1983).

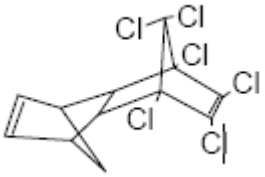
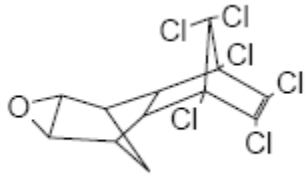
2.3.1 Organochlorines Pesticides

Organochlorines pesticides are organic compounds with five or more chlorine atoms. Organochlorines were the first synthetic organic pesticides to be used in agriculture and in public health. Most of them were widely used as insecticides for the control of a wide range of insects and they have a long-term residual effect in the environment since they are resistant to most chemical and microbial degradations. Organochlorine insecticides act as nervous system disruptors leading to convulsions and paralysis of the insect and its eventual death. Some of the commonly used representative examples of organochlorine pesticides are DDT, lindane, endosulfan, aldrin, dieldrin and chlordane and their chemical structures are presented here under (Zacharia, 2011).

2.3.1.1 Aldrin

Aldrin is an insecticide that enters the insect's body (and in the environment) and quickly converts to dieldrin. It is harmful and it is a persistent environmental contaminant. Aldrin and dieldrin are the common names of two structurally similar compounds that were once used as insecticides (Table 2.1).

Table 2.1 Chemical identity of aldrin and dieldrin (Gilbert, 2014)

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	C12H8Cl6	C12H8Cl6O
Chemical structured		

Aldrin can enter the body dermally, through the lungs when inhaled, or by ingesting contaminated dirt or food. Once aldrin is ingested it is converted in by the body into dieldrin which is then stored in fat throughout the body. The body metabolizes the stored dieldrin slowly, excreting it mainly through feces though this process can take years to totally rid the body of the insecticides (Gilbert, 2014).

Aldrin was used extensively from the 1950s to the early 1970s on crops such as corn an cotton and later used, until 1987, against termites. Aldrin has been seen to cause severe health problems when ingested or inhaled in a significant quantity. Nervous system affects, including convulsions, headaches, irritability and nausea are witnessed in many people with extreme exposure to the insecticides. Research on additional health problems related to aldrin is sparse. A few cancer registries have stated that there is not enough evidence to list aldrin as a carcinogen (Gilbert, 2014).

2.3.1.2 Hexachlorobenzene (HCB)

Hexachlorobenzene (HCB) is a fully chlorinated industrial hydrocarbon chemical. It is insoluble in water, but is very soluble in fat, oils, and organic solvents. HCB is one of the most POPs and bioaccumulates in the environment, in animals, and in humans. It is not currently manufactured as a commercial product in the United States and virtually all commercial production ended in the late 1970s. However some HCB is produced as a by product or impurity in the manufacture of chlorinated solvents and other chlorinated compounds, including several pesticides currently in use (pentachloronitrobenzene, chlorothalonil, dacthal, picloram, pentachlorophenol, atrazine, simazine, and lindane). It is estimated that 3,500-11,500 kg of hexachlorobenzene were in advertently produced in the manufacture of chlorinated solvents in 1984. There are current commercial uses of HCB in the United States, Although HCB was used as a fungicide on these eds of onions, sorghum, wheat, and other grains until 1984, when its registration as a pesticide was voluntarily canceled (ATSDR ToxFAQs, 2002). Due to HCB's persistence in the environment, it has been banned globally under the Stockholm Convention.

Although HCB is no longer directly used, it is still found in our environment as a by-product of certain activities and because of past use. HCB is a white crystalline solid which is not very soluble in water. The odor threshold for HCB is not available. The chemical formula for HCB is C6Cl6, and the molecular weight is 284. 8 g/mol.

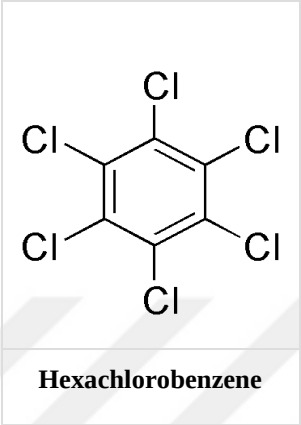


Figure 2.1 Chemical structure of HCB (Hexachlorobenzene, 2015)

HCB can enter your body when you eat food contaminated with it, when you breathe particles of it in the air or when it gets on your skin. After it enters your body, it rapidly spreads through your blood to many tissues in the body, especially to fat. This probably happens within a few hours. Based on the results of a survey of this substance in people's tissues, it will remain in your body, especially in fat, foryears. A large portion of HCB in the fat of a mother can be transferred to her baby in breast milk (ATSDR, 2002).

HCB is listed as a "possible carcinogen" by the IARC (International Agency for Research on Cancer). On the U.S. National Toxicology Program's (NTP) Carcinogen List, it is ranked as "Reasonably Anticipated to Be a Carcinogen" and the U.S. EPA lists it as a "probable carcinogen".

HCB tends to remain in the environment for a long time. If it is released to the soil, it has a half-life of 3-6 years. If it is released to surface waters such as lakes, rivers and streams, the half-life is 2.7-5.7 years, and if it is released to groundwater, the half-life is 5.3-11.4 years. Since HCB does not dissolve in water very well, most

of it will remain in particles on the bottom of lakes, rivers, or streams. The evaporation of HCB into the air is not significant under ordinary conditions. Once in the air, it can be carried over wide geographic areas. Its half-life in air ranges from 0.63 to 6.28 years (ATSDR, 2002).

2.3.1.3 Dieldrin

Dieldrin is an organochlorine insecticide that is structurally very similar to aldrin. Aldrin quickly breaks down into dieldrin once it enters the atmosphere. It is a persistent environmental contaminant and was once found in most watersheds, soil, and animal fat, though detection levels have decreased since its cancellation in 1974 in the U.S. Pure dieldrin is a white powder with a mild odor, and technical-grade dieldrin is a tan powder. Neither are readily soluble in water.

Dieldrin is readily absorbed by inhalation, ingestion or the skin. Once it is in the body, the majority is metabolized and excreted in the feces, and the rest is stored in fat cells. It can take many weeks or years for all the dieldrin to leave one's body, assuming additional exposures do not ocur.

Dieldrin was used extensively from the 1950s to 1970 as an insecticide on corn and cotton. The USDA canceled its use in 1974 for all purposes except for controlling termite populations (ATSDR, 2002). The manufacturer voluntarily canceled its use in 1987.

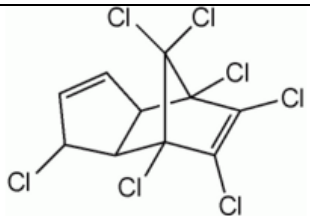
People exposed to large amounts of dieldrin, by any route of exposure, have been seen to experience convulsions and death. Chronic exposure to low to moderate levels of dieldrin has been shown to cause headaches, dizziness, irritability, vomiting and uncontrolled muscle movements. Workers removed from the source of exposure rapidly recovered from most of these effects (ATSDR ToxFAQs, 2002).

2.3.1.4 Heptachlor

Heptachlor is a non sytemic stomach and contact organochlorine insecticide first synthesized in 1946 and banned in 1988 (ATSDR, 2002). It was used extensively in the 1960s and 1970s in household and agricultural settings (Table 2.2). Studies link heptachlor to cancer, endocrine disruption and developmental toxicity, but the full extent of heptachlor's health effects are currently unknown. Heptachlor is extremely persistent and is found throughout the United States nearly twenty years after its cancellation. Heptachlor is readily converted to more potent heptachlorepoxide once it enters the environment or the body (Extension toxicology network, pesticide information profile heptachlor, 1996).

Heptachlor is an insecticide used heavily in the 1960s and 1970s in household and agricultural settings (Caudle et al., 2005). It was used extensively to control termites and pests on corn crops. Heptachlor's use was canceled in 1988, though it is still registered for use to kill fire ants in power transformers and in underground cable television and telephonecable boxes (ATSDR, 2002).

Table 2.2 Chemical identity of heptachlor (Heptachlor, n.d)

Characteristic	**Heptaclor**
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
Chemical formula	C10H5Cl7
Chemical structured	

Heptachlor can enter the body through absorption from contaminated soil, from eating or drinking contaminated products, and through inhalation by breathing air contaminated with heptachlor (ATSDR, 2002). Nursing mothers also can pass heptachlor on to their children.

Heptachlor and heptachlor epoxide are readily stored in fatty, liver and kidney tissues in mammals. Heptachlor also passes the placenta and is found in breastmilk (Extension toxicology network, pesticide information profile heptachlor , June 1996). The results of the animal studies are a serious enough concern for the EPA to list haptachlor as a probable cancer-causing agent (ATSDR, 2002).

Heptachlor and heptachlor epoxide are both highly persistent in the environment, with a half-life of around 250 days depending on the soil type. Both bond strongly to soil and tend not to leach into groundwater (ATSDR, 2002 & Extension toxicology network, pesticide information profile heptachlor, 1996). Heptachlor is practically insoluble in water (heptachlor epoxide is more soluble) and neither heptachlor nor heptachlor epoxide readily evaporate from water. Additionally, heptachlor, because of its high use and its ability to bond to soil, was often unintentionally carried away by the wind (ATSDR, 2002).

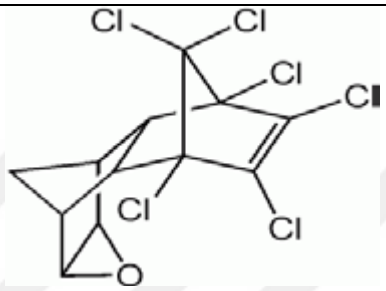
2.3.1.5 Endrin

Endrin is an organochlorine insecticide and rodenticide most commonly used on cotton, maize and sugarcane (Table 2.3). Endrin, a white, odorless substance, is lethal if ingested in large quantities, and has been outlawed in the United States since 1986 (Mergel, 2009).

Endrin released to soils will persist for extremely long periods of time (up to 14 yr or more) (Technical Factsheet on: Endrin, n.d).

Endrin and its metabolic products pass through the body in a few days, although studies suggest that some small amounts of endrin remain in thebody's fatty tissues if exposure to the substance is high (Mergel, 2009).

Table 2.3 Chemical identity of endrin (Endrin, n.d.)

Characteristic	**Endrin**
Synonyms	Octachloro-4,7-methanohydroindane
Chemical formula	C12H8Cl6O
Chemical structured	

Swallowing large amounts of endrin can cause convulsions and lead to death within a few minutes or hours. Less serious exposure to endrin can result in headaches, dizziness, confusion, nervousness, nausea or vomiting. Long term effects have not been noted in laborers who have been exposed to endrin through inhalation or dermal contact (ToxFAQs, 2007).

The EPA does not classify endrin as a carcinogen. Endrin has been found at low levels in surface and groundwater, although exposure to endrin through drinking water is very low. Endrin does not break down easily within water, and can accumulate in the tissues of aquatic organisms. Endrin can be transmitted to nursing babies through contaminated breast milk (ToxFAQs, 2007).

2.3.1.6 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%),

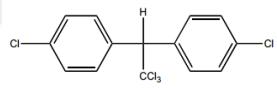
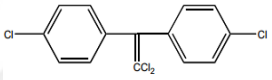
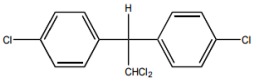
and o,o'-DDT (trace amounts). All of these are white, crystalline, tasteless and almost od or less solids. Technical grade DDT may also contain DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene) and DDD (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane) as contaminants. DDD was also used to kill pests, but 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.

Large amounts of DDT were released into the air and on soil or water when it was sprayed on crops and forests to control insects. DDT was also sprayed in the environment to control mosquitos. The half-life of these chemicals in the atmosphere as vapors (the time it takes for one-half of the chemical to turn into something else) has been calculated to be approximately 1.5-3 days.

However, in reality, this half-life estimate is too short to account for the ability of DDT, DDE and DDD to be carried long distances in the atmosphere. DDT, DDE and DDD last in the soil for a very long time, potentially for hundreds of years. Most DDT breaks down slowly into DDE and DDD, generally by the action of microorganisms. These chemicals may also evaporate into the air and be deposited in other places. They stick strongly to soil and therefore generally remain in the surface layers of soil. Some soil particles with attached DDT, DDE or DDD may get into rivers and lakes in runoff. DDT initially present usually disappears in about 5 years. However, in some cases, half life of the DDT initially present will remain for 20, 30 or more years (Table 2.4).

In surface water, DDT will bind to particles in the water, setle and be deposited in the sediment. DDT is taken up by small organisms and fish in the water. It accumulates to high levels in fish and marine mammals (such as seals and whales), reaching levels many thousands of times higher than in water. In these animals, the highest levels of DDT are found in their adipose tissue. DDT in soil can also be absorbed by some plants and by the animals or people who eat those crops.

Table 2.4 Chemical identity of *p,p*'-DDT, *p,p*'-DDE and *p,p*'-DDD (Toxicological profile for DDT, DDE and DDD, 2002)

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; dichlorodiphenyltrichloroethane; 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	C14H9Cl5	C14H8Cl4	C14H10Cl4
Chemical structure			

Studies in animals have shown that oral exposure to DDT can cause liver cancer. Studies of DDT-exposed workers did not show increases in deaths or cancers. Based on all of the evidence available, the Department of Health and Human Services has determined that DDT is reasonably anticipated to be a human carcinogen. Similarly, the International Agency for Research on Cancer (IARC) has determined that DDT is possibly carcinogenic to humans. EPA has determined that DDT, DDE and DDD are probable human carcinogens (ATSDR, 2002).

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, stillused 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.

2.4 Pesticide Toxicity

Pesticide applicators should understand the hazards and risks associated with the pesticides they use. Pesticides vary greatly in toxicity. Toxicity depends on the chemical and physical properties of a substance, and may be defined as the quality of being poisonous or harmful to animals or plants. Poisons have many different modes of action, but in general cause biochemical changes which interfere with normal body functions.

The toxicity of any compound is related to the dose. A highly toxic substance causes severe symptoms of poisoning with small doses. A substance with a low toxicity generally requires large doses to produce mild symptoms. Even common substances like coffee or salt become poisons if large amounts are consumed.

Toxicity can be either acute or chronic. Acute toxicity is the ability of a substance to cause harmful effects which develop rapidly following absorption, i.e. a few hours or a day. Chronic toxicity is the ability of a substance to cause adverse health effects resulting from long-term exposure to a substance (Pesticide wise, toxicity & hazard n.d).

2.5 Pesticide Movement and Degradation in Environment Movement and Degradation Mechanisms

Pesticides enter the atmosphere either by application drift, post-application vapour losses or wind erosion of pesticide treated soil. They and their photo degradation products may be transported long distances before the removal processes of atmospheric wet and dry deposition return them to the earth's surface (Cessna et al., 2005; Cessna et al., 2006)

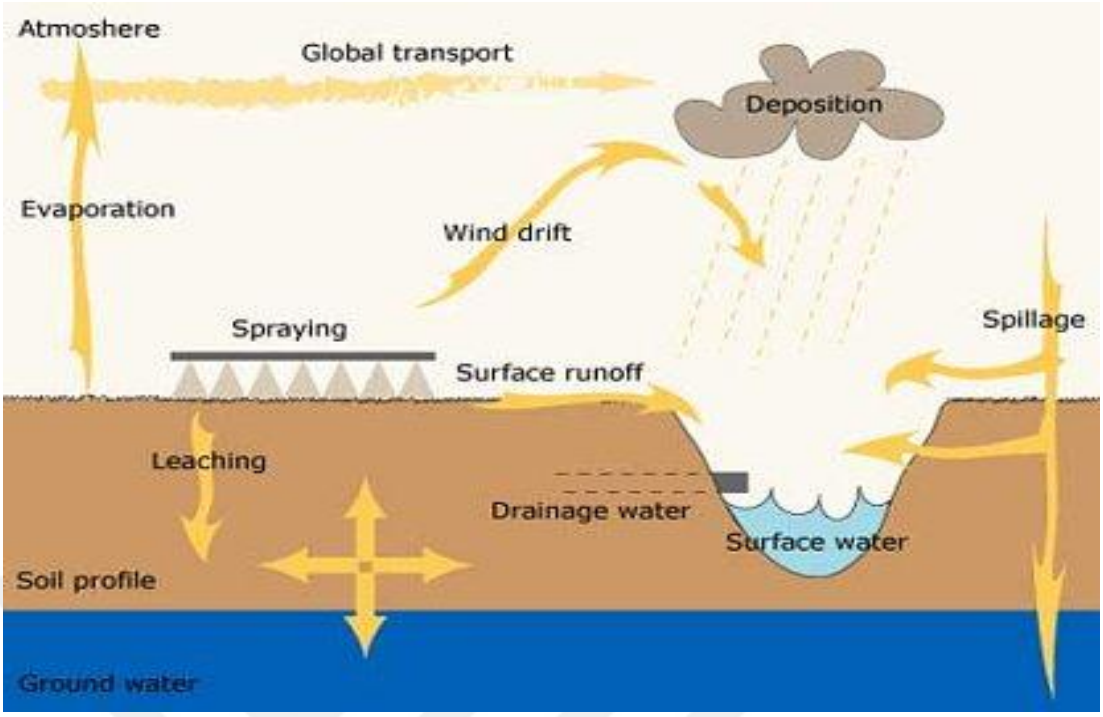


Figure 2.2 Pathways of pesticide into aquatic system (Information about pesticides in the environment pathways of pesticide spread in the environment , 2015).

2.6 Polychlorinated Biphenyls (PCBs)

PCBs comprise a class of 209 individual compounds. The chemical structure and the numbering of the C-atoms are shown in Figure 1.

The two main sources of PCBs are:

- Commercial production, and
- by-product in combustion processes as thermodynamically stable compound.

PCBs are produced by chlorination of biphenyl; its commercial production started about 60 years ago. The total amount produced world-wide is estimated at 1.5 million tons (Ivanov & Sandell, 1992; Rantanen, 1992)

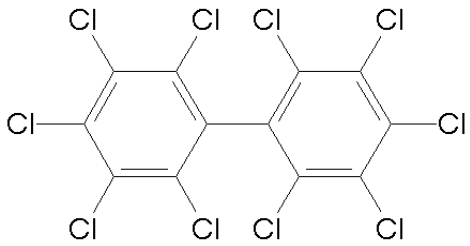


Figure 2.3 Structure and numbering for PCBs (Fiedler, n.d)

Depending on the degree of chlorination of the PCBs, their physico-chemical properties, like inflammability or electric conductivity, brought about a wide field of application. Thus, PCBs have been used as electric fluids in transformers and capacitors, as pesticide extenders, adhesives, dedusting agents, cutting oils, flame retardants, heat transfer fluids, hydraulic lubricants, sealants, paints, and in carbonless copy paper. Some of their applications resulted in a direct or indirect release of PCBs into the environment. Relatively large amounts were released due to inappropriate disposal practices, accidents and leakages from industrial facilities.

Reports on the occurrence of PCBs in fish, mussels, seals, sea birds and birds of prey first appeared in 1966, and in 1967, PCBs were detected in human adipose tissue, albeit in low concentrations. In 1968, PCBs from a leaking cooling system contaminated a rice oil tank at a food factory in Japan. As a result of the consumption of the contaminated rice oil which had reached the stores, 1,000 people fell ill with a disease subsequently known world-wide as Yusho Disease.

Substances of low biological degradability tend to accumulate throughout trophic levels of the food net. For example, concentrations of total PCB increases with the trophic level. Only concentrations of PCBs in sediments are higher than levels in the subsequent trophic levels In all cases an exchange between trophic levels (sediment→algae→plankton→planktivores→piscivorousfish→piscivorousbirds) resulted in an increase of total PCB concentration called biomagnification (Fiedler et al., 1994).

Chlorinated hydrocarbons (CHC), such as the pesticides chlordane and toxaphene (polychlorinated camphenes, PCC), hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and DDT, and industrial chemicals, such as PCBs have been identified in air, snow, ocean water and biota in the marine ecosystem. The presence of persistent polychlorinated compounds in remote areas such as the Arctic and the Antarctic has been reported. PCB, PCDD/PCDF, HCH and HCB were found in marine organisms such as seal blubber and pinniped milk as well as in lake and sea sediments. The occurrence of mainly man-made organochlorines in regions far away from industrialised and densely populated areas indicates that atmospheric transport is an important route to disperse these compounds.

In the Aroclor series, a 4-digit code is used. Most are given a numerical designation beginning with 12 (in the first two positions) for 12 carbon atoms and ending with two digits expressing the percentage by weight of chlorine in the mixture. Aroclor 1254 is 54% chlorine by weight and averages five chlorine per molecule. Aroclor 1260 contain 60% chlorine by weight, with six chlorine per biphenyl molecule. In this study, Aroclor 1254 and 1260 were detected all biota samples.

Due to their world wide distribution, persistence in the environment, and their possible health effects, PCBs have attracted great concern over the past years. Their ability to bioaccumulate in fatty tissues and their lipophilic behavior, pose a serious threat to mammalian systems (Brunner et al., 1985). PCBs can enter the body through skin contact, by the inhalation of vapors or by ingestion of food containing PCB residues. PCBs are not particularly toxic in acute or short-term chronic testing. High dosages are necessary to induce a lethal response in most trophic levels.

Chronic exposure to sublethal concentrations combined with high lipid solubility and resistance to metabolism can result in PCB accumulation and a toxic response (Exner, 1982). PCBs can be toxic to higher plants, marine biota and birds. PCBs may interfere with the overall growth of some plant species, by inhibiting cell division,

and also disturb photosynthesis in some plants. PCBs can induce mixed function oxidase (MFO) enzymes and can inhibit ATPases in marine biota. PCBs are known to effect hormones in fish and in birds, they can cause teratogenic and behavioral effects (Waid, 1986). PCBs can also be toxic to some microorganisms, including the fresh-water, marine and soil microorganisms (WHO, 1993).

Because PCBs are water insoluble and resistant to chemical decomposition and biodegradation, these compounds persist in the environment. PCBs pose a serious health hazard due to the potential for long-term toxic effects (Das, 1998).

2.7 Pesticide and PCB Usage in 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 1980s (Tablo 2.5). 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).

Table 2.5 Pesticides banned years in Turkey (ÇOB, 2008)

Pesticides	**Banned Years**
Dieldrin	1971
Aldrin	1979
Endrin	1979
Lindane	1979
Heptachlor	1979
HCB	1982
DDT	1985

According to "Ziraî Mücadelede Kullanılan Pestisit ve Benzeri Maddelerin Ruhsatlandırılması Hakkında Yönetmelik Resmi Gazete: 17 Şubat 1999 no:23614" insecticides can include only 1ppb POPs (aldrin, chlordane, dieldrin, DDT, endrin, % 0-99.0 γ izomer içeren HCH, heptachlor, heksachlorohekzan) (ÇOB, 2008). However, derivates of DDT, including DDE, DDD have been detected in surface

waters, in sediments and as suspended solids more than 25 years after DDT was prohibited (e.g., Chan et al., 1994 ; Barlas, 1999; Hung & Thiemann, 2002).

PCBs are introduced into the environment through human activities. In particular, they are derived from the discharged waste of some chemical and electrical industries (Connell et al., 1998; Haynes & Johnson, 2000). Although the use of PCBs was banned in Turkey in 1996, the import of PCBs continued illegally until the 2000s.

CHAPTER THREE
STUDY AREA

3.1 Study Area

Fish and blue crab samples were collected in Dalyan, Fethiye, Beymelek Lagun (Antalya), İskenderun, Göksu Delta (Taşucu), Karataş Lagun (Adana) in 2013 (Figure 3.1).



Figure 3.1 Sampling locations (A: Dalyan, B: Fethiye, C:Beymelek Lagun (Antalya) D: Göksu Delta (Taşucu) E: Karataş Lagun (Adana) F: İskenderun

3.1.1 Dalyan

Dalyan is a town in Muğla Province located between the well-known districts of Marmaris and Fethiye on the south-west coast of Turkey (Dalyan, n.d). Dalyan means "fishing weir" in Turkish. Bass, mullet and sea bream swim upstream from the sea to Köyceğiz Lake where another large town of the region, Köyceğiz, is located. The fish spawn there, and when returning to the sea they are caught in the dalyans (Dalyan, n.d). The surface area of the Lagoon which is 5500 ha, take place agricultural areas and small settlements. Köycegiz Lagoon System is rich in terms of biological resources. In this region the most important economic activities are tourism and fisheries. Over the last decades the aquatic ecosystems in the region have been contaminated by persistent pollutants of agricultural and industrial origin. OCPs were the first synthetic organic pesticides that were used in agriculture (Çalıskan & Yerli, 2000). The Dalyan River, outflow channel of the estuary to the

sea, follows a meandering bed that widens into a labyrinth-like channel system discharging into the Mediterranean Sea at Dalyanagzi (Kazanci et al., 1992) The entire Delta is a protected National Conservation area and is home to over 100 species of birds along with no less than three varieties of turtle, including the Loggerhead Caretta Caretta (Dalyan guide, n.d).

3.1.2 Fethiye

Fethiye harbor located between 36° 37′- 36° 39′ N and 29° 05′- 29° 08′ E and covers an area of 9 km^2 .In the south west coast of Turkey. In the harbour city effluence and effluents from mineral deposits in the environment as a results of heavy metal accumulation. Fethiye is a semi enclosed sea; water circulation is limited among the factors that increase pollution (Yılgör & Avcı, 2004).

Natural and historical charms of Fethiye Gulf attract domestic and foreign tourists. Besides, fertile plain in the region makes Fethiye an unique center in terms of agricultural activities. Water depth in gulf varies greatly. In eastern part of the gulf, the depths are quite shallow; however, in the middle parts the depth rises to 20 m. Fethiye Gulf is the natura discharge point of Susambeleni, Uzumlu, Eldirek, Kosebuku, Iplikci, and Murt streams. Irregular flow conditions of those streams which run disorderly in the plain and cause floods from time to time were overcomed by stream reclamation plans by DSI (State Hydraulic Works). The climate of the region is typical Mediterranean climate with hot summers and mild and rainy winters (Koç, 2012).

3.1.3 Antalya (Beymelek Lagoon)

Beymelek Lagoon (36°15′39″–36°16′32″N, 30°02′26″–30°04′10″E) is located in the Western Mediterranean Coast of Turkey. Beymelek Lagoon has a great importance for fisheries activities. The economically important fish species migrated to the Beymelek Lagoon for the purpose of feeding are caught at the end of dens feeding period. The sea bass and bream culture station of The Mediterranean

Fisheries Research, Production and Education Institute is also here. On the other hand, because of its proper climate, dense agricultural activities in the surroundings of this lagoon have been done and a lot of fertilizers and pesticides has been used. This region is also an important touristic area. It is likely that some heavy metals result from agricultural reasons as well as other anthropogenic activities that accumulate in fish in this lagoon (Uysal, Emre & Köse, 2008).

3.1.4 Adana (Karataş, Akyatan Lagoon)

Akyatan is the biggest fisheries lagoon located in the Iskenderun Bay, Mediterranean coast of Turkey. Akyatan lagoon habitats may be influenced by a number of pollution sources. Besides domestic wastes, for example lagoons may face serious threats from agriculture, since the adjacent regions support extensive farming activity with corresponding use of pesticides and fertilisers. However, heavy industrial activities in the region, the bay have the polluted coastal waters of Turkey. The potential for damaging the fragile ecological equilibrium of these unique ecosystems as a result of unstable environment factors and enhanced anthropogenic pressure justifies attempts at pollution monitoring (Dural & Göksu, 2007).

3.1.5 İskenderun Bay

Along the coast of Iskenderun Bay that an economically important location for fishery there are many towns, agricultural lands, industrial plants (iron-steel plants, beverage, LPG plants, oil transfer docks, other industrial plants and cargo ships ballasts water). Therefore mainly untreated agricultural, municipal and industrial wastes affect the bay direct or indirectly (Turkmen et al., 2005). This area, in which there are large quantities of untreated industrial and domestic sewage, has one of the most polluted coastal waters of Turkey (Yılmaz, 2005). During recent years, the levels of pollutants in the Iskenderun Bay have come to the fore following the sinking of the ship, M/V Ulla, in 2004. This event caused a sensation in the media as chromium, petroleum and PCB pollution. Since the bay is a semi-closed zone, settling time for

contaminants is relatively long and this may be one of the reasons for increasing amounts of pollutants (Yılmaz, 2010).

3.1.6 Göksu Delta (Taşucu, Mersin)

Göksu Delta is an important wetland (15000 ha) where the Göksu River reaches the Mediterranean Sea in the eastern town of Taşucu-Mersin. The delta is classified as a Wetland of International Importance according to the Ramsar Convention on Wetlands of International Importance. The Göksu Delta is additionally significant for being one of the few remaining areas in the world where sea turtles (Caretta caretta, Cheloniamydas) and blue crabs (*Callinectes sapidus*) lay their eggs (Demirel, 2011). The Mediterranean coastline, stretching from the district of Silifke to the Susanoğlu region, is heavily populated due to urban developments and increased population influx from the surrounding cities, especially during the summer. The Göksu Delta is not only an urban area but it is also surrounded by densely cultivated orchards (mostly citrus), traditional vegetable farms, and greenhouse cultivations where farming activities continue all year long due to the favorable climate and fertilizers and pesticides used intensively during the year. In the previous studies, data showed that about 94 tons of pesticides and 520 kg/ha of mineral fertilizers were used within a year in the Göksu Delta **(**Çetinkaya, 1996). Ayas et al., (1997) reported that various environments (e.s river and lake) and organisms were contaminated by 13 different pesticides and their residues. It was determined that the use of pesticides in the Mediterranean region is more than the average consumption of all of Turkey (Delen, Durmuşoğlu, Güncan, Güngör, Turgut & Burçak, 2005; Erdoğan & Karaca, 2001), reported that pesticide consumption was 9.9 kg per ha the types of pesticides are increased and 102 different types of pesticides were used in agricultural areas in the Göksu Delta. Additionally, the amount of fertilizers was 7200 tons in 2006. These pollutants affect the surface and groundwater quality negatively.

CHAPTER FOUR
MATERIAL AND METHODS

4.1 Material

4.1.1 Blue Crab

Atlantic blue crabs, or simply “blue crabs,” are given their name not from the color of their shell, but rather the blue colored tips of the male’s claws. The blue crab’s scientific name *(Callinectes sapidus)* is derived from the Greek and Latin languages, respectively. This name literally translates to “beautiful, savory swimmer.” These crabs are benthic (bottom) dwelling animals. Blue crabs are typically carnivorous (meat/flesh-eating). Their preferred diet includes small fish, bivalves, and even other crustaceans. It is not uncommon, however, for a blue crab to eat plants or detritus (dead and decaying plant and animal matter). Throughout their lives, blue crabs travel and live within a wide range of salinities (salt concentration). Generally remaining in a low salinity waters, female blue crabs often migrate to higher salinity estuaries and bays to hatch their eggs. A blue crab’s average life span in the wild is three to four years. Blue crabs have 10 legs: two claws (chilipeds), six walking legs, and two swimming legs. In general, it is easy to distinguish between male and female crabs by viewing their “apron” or underside. Male crabs possess a shape resembling inverted “T.” Immature females have a triangular shape on their aprons, while the mature females’ aprons are more circular in shape (Figure 4.1 and Figure 4.2) (Welsh, 2012).

Blue crab was introduced artificially between 1935 and 1945 to the northern Aegean Sea, and gradually came to occupy the Turkish coasts in the northeastern Mediterranean (Artuz, 1990). Enzenrob et al., (1997) reported the occurrence of the blue crab in 15 lagoons of the Mediterranean coastline of Turkey (such as Dalyan, Fethiye, Antalya, Adana, Mersin, İskenderun). The blue crab is one of the most commercially harvested species for the lagoons of the Mediterranean coastline of Turkey.



Figure 4.1 Female blue crab *(Callinectes sapidus)*



Figure 4.2 Male blue crab *(Callinectes sapidus)*

4.1.2 Sea Bream (Sparus aurata, Lin., 1758)

Gilthead sea bream (*Sparus aurata*) is the only species of sea bream which is currently farmed on a large scale. It is common throughout the Mediterranean and is also found along the Eastern Atlantic coasts, from the United Kingdom to the Canary Islands. Its latin name comes from the characteristic golden band between its eyes

(Figure 4.3). It can live in marine waters as well as in the brackish waters of coastal lagoons. Commonly seen in rocky or sandy bottoms, it can also be found in sea-grass beds. During the spawning period (October to December), adults move into deeper waters. The young fry migrate to coastal or estuarine water in early spring. This species is hermaphrodite, maturing as a male throughout the first or second year of its life and then as a female throughout the second or third year. It feeds on molluscs, crustaceans and small fish (Fisheries and aquaculture in Europe, 2012).



Figure 4.3 Sea bream (*Sparus aurata*)

4.1.3 Gray Mullet

Gray mullet is a shoaling species, usually found in inshore waters, entering estuaries and lagoons. It spawns in the Channel and in Irish waters in July to August, earlier in the southern part of the distribution. It can reach up to 75 cm in length and 4.5 kg in weight. The maximum reported age is 25 years. As larvae they feed on zooplankton, but the juveniles and adults mostly feed on detritus, bottom algae and small organisms, gray mullet are mature at 30 to 35 cm and an age of three to four years (Seafish Species Guide, 2014).

4.1.3.1 Gray Mullet (Liza aurata, Risso 1810)

Liza aurata, is one of the target fish species of commercial fishing along Aegean coasts (Figure 4.4).

Diagnosis: head broad, space between eyes about equal to width of mouthcleft; adipose eyelidrudimentary; upper lip thin, less than pupil diameter; corner of mouthcleft reaching to below front nostril; hind edge of preorbital pointed. No pectoralaxillary scale. Scales on head extend forward to level of posteriornostril.

Colour: back grey/blue, flanks and belly pale or silvery; a golden blotch on operculum.

Size: to 50 cm SL.

Habitat: pelagic, usually inshore, entering lagoons and estuaries, but rarely moves into freshwater.

Food: small benthic organisms, detritus, occasionally insects and plankton.

Reproduction: July-November.

(Marine species identification portal, Golden grey mullet , *Liza aurata*, n.d).



Figure 4.4 Gray mullet *(Liza aurata)*

4.1.3.2 Gray Mullet (Mugil cephalus Linnaeus, 1758)

Diagnosis: head broad, its width more than width of mouthcleft; adipose eyelid well developed, covering most of pupil; upper lip thin, without papillae, labialteeth of upper jaw small, straight, and dense, usually in several rows; mouthcleft ending below posteriornostril. Pectoralaxillary scale about one-third length of fin; 8 soft anal finrays.Pyloric caeca 2.Scales in lateral series 36-45 (Figure 4.5).

Colour: back blue/green, flanks and belly pale or silvery; scales on back and flanks usually streaked to form longitudinal stripes; dark pectoral axillary blotch.

Size: to 100 cm SL.

Habitat: pelagic, usually inshore, entering estuaries and lagoons.

Food: juveniles on invertebrates, adults mostly on detritus, bottom algae and small organisms, occasionally on plankton.

Reproduction: July-October. In some countries these fishes are cultured in ponds or grown in enclosures. **(**Marine species identification portal, Flathead grey mullet, *Mugil cephalus*, n.d).



Figure 4.5 Gray mullet (*Mugil cephalus)*

4.1.3.3 Gray Mullet (Liza saliens Risso, 1810)

Diagnosis: head broad, space between eyes about equal to width of mouthcleft; adipose eyelid poorly developed; upper lip thin, less than pupil diameter; corner of mouthcleft reaching to below front nostril. No pectoralaxillary scale. Scales on head extend forward to level of front nostrils, mostly bearing 2 grooves. Pyloric caeca 7-8.

Colour: back blue/grey, flanks and belly pale or silvery. *Size:* to 35 cm SL.

Habitat: pelagic, usually inshore, entering lagoons and estuaries. *Food:* bottom and planktonic organisms.

Reproduction; summer months.

Distribution: Atlantic coasts northward to the Bay of Biscay; also, whole of Mediterranean, Black Sea and Sea of Azov. Elsewhere, southward, perhaps as far as Angola; introduced into the Caspian Sea (Figure 4.6).

(Marine species identification portal, Leaping mullet, *Liza saliens*, n.d).

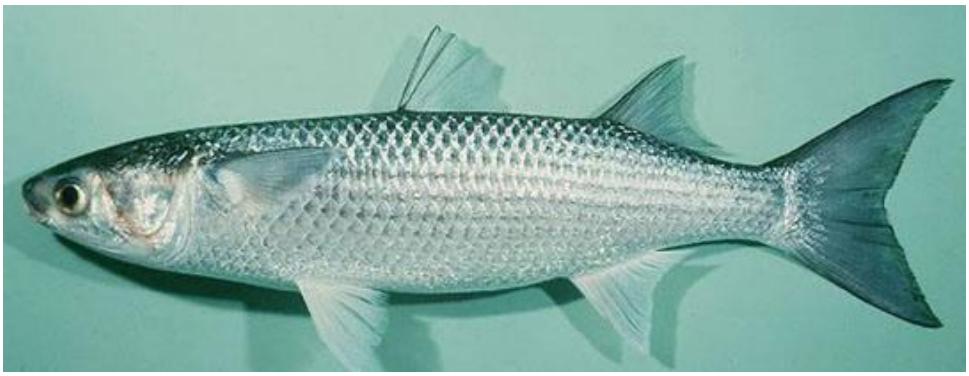


Figure 4.6 *Mugil cephalus Linnaeus*, 1758

4.2 Sampling

A total of fifty nine blue crabs (thirty five female and twenty four male), thirty sea bream and thirty gray mullet were collected from Dalyan, Fethiye, Beymelek (Antalya), İskenderun, Göksu Delta (Taşucu) and Karataş (Adana) in 2013 (Table 4.1). Blue crab's carapace length and weight, fish's weight and length were recorded and the soft tissues were removed (Table 4.2 and 4.3). The biota samples were freeze-dried and homogenized using blender.

Table 4.1 Sampling locations, date and number of samples

Sampling Area	**Sampling Date**	**Blue Crab**	**Sea Bream**	**Gray Mullet**
Dalyan	30.March.2013	5 F+4 M	5	5 *(L. aurata)*
Fethiye	30.March.2013	1 F+5 M	5	5 *(L. aurata)*
Antalya (Beymelek L.)	12.April.2013	5 F+4 M	5	5 *(L. aurata)*
Adana (Karataş L)	13.May.2013	7 F+ 3 M	5	5 (*M. cephalus)*
Göksu Delta (Taşucu)	27.May.2013	9 F+5 M	5	*5 (M. saliens)*
İskenderun	5.Sept.2013	8 F+ 3 M	5	5 *(L. aurata)*
F: Female M: Male				

Table 4.2 Specifications of fish samples

	Species	**Length (cm)**	**Weight (gr)**
Dalyan	Sea bream	22.5	242
		23.0	244
		24.0	285
		24.5	289
		25.5	255
	Gray mullet *(L. aurata)*	27.0	193
		27.5	193
		28.0	200
		28.0	203
		27.5	208
Fethiye	Sea bream	23.5	242
		22.0	236
		21.5	203
		22.0	216
		23.0	230
	Gray mullet *(L. aurata)*	23.5	140
		24.0	152
		22.5	121
		23.0	139
		22.5	128
Beymelek L.	Sea bream	18.0	111
		17.0	91
		17.0	98
		17.5	97
		18.0	117
	Gray mullet *(L. aurata)*	22.5	162
		23.0	174
		23.5	195
		22.0	140
		22.0	162
Adana Karataş L.	Sea bream	10.0	58
		14.8	72
		14.0	57
		15.5	72
		13.6	52
	Gray mullet *(M. cephalus)*	33.0	466
		29.7	339
		35.0	524
		33.2	525
		30.3	356
Taşucu Göksu Delta	Sea bream	14.5	89
		15.0	90
		18.0	127
		19.0	143
		17.5	100
	Gray mullet (*M. saliens)*	22.5	116
		22.5	126
		24.5	158
		24.0	161
		22.5	126
İskenderun	Sea bream	15.0	80
		16.7	98
		15.5	90
		15.5	77
		17.0	90
	Gray mullet *(L. aurata)*	19.5	116
		19.5	134
		21.5	131
		21.0	63
		19.5	137

Table 4.3 Specifications of blue crab samples

Region	Sexuality	Long carapace width (cm)	Carapace length (cm)	Weight (gr)
Dalyan	Female	14	7.5	200
		15.2	6.9	234
		16	7.2	221
		16	7.2	200
		15.9	7.4	203
	Male	14.9	7.5	239
		13.3	6.6	143
		16.5	7	232
		16.1	7.6	205
Fethiye	Male	16	7.2	243
		14	7.3	198
		15.5	8	240
		13.2	6.5	154
		13.3	6.1	102
	Female	16.5	7.2	199
Antalya Beymelek L.	Male	15	7	242
		14	7	180
		14	7	182
		11	5	94
	Female	14.5	7	181
		14.5	8.5	209
		15	7.5	204
		14	6.5	152
		14	6.5	135
Adana Karataş L.	Male	16.5	9.5	268
		10.0	5.5	64
		7.5	4.5	34
	Female	8.5	5.0	35
		15	8.0	190
		7.0	5.0	45
		8.5	4.5	38
		7.5	5.0	45
		7.5	4.0	25
		7.0	3.6	30
Göksu Delta Taşucu	Female	14.0	9.5	165
		15.0	10.5	196
		13.5	9.5	178
		13.5	9.5	188
		15.5	7.5	172
		14.5	9.0	153
		13.5	7.5	101
		15.0	7.0	157
		14.5	7.0	148
	Male	5.0	5.0	84
		5.0	5.0	99
		5.0	5.0	102
		5.4	5.4	108
		5.0	5.0	120
İskenderun	Male	15.0	7.5	353
		15.0	8.5	360
		14.0	8.5	334
	Female	11.5	6.5	95
		12.0	7.5	170
		7.0	13.5	132
		12.0	6.5	105
		12.5	6.0	119
		14.5	7.5	186
		6.5	13.5	177
		14.0	7.0	234

Pollutant concentrations in wet weight were calculated according to Table 4.

Table 4.4 Dry weight/Wet weight (DW/WW)

Sample	DW/WW
Sea bream	0.21
Gray mullet	0.26
Blue crab	0.22

4.3 Method

4.3.1 Analytical Procedures

Analytical Procedures which is called “Modular Multiple Analytical Method for the Determination of Pesticide Residues in Foodstuffs” included in the Official German Manual as Method L 00.00-34 (DFG Method S 19, 1999).

4.3.2 Analytical Method

MODULE E 7 Extraction in the presence of large amounts of fat

1. Outline

Fat or a dry sample with high fat content (e.g. oil seed) is mixed intensely with the suspension of a synthetic calcium silicate (trade name: Calflo E) in acetonitrile. The suspension is filtered and the volume of the filtrate measured. The solution is evaporated to dryness and the remaining residue is dissolved in GPC eluting mixture. The extract is used for clean-up by gel permeation chromatography (module GPC).

2. Reagents

2.1. Calflo E (Johns-Manville Prod. Corp. New York; obtainable from Dr. Ehrenstorfer, Augsburg), heated at 550 °C for at least 2 h

2.2. Filter aid, e.g. Celite 545 (Roth, Karlsruhe), heated at 550 °C for at least 2 h

2.3 Acetone, for residue analysis

2.4. Acetonitrile, for residue analysis

2.5. Cyclohexane, for residue analysis

2.6. Ethyl acetate, for residue analysis

2.7. Isooctane, for residue analysis

2.8. GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); if necessary, redistilled as an azeotropic mixture

3. Apparatus

3.1. High-speed homogenizer, e.g. Ultra-Turrax (Janke u. Kunkel, Staufen/Br)

3.2. Glass jar, 500 mL or 750 mL, with a screw cap lined with aluminium foil

3.3. Buchner porcelain funnel, 12.5 cm dia., or glass filter funnel, 9.0 cm dia.

3.4. Filtration flask, 1 L

3.5. Glass funnel, 100 mm dia.

3.6. Graduated cylinders, 250 mL and 25 mL

3.7. Volumetric pipette, 10 mL

3.8. Round-bottomed flask, 250 mL, with ground joint

3.9. Rotary vacuum evaporator, water bath temperature 40 °C

3.10. Round filter paper, 12.5 cm or 9.0 cm dia., fastflow rate, extracted exhaustively with acetone

3.11. Fluted filter paper, 20 cm dia., extracted exhaustively with acetone

3.12. Membrane filter, 0.45 µm pore size, 25 mm dia. (e.g. Chromafil, type 0-45/25 organic, Macherey-Nagel Nr. 718 005)

Note: Glassware cleaned with detergents must be thoroughly rinsed with distilled water and acetone.

4. Procedure

Sampling of the fish and blue crab muscle were kept at (-20 °C) until analysis (UNEP/IOC/IAEA/FAO, 1991). The samples were freeze-dried, and homogenized. 10 grams of dried biota sample was used for OC compounds analysis.Weigh 10 g (mA) of fat or an equivalent amount of a high-fat material into a glass jar containing 20 g Calflo E and 10 g Celite 545. Add 240 mL acetonitrile and 10 mL internal (Aldrin) (Sum $V=V_{Ex}$). Homogenize the mixture for 2 min with the homogenizer and filter the suspension with suction through a filter paper in a porcelain or glass filter funnel. Apply only gentle suction to ensure that not more than minimal portions of the filtrate evaporate. In addition, filter only for a short time, even if only 100 to 150 ml of filtrate is collected. With less than 100 ml of filtrate, repeat the procedure with

a smaller amount of sample. Then filter the filtrate through a dry fluted filter paper, covered with 0.5 g Calflo E, into a 250-mL graduated cylinder and measure the volume obtained. Transfer the filtrate quantitatively, rinsing with acetone, into a weighed round-bottomed flask, add 10 mL isooctane and evaporate the solution to 0.5 to 1 mL using a rotary evaporator. Evaporate the remaining traces of solvent with a gentle stream of air. Weigh the flask again and calculate the mass of the residue. If less than 2 g of fat remain, dissolve it in approx. 10 mL GPC eluting mixture. Transfer the solution into a 25-mL graduated cylinder, make up to 15 mL (V_{End}) with GPC eluting mixture and filter through a membrane filter, if necessary. If more than 2 g of fat remain, dissolve it in GPC eluting mixture and make up to an appropriate larger volume (V_{End}). With the solution, proceed as described in the module GPC.

MODULE GPC Gel permeation chromatography

1. Outline

The extract solution derived from one of the modules E is cleaned up by gel permeation chromatography using the polystyrene gel Bio-Beads S-X3 and elution with a mixture of cyclohexane and ethyl acetate.

2. Reagents

2.1. Bio-Beads S-X3, 200-400 mesh (Bio-Rad Laboratories GmbH, München)

2.2. Cyclohexane, for residue analysis

2.3. Ethyl acetate, for residue analysis

2.4. GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); if necessary, redistilled as an azeotropic mixture

2.5. GPC test solution, e.g. approx. ρ= 0.035 µg/mL HCB, 0.13 µg/mL trifluralin, 0.2 µg/mL flucythrinate and 0.25 µg/mL chinomethionat in GPC eluting mixture

3. Apparatus

3.1. Automated equipment for gel permeation chromatography, e.g. Gilson/Abimed Clean-Up XL system (ABIMED Analysen-Technik GmbH, Langenfeld) or Gel chromatograph GPC Autoprep 1002 (Analytical Biochemistry Laboratories, Columbia, Mo., USA)

Supplier ANTEC GmbH, Pinneberg) in both cases: chromatography column with end adapters length 40 cm, 25 mm i.d., sample loop 5.0 mL

3.2. Glass syringe, 10 mL, with Luer-lock fitting (or disposable polypropylene syringes)

3.3. Long-neck round-bottomed flask, 150 mL, with ground joint

3.4. Pear-shaped flask, 250 mL, with ground joint

3.5. Rotary vacuum evaporator, water bath temperature 40 °C

3.6. Pasteur pipettes

3.7. Graduated test tubes, e.g. 12 to 15 mL, with ground stopper and graduation marks at 2.5, 5.0 and 10.0 mL

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4.1 Packing gel permeation column

Suspend 50 g of Bio-Beads in the GPC eluting mixture and allow them to swell overnight. Pour the suspension all at once into the chromatographic column (capacity approx. 180 mL). Once the gel has settled to a height of approx. 32 cm and is free from air bubbles, insert the end adapter and lower it down to the bed level. If the gel bed is compressed further after prolonged use, adjust the adapter accordingly. For further details refer to manufacturer's instructions.

4.2 Checking elution volumes

Check the elution conditions for every new gel permeation column and for a column whose separation efficiency has diminished. To do so, set the following parameters:

Dump 0 min to discard 0 mL

Collect 2 min to collect 10 mL

Inject 5.0 mL of the GPC test solution and elute with the GPC eluting mixture at 5.0 mL/min. Discard fractions 1 to 7. Collect the fractions 8 to 23 separately and analyze them by gas chromatography mass spectrometry (module D 1). From the recoveries obtained for the four analytes determine the appropriate range of elution volumes.

4.3 Cleanup of crude extracts

Inject approx. 10 ml of the filtered extract solution derived from one of the modules E into the 5-ml sample loop (5.0 mL = V_{GA}: is the aliquot portion of the extract volume injected onto the GPC column).

Elute the gel permeation column with the GPC eluting mixture at 5.0 mL/min. To do so, set the determined parameters beforehand, e.g. Discard ("Dump") 17 min corresponding to 85 mL Collect ("Collect") 22 min corresponding to 110 mL.

The "Dump"-phase is discarded. Collect the "Collect"-fraction in a 150-mL long-neck round-bottomed flask or in a 250-mL pear-shaped flask. Concentrate it to approx. 1 mL in a rotary evaporator (rotate slowly, immerse the flask only slightly in the water bath). Pipet the remaining solution quantitatively into a ground-stoppered graduated test tube, rinse the flask with acetone, and make up to 1.0 mL (V_{GE}:is the final volume of GPC eluate after concentration with acetone.)

4.3.3 Extractable Organic Matter (EOM)

Extractable organic matter (EOM) was determined gravimetrically (UNEP, 1996). The EOM is determined in the following manner. On the weighing pan of an electrobalance, a known volume of the extract is evaporated (up to 100 µl) and the residue is weighted with a precision of about ± 1 µg. If the residue is less than 2 µg, preconcentration of the original extract is required. The quantity of EOM is :

$$\text{EOM}(\mu g/g) = \frac{\textit{Weight}\ \text{of residue (}\ \mu g\text{) x volume of the extract}\left(\text{ml}\right)\ \text{x 1000}}{\textit{Volume evaporated}\ \left(\mu l\right)\ \text{x quantity of sample extracted}\ \left(\text{g}\right)}$$

When the lipid content of the extract exceeded 100-150 g, sulphuric acid was used for the removal of lipids (UNEP, 1996).

4.3.4 Gas Chromotography Conditions for Halogenated Hydrocarbons

Eluate concentrated to 1 ml under a stream of N_2 gas and injected to gas chromatography. Quantitative analysis was performed with Agilent 5975C GC-MS. An analytical column DB-5MS 30m×0.25mm×0.25µm was used.

To analyze organochlorinated compounds, the temperature program of GC/MS was as follows: initially 70°C for 2min, then increase to 150°C with a velocity of 25°C/min then increase to 200°C with a velocity of 3°C/min and up to 280°C with a velocity of 8°C/min held for 10 min.

The nine OCPs (p,p'-DDE, p,p'-DDD, p,p'-DDT, lindane, HCB, aldrin, dieldrin, endrin, heptachlor) and PCBs: such as commercial mixtures, Arochlor 1254 and 1260 were analyzed in the biota samples collected from the Aegean and Eastern Mediterranean coasts.

4.3.5 Quality Assurance for OCPs

The quality of the analytical data was assured using the reference material of IAEA-435 the biota sample (from IAEA). The whole methodology was verified on this reference material, obtaining results in good agreement with the certified values. Blanks were run periodically during the analysis to confirm the absence of contaminants. The blank values of the analytical procedure remained always below the detection limits. The recoveries for sediments fell with a fairly narrow range between 70.0 and 96.1%. The detection limits were given in 0.10-0.57 pgg^{-1} for OCPs and 2.4-4.5 pgg^{-1} for PCB (Table 4.5).

Table 4.5 Observed and certified values of elemental concentrations in reference material (IAEA-435) as ng g^{-1}dry weight

	Measured value	**Certified value**
HCB	0.28	0.20
Heptachlor	0.82	1.00
Lindane	0.42	0.58
DDE	1.90	2.10
Dieldrin	1.55	1.30
Endrin	6.00	5.40
DDD	0.58	0.88
DDT	0.50	0.67
Aro.1254	78	84
Aro.1260	711	716

4.3.6 Statistical Analysis

4.3.6.1 Cluster Analysis

Cluster analysis or clustering is the task of grouping a set of objects in such a way that objects in the same group (called a cluster) are more similar (in some sense or another) to each other than to those in other groups (clusters). It is a main task of exploratory data mining, and a common technique for statisticaldata analysis, used in many fields, including machine learning,pattern recognition, image analysis, information retrievaland bioinformatics (Cluster analysis, n.d).

The data, obtained at all stations, were analyzed using cluster techniques based on the Bray-Curtis similarity using the PRIMER package (Clarke & Warwick, 2001). Before the analysis, the raw data expressed as the number of individuals in each sample, were transformed using the Log (x + 1) transformation.

CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 OCP Levels

Table 5.1 illustrates the concentrations of OCPs (ng g^{-1}) in biota samples collected from Aegean and Mediterranean coast of Turkey (Figure 3.1). The eight OCPs (ppDDE, ppDDD, ppDDT, lindane, HCB, dieldrin, endrin, heptachlor) together with PCBs: such as commercial mixtures, Aroclor 1254 and 1260 were analyzed in blue crab, gray mullet, sea bream samples. Some examples of chromatograms OCPs and PCBs for the biota saamples collected from Aegean and Mediterranean coasts of Turkey were illustrated in Figure 5.1.

The concentrations of ΣOCPs were in the range of 0.87-33.15 ng g^{-1} dry wt. The maximum concentration of ΣOCPs (33.15 ng g^{-1}) was found in gray mullet samples collected from Antalya due to dense agricultural activities in the surroundings of Beymelek Lagoon (Antalya). The minimum concentration of ΣOCPs (0.87 ng g^{-1}) was found in male blue crab samples collected from Mersin (Table 5.3, Figure 5.2).It is expected that minimum value was found in Goksu Delta (Mersin) is classified as a Wetland of International Importance according to the Ramsar Convention on Wetland.

The concentrations of ppDDE were in the range of 0.40-12.87 ng g^{-1} dry wt. The highest concentration of ppDDE was found in gray mullet samples in Antalya (12.87 ng g^{-1} dry wt). The lowest concentration of ppDDE was found in male blue crab samples in Mersin (0.40 ng g^{-1} dry wt). The concentrations of ppDDD were detected in the range of 0.02-3.90 ng g^{-1} dry wt. The maximum concentration of ppDDD was found in gray mullet samples Antalya (3.90 ng g^{-1} dry wt) similar to ppDDE. The minimum concentration of ppDDD was found both male and female blue crab samples in Adana (0.02 ng g^{-1} dry wt). The concentration of ppDDT was in the range of bdl-6.10 ng g^{-1} dry wt. The highest concentrations of ppDDT was found in sea

bream samples Antalya (6.10 ng g^{-1} dry wt). ppDDT was only found below detection limit (bdl) in male blue crab samples in Mersin (Table 5.1).

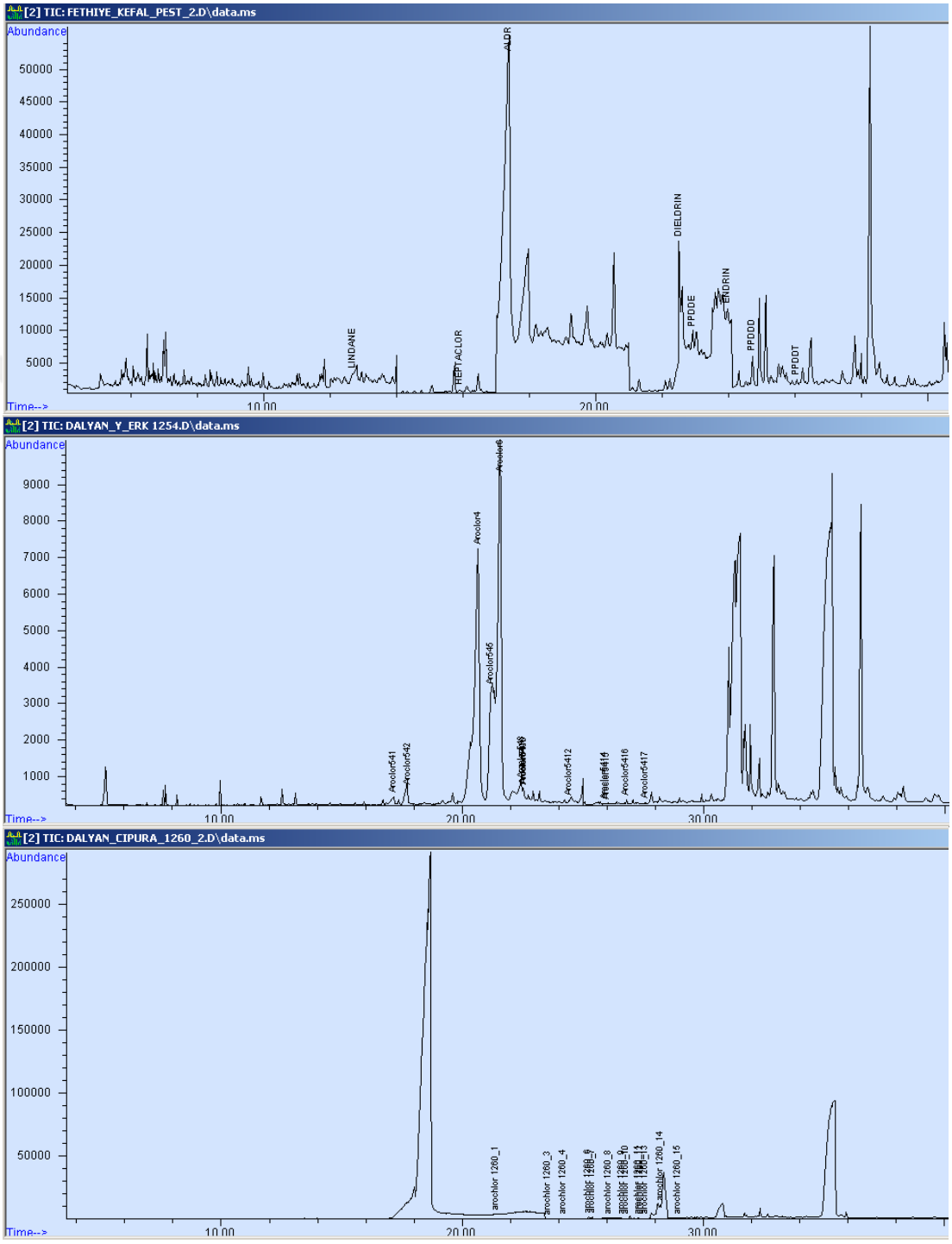


Figure 5.1 Chromatograms of OCPs and PCBs for the biota saamples collected from Aegean and Mediterranean coasts of Turkey

Table 5.1 Concentrations of OCPs in biota samples collected from Aegean and Mediterranean coast of Turkey (ng g^{-1}) dry weight

Region	Sample	HCB	Lindane	Heptachlor	Endrin	Dieldrin	ppDDE	ppDDD	ppDDT
Dalyan	Sea bream	8.71	0.23	1.00	2.50	1.60	6.80	1.64	5.40
	Gray mullet	1.80	0.04	0.97	2.90	1.81	7.50	3.90	4.80
	Blue crab (F)	0.56	0.02	0.12	0.88	0.65	4.61	0.65	2.30
	Blue crab (M)	0.45	Bdl	0.05	0.61	3.15	5.33	0.10	4.90
Fethiye	Sea bream	3.14	0.08	0.02	2.60	2.10	4.00	0.94	4.50
	Gray mullet	1.50	0.04	1.34	1.70	1.90	8.65	1.01	4.40
	Blue crab (F+M)	0.20	0.01	Bdl	0.60	1.00	2.20	0.05	1.40
Antalya	Sea bream	0.06	Bdl	0.02	0.71	1.20	7.72	0.16	6.10
	Gray mullet	7.60	0.22	2.75	0.60	1.80	12.9	3.02	4.30
	Blue crab (F)	0.78	0.02	0.01	1.73	0.85	9.60	0.50	0.80
	Blue crab (M)	0.06	Bdl	0.18	0.85	0.67	1.24	0.22	0.94
Adana	Sea bream	5.97	0.20	0.04	1.50	1.80	6.17	1.30	6.00
	Gray mullet	0.76	0.02	8.56	1.60	2.00	5.50	2.00	4.00
	Blue crab (F)	0.00	0.00	0.03	0.39	0.60	1.32	0.02	1.00
	Blue crab (M)	0.00	0.00	0.08	0.14	0.80	1.20	0.02	2.12
Iskenderun	Sea bream	4.10	0.11	0.75	2.10	0.80	4.00	0.65	2.56
	Gray mullet	0.46	0.01	0.80	2.00	1.10	3.45	1.77	0.88
	Blue crab (F)	0.08	0.00	0.01	0.50	1.75	1.70	0.18	1.00
	Blue crab (M)	0.02	Bdl	Bdl	0.23	1.74	3.40	0.21	0.46
Mersin	Sea bream	1.25	0.03	0.16	1.20	1.48	6.75	0.47	3.00
	Gray mullet	0.36	0.01	0.45	1.30	0.95	2.60	0.99	1.20
	Blue crab (F)	0.00	Bdl	0.02	0.54	0.89	9.40	0.16	0.10
	Blue crab (M)	0.00	Bdl	0.04	0.10	0.18	0.40	0.16	0.00

Bdl: below detection limit

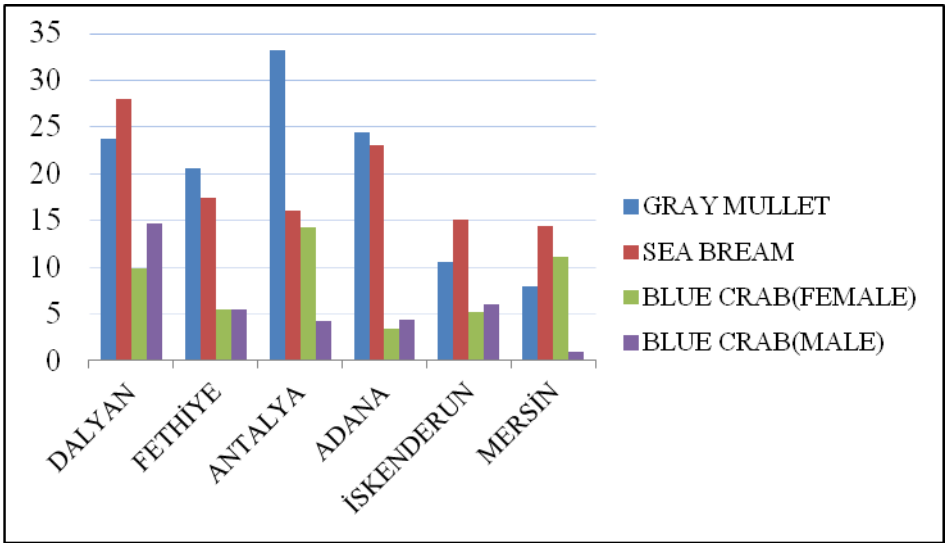


Figure 5.2 Total concentrations of OCPs (ng g^{-1}) dry weight

5.2 PCB Levels

Arochlor 1254 and 1260 concentrations in the biota samples collected from Aegean and Mediterranean coast of Turkey were presented in Table 5.2. Arochlor 1254 ranged from 28-197 and Arochlor 1260 ranged between 5-53 ng g^{-1}dry wt.The highest concentration of ΣPCBs (226 ng g^{-1}) and the high concentration of ΣOCPs was found in samples collected in sea bream in Dalyan. The minimum concentration of ΣPCBs was found in sea bream samples in Antalya (43 ng g^{-1}dry wt) (Table 5.3, Figure 5.3).

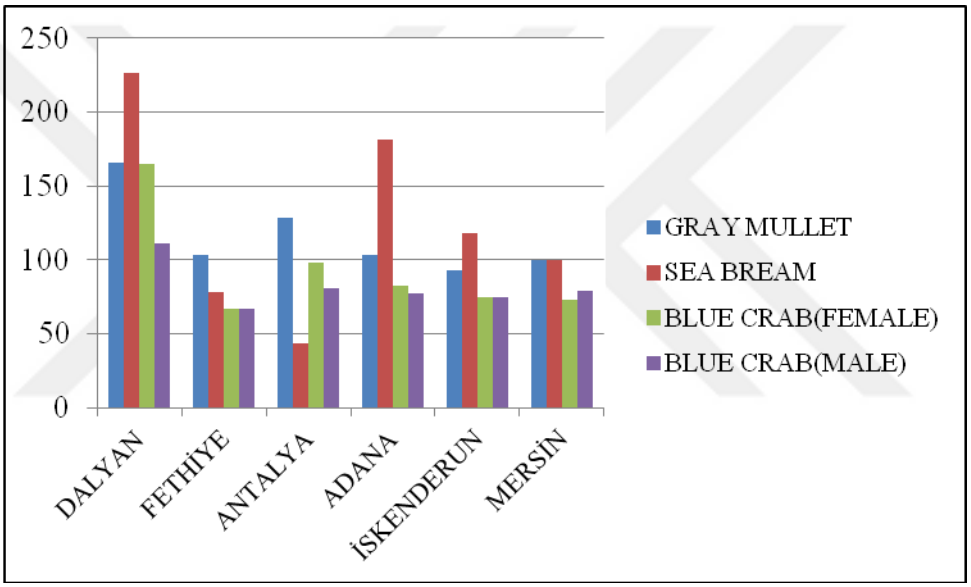


Figure 5.3 Total PCB Concentrations (ng g^{-1})

Concentrations of the total DDT ranged from 0.56 to 20.19 ng g^{-1}dry wt in all sampling regions (Table 5.4). The highest ΣDDTs concentrations were found in gray mullet samples in Antalya, Dalyan and Fethiye respectively (Figure 5.5). Lowest ΣDDTs concentrations were found in male blue crab samples in Mersin similar to lowest ΣOCPs, followed by male blue crab samples in Antalya and female blue crab samples in İskenderun (Figure 5.2, 5.6, 5.7).

Table 5.2 Concentrations of Arochlor 1254 and Arochlor 1260 in biota samples collected from Aegean and Mediterranean coast of Turkey (ng g^{-1})

Region	Sample	Aro.1254	Aro.1260
Dalyan	Sea bream	197	29
	Gray mullet	145	21
	Blue crab (F)	152	13
	Blue crab (M)	99	12
Fethiye	Sea bream	63	14
	Gray mullet	55	48
	Blue crab (F+M)	59	8
Antalya	Sea bream	28	15
	Gray mullet	74	53
	Blue crab (F)	55	44
	Blue crab (M)	76	5
Adana	Sea bream	146	36
	Gray mullet	74	29
	Blue crab (F)	60	22
	Blue crab (M)	58	19
Iskenderun	Sea bream	79	39
	Gray mullet	68	24
	Blue crab (F)	59	16
	Blue crab (M)	61	14
Mersin	Sea bream	78	22
	Gray mullet	68	31
	Blue crab (F)	65	8
	Blue crab (M)	58	21

Aro.1254: Arochlor1254

Aro.1260: Arochlor1260

Table 5.3 Total concentration of Cyclodienes, OCPs, PCBs and EOM in biota samples collected from Aegean and Mediterranean coast of Turkey

Region	**Sample**	**∑OCPs (ng g^{-1})**	**∑Cyc (ng g^{-1})**	**∑ PCBs (ng g^{-1})**	**EOM (mg/g)**
Dalyan	Sea bream	27.88	5.10	226	110
	Gray mullet	23.72	5.68	166	184
	Blue crab (F)	9.78	1.65	165	87
	Blue crab (M)	14.59	3.81	111	103
Fethiye	Sea bream	17.37	4.72	78	175
	Gray mullet	20.54	4.94	103	160
	Blue crab (F+M)	5.46	1.60	67	186
Antalya	Sea bream	15.97	1.93	43	143
	Gray mullet	33.15	5.15	128	136
	Blue crab (F)	14.28	2.59	98	190
	Blue crab (M)	4.16	1.70	81	173
Adana	Sea bream	22.97	3.34	181	50
	Gray mullet	24.44	12.16	103	87
	Blue crab (F)	3.36	1.02	82	122
	Blue crab (M)	4.36	1.02	77	67
Iskenderun	Sea bream	15.07	3.65	118	181
	Gray mullet	10.47	3.90	93	167
	Blue crab (F)	5.22	2.26	75	162
	Blue crab (M)	6.06	1.97	75	83
Mersin	Sea bream	14.34	2.84	100	123
	Gray mullet	7.85	2.70	100	189
	Blue crab (F)	11.10	1.45	73	187
	Blue crab (M)	0.87	0.32	79	145

Cyc: Cyclodienes

PCBs: Arochlor 1254 + Arochlor 1260

∑Cyc: Total cyclodiens (Dieldrin+Endrin+Heptachlor)

The concentrations of HCB were in the range of bdl-8.71 ng g^{-1}dry wt.The concentrations of lindane were in the range of bdl-0.23 ng g^{-1}dry wt^{-1}.The highest concentrations of HCB (8.71 ng g^{-1}) and lindane (0.23 ng g^{-1}dry wt) were found in

sea bream samples in Dalyan because OCPs were used in agriculture in the surrounding area of Dalyan. The highest levels of HCB were also found for gray mullet samples in Antalya and sea bream in Adana. HCB and lindane were only observed below detection limit in blue crab samples in Adana and Mersin.

Table 5.4 presented the ratios of (DDE+DDD)/ΣDDT and DDD/DDE in biota samples collected from Aegean and Mediterranean coast of Turkey. In the study,the relative percentages of p,p'-DDT, p,p'-DDE and p,p'-DDD, highlights that p,p'-DDT not exceeded 50% of the ∑ DDTs in samples (Table 5.4). Given the relatively slow degradation rate of DDT in the environment (Woodwell et al., 1971), the results indicate recent DDT influxes not identified. In general, the ratio of (p,p'-DDE+p,p'-DDD)/ ∑ DDTs>0.5 indicates long-term weathering (Schmitt et al., 1990). The (p,p'-DDE + p,p'-DDD)/ ∑DDT ratio was<0.5 at all sites where relatively higher percentages of p,p'-DDT were found. The low (p,p'-DDE+p,p'DDD)/ ∑ DDT ratios point to a current DDT usage in these sites, probably linked to public health emergencies. The ratio of (DDE+DDD)/ ∑DDTs>0.5 in all biota samples. Generally, this result indicates that DDTs input at the sampling sites was historical and significant degradation has occurred (Table 5.4). The DDE/DDD ratio could be an indicator of the aerobic/anaerobic conditions in the environment (Liu et al., 2008). As shown in Table 5.4, DDD/DDE ratios in biota samples were lower than 1, indicating relatively aerobic conditions for Aegean and Eastern Mediterranean coast of Turkey.

Concentrations of the Σcyclodienes (including heptachlor, dieldrin, endrin) ranged from 0.32 to 12.16 ng g^{-1} dry wt (Table 5.1). Highest Σcyclodienes concentrations occurred in gray mullet samples (12.16 ng g^{-1}dry wt) in Adana (Table 5.3, Figure 5.9). Although maximum dieldrin level (3.15 ng g^{-1}dry wt) was found in male blue crab samples, maximum endrin level (2.90 ng g^{-1}dry wt) was detected gray mullet samples in Dalyan. However maximum heptachlor level was found in gray mullet samples in Adana (8.56 ng g^{-1}dry wt) (Table 5.1).

The EOM values ranged between 67-190 for blue crab, 50-181 for sea bream and 87-189 mg/g for gray mullet (Table 5.3). The lipid content of fish tissue is influenced by severalfactors, such as sex, age, species, nourishment and spawning status (Larsson et al., 1993; Kozlova, 1997).

Table 5.4 Total concentration of DDTs (ng g^{-1}), and the ratios of DDT concentrations in biota samples collected from Aegean and Mediterranean coast of Turkey

Region	**Sample**	**∑DDTs**	***p.p'*-DDD%**	***p.p'*-DDE%**	***p.p'*-DDT%**	**DDD/DDE**	**(DDE+DDD)/∑DDT**
Dalyan	Sea bream	13.84	11.81	49.13	39.02	0.24	0.61
	Gray mullet	16.20	24.07	46.30	29.63	0.52	0.70
	Blue crab (F)	7.56	8.60	60.98	30.42	0.14	0.70
	Blue crab (M)	10.33	0.97	51.60	47.43	0.02	0.53
Fethiye	Sea bream	9.44	9.96	42.3	48.00	0.24	0.52
	Gray mullet	14.06	7.18	61.52	31.29	0.12	0.69
	Blue crab(F+M)	3.65	1.37	60.27	38.36	0.02	0.62
Antalya	Sea bream	13.98	1.14	55.22	43.63	0.02	0.56
	Gray mullet	20.19	15.00	63.74	21.30	0.23	0.79
	Blue crab (F)	10.90	4.59	88.07	7.34	0.05	0.93
	Blue crab (M)	2.40	9.17	51.67	39.17	0.18	0.61
Adana	Sea bream	13.47	9.65	45.81	44.54	0.21	0.55
	Gray mullet	11.50	17.39	47.83	34.78	0.36	0.65
	Blue crab (F)	2.34	0.85	56.0	43.0	0.02	0.57
	Blue crab (M)	3.34	0.60	36	63	0.02	0.57
Iskenderun	Sea bream	7.21	9.00	55.48	35.51	0.16	0.64
	Gray mullet	6.10	29.02	56.56	14.43	0.51	0.86
	Blue crab (F)	2.88	6.25	59.03	34.72	0.11	0.65
	Blue crab (M)	4.07	5.16	83.54	11.30	0.06	0.89
Mersin	Sea bream	10.22	4.60	66.05	29.35	0.07	0.71
	Gray mullet	4.79	20.67	54.28	25.05	0.38	0.75
	Blue crab (F)	9.66	1.66	97.31	1.04	0.02	0.99
	Blue crab (M)	0.56	28.57	71.43	0.00	0.40	1.00

p,p'-DDD%: *p,p'*-DDD/∑DDTs *p,p'*-DDT%: *p,p'*-DDT/∑DDT

p,p'-DDE%: *p,p'*-DDE/∑DDTs

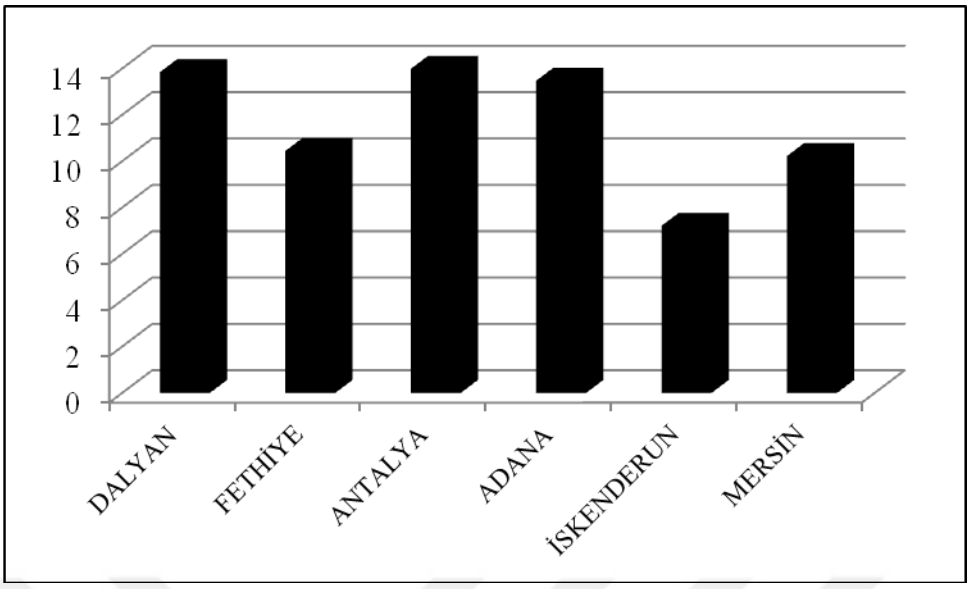


Figure 5.4 Total DDT concentrations in sea bream (ng g^{-1})

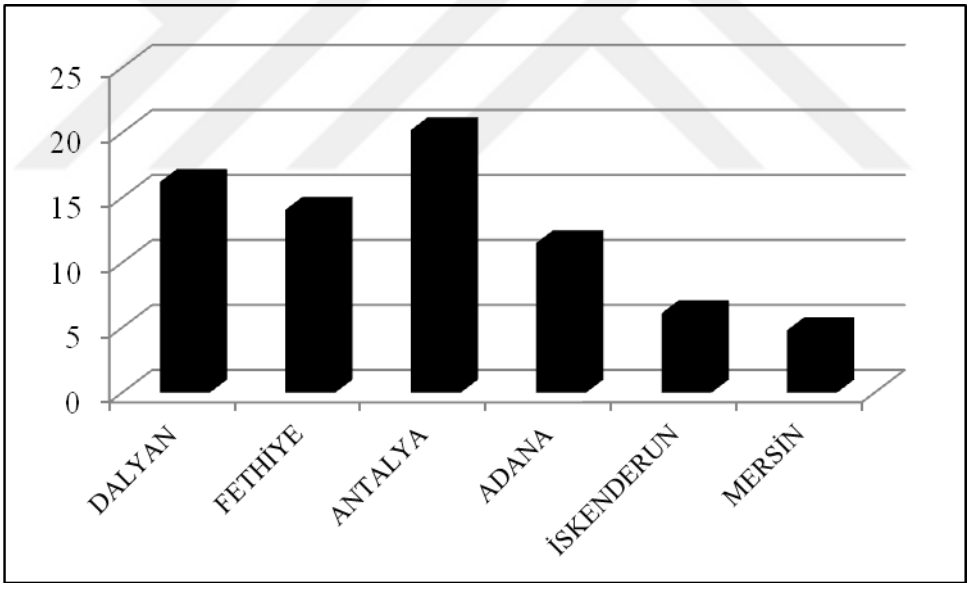


Figure 5.5 Total DDT concentrations in gray mullet (ng g^{-1})

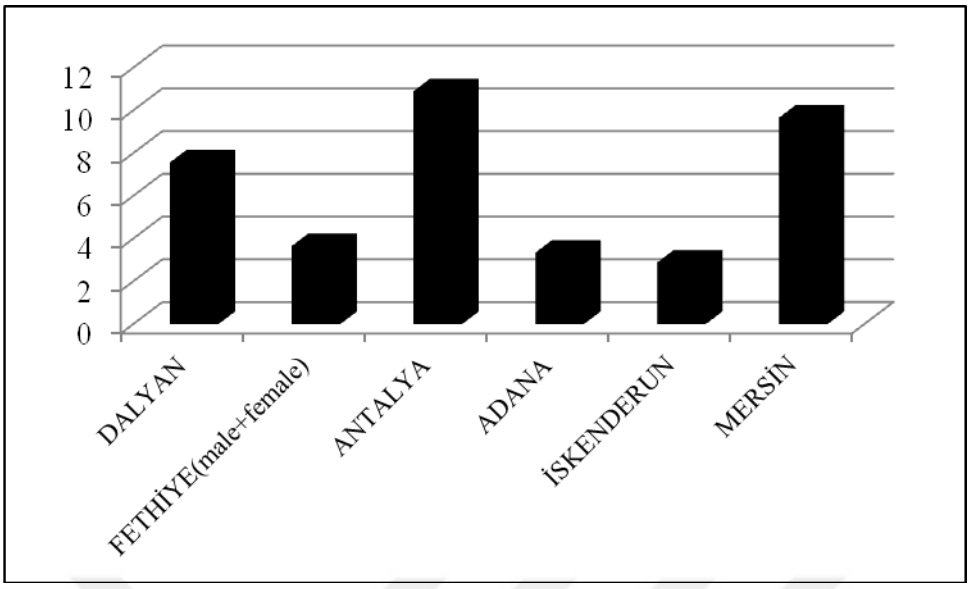


Figure 5.6 Total DDT concentrations in female blue crab (ng g^{-1})

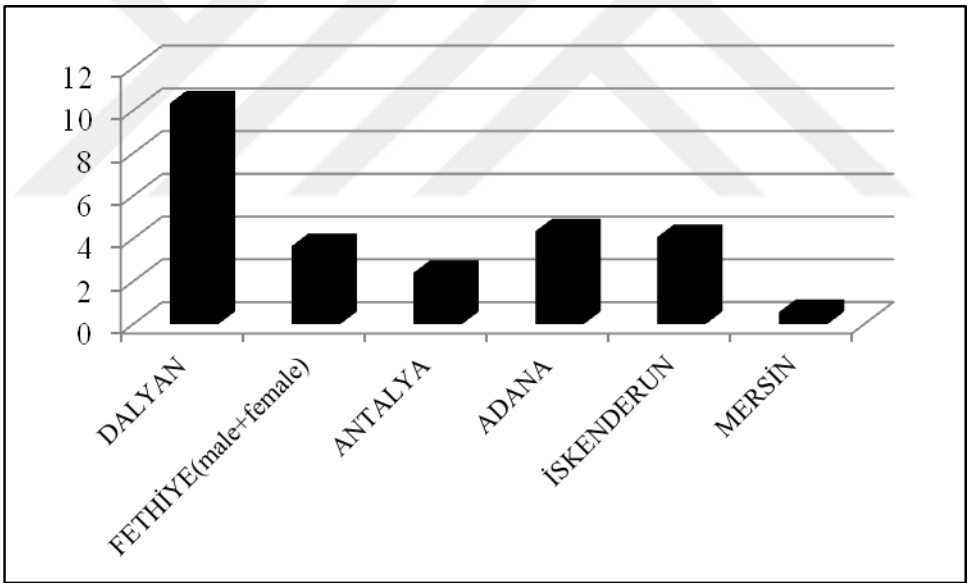


Figure 5.7 Total DDT concentrations in male blue crab (ng g^{-1})

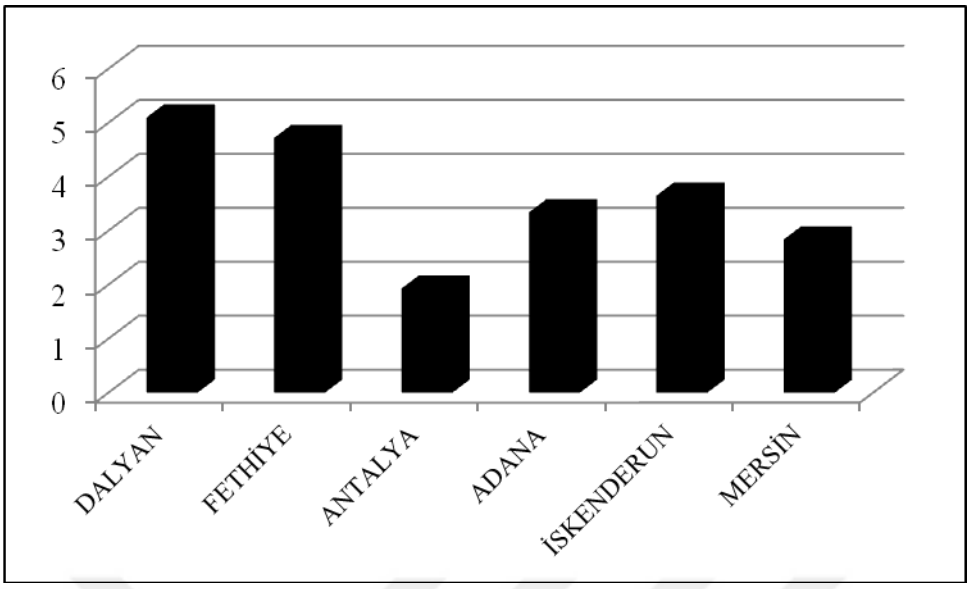


Figure 5.8 Total cyclodiens concentrations in sea bream (ng g^{-1})

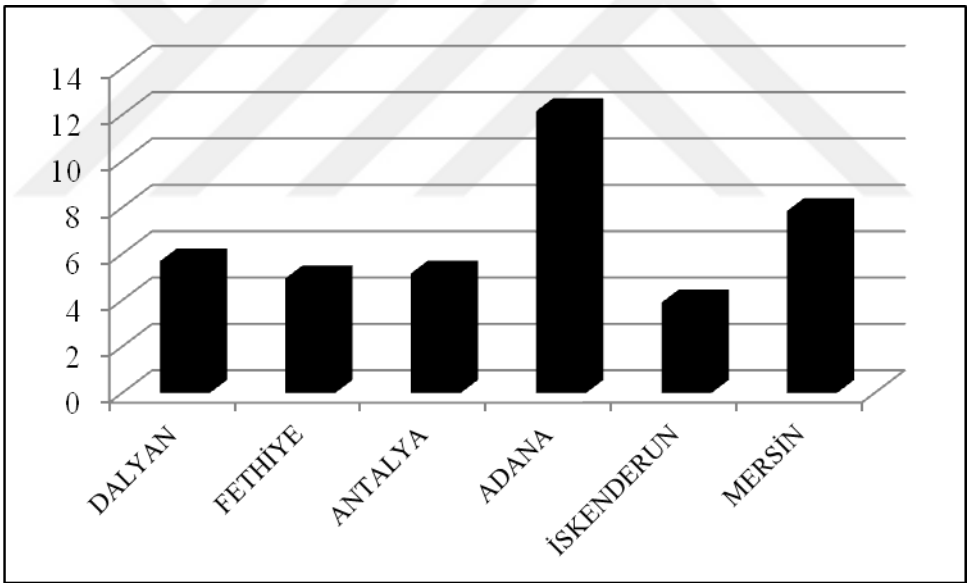


Figure 5.9 Total cyclodiens concentrations in gray mullet blue crab (ng g^{-1})

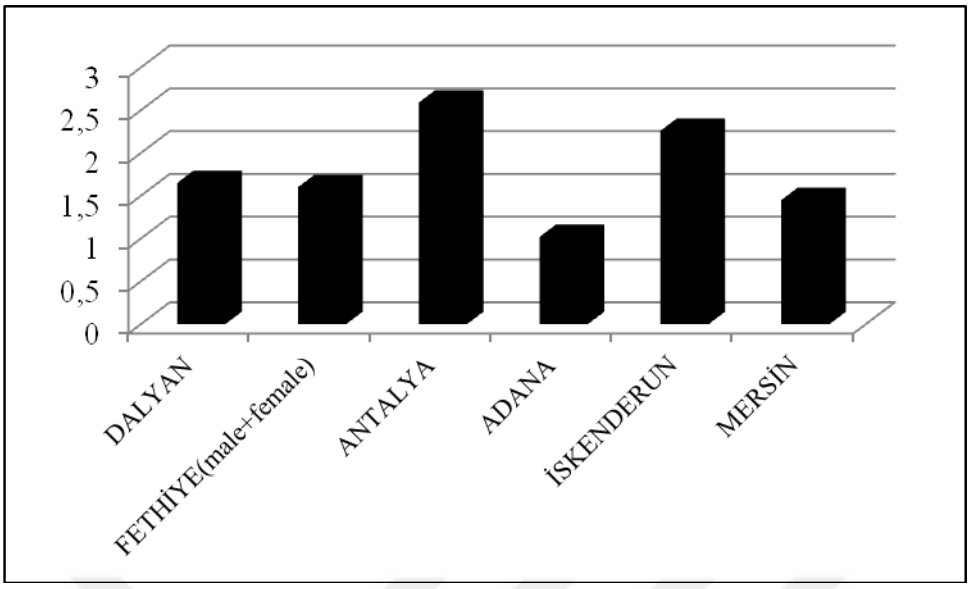


Figure 5.10 Total cyclodiens concentrations in female blue crab (ng g^{-1})

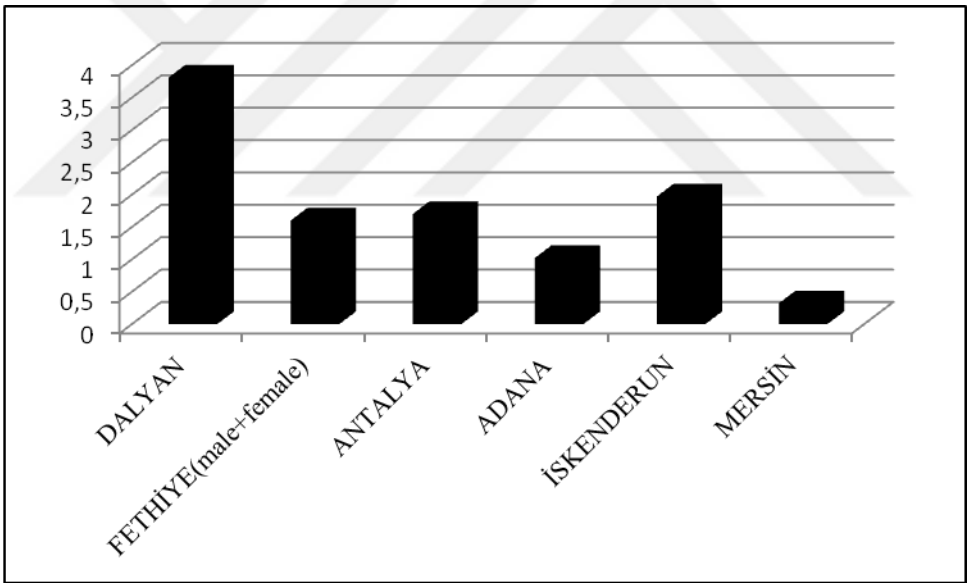


Figure 5.11 Total cyclodiens concentrations in male blue crab (ng g^{-1})

Organochlorinated pesticides and PCBs levels in biota samples from different areas in the world were given in Table 5.5. The contamination levels of OCPs and PCBs in fish and crabs from the Aegean and Mediterranean coast of Turkey were lower than samples collected from a Southern Atlantic Coastal Lagoon Watershed Argentina (Menone et al., 2001), Qiantang River China (Zhou et al., 2008), sandy beaches in California (Dugan et al., 2005) Gulf of Naples, Southern Italy (Naso et al., 2005). Lagoon of Venice (Ricciardi et al., 2010).Danube Delta Romania (Covaci et al., 2006), and Castellon Coast Spanish Mediterranean Coast (Serrano et al., 2008). This means that the contamination of OCPs and PCBs in fish and crabs from the Aegean and Mediterranean coasts of Turkey is low as compared to the other areas.

Table 5.6 Maximum residue limits for various types of POPs in seafood for various countries (ngg^{-1} ww)

	USFDA[a]	EU[b]/OsPAR	China[c]	Canada[d]	Japan[a]	This study
ΣDDT	5000	Finland: 500	10	5000		0.8-9.3
ΣPCB	2000			2000	Offshore: 500 Coastal: 3000	9-47.5

[a] Food and Drug Administration (U.S.Food and Drug Administration, 2009)
[b] FAO Fisheries Technical Paper 473.(Ababouch et al., 2005)
[c] GB18421-2001.
[d] Canadian Food Inspection Agency (Canadian guidelines for chemical contaminants and toxins in fish and fish products, 2010).

In this study the contamination levels of ΣPCB and ΣDDT in sea food samples from the Aegean and Mediterranean coast of Turkey ranging from 79-487 and 0.7-27 ng/g wet weight respectively. Table 5.6 lists Maximum Residue Limits (MRL), tolerances and guidance levels established by the Food and Drug Administration (FDA) and various countries for poisonous or deleterious substances in seafood. The action level established by the FDA is 5000 for ΣDDT and 2000 ng g^{-1}wet wt for PCB for all species. Concentrations of ΣDDT and ΣPCB in seafood samples from the Aegean and Mediterranean coast of Turkey lower than the action level established by the FDA.

Table 5.5 Chlorinated organic pesticides and PCBs pollution levels in biota samples from different areas in the world as ng/g lipit weight

Location	Year	Sample	Heptachlor	Dieldrin	Lindane	HCB	∑DDT	∑PCB	DDT(metabolite
S Atlantic Coastal Lagoon Argentina[1]	1995-1996	Crab (Cyrtograpsus angulatus)	1-16.0	36-123	36-164	7-17.7	66-241	-	p,p'-DDT, p,p'-DDE, p,p'-DDD
Qiantang River, China[2]	2006	Crab (Eriocheir sinensis)	79-141	46	238-444	-	526	-	p,p'-DDT, p,p'-DDE, p,p'DDD, o,p'-DDT
Sandy beaches California[3]	2000-2001	Sand crab	-	-	-	-	179-6488	22-2247	p,p'-DDT, p,p'-DDE, p,p'-DDD
Venice Lagoon (Italy)[4]	2007	Crab (Carcinus aestuarii)	-	-	nd-0.18	-	558-3392	670-3695	p,p'-DDT, p,p'-DDE, p,p'DDD,o,p'DDD, o,p'-DDE
Fish Market of Istanbul,. Marmara Sea[5]	2003	Mullet (Mugil cephalus)	2.26	-	9.03	8.71	810	508.71	p,p'-DDT, p,p'-DDE, p,p'DDD, o,p'-DDT, o,p'-DDD,o,p-DDD
Gulf of Naples S Italy[6]	2003	Gray mullet (Mugil cephalus)	-	-	-	nd-32.6	nd-2095.5	3134.6-47909	p,p'-DDT, p,p'-DDE, p,p'-DDD
Danube Delta, Romania[7]	2001	Bream (Abramis brama)	-	-	50-53	7.4-33	678-2962	249-540	p,p'-DDT, p,p'-DDE, p,p'-DDD

Table 5.5 Chlorinated organic pesticides and PCBs pollution levels in biota samples from different areas in the world as ng/g lipit weight (continue)

Location	**Year**	**Sample**	**Heptachlor**	**Dieldrin**	**Lindane**	**HCB**	**Total DDT**	**Total PCB**	**DDT(metabolite)**
Castellon Coast (Spanish Medit. Coast)[8]	2001-2002	Wild and cultured gilthead seabream (Sparus aurata)	-	-	nd-37	nd-173	270-995	nd-589	p,p'-DDT, p,p'-DDE, p,p'-DDD
This study	2013	Seabream	0.02-1.8	1.3-3.5	nd-0.4	0.01-11	12-26	48-347	p,p'-DDT, p,p'-DDE, p,p'-DDD
This study	2013	Gray mullet	0.8-12.1	1.7-5.8	0.02-0.5	0.7-16	9-43	153-487	p,p'-DDT, p,p'-DDE, p,p'-DDD
This study	2013	Crab	nd-0.27	0.2-8.4	nd-0.03	nd-1.2	0.7-27	79-295	p,p'-DDT, p,p'-DDE, p,p'-DDD

nd:not detected [1]Menone et al., 2001 [2]Zhou et al., 2008
[3]Dugan et al., 2005 [4]Ricciardi et al., 2010 [5]Coelhan et al., 2006
[6]Naso et al., 2005 [7]Covaci et al., 2006 [8]Serrano et al., 2008

5.3 Health Risks Assesment

A health risk assessment is a health questionnaire, used to provide individuals with an evaluation of their health risks and quality of life (Baker, Dejoy, Wilson, 2007). In this study, health risk assesment was analyzed about OCPs and PCBs due to consumed sea food. Annual per capita fish consumption is 7,081 kg in Turkey (TÜİK, 2013). Fish consumption is very low in comparison to many European countries. While the annual average fish consumption in the world is about 20,7 kg, this rate increase to 25 kg in the European Union countries (World Review of Fisheries and Aquaculture Part 1, 2012). Fish consumption per person is 0.89 kg monthly in West Mediterranean Region in Turkey.

In Tables 5.7 the Acceptable Daily Intake (ADI) for each pesticide is reported (WHO, 2003). ADI was defined on experimental basis and represents the quantity of a contaminant ingested daily (ng per kg of body weight) with which no adverse health effects should be observed. Together with ADI in Tables 5.7 is reported the Total ADI for a person weighing 70 kg (simply the ADI multiplied by 70) and the average daily intake in West Mediterranean Region in Turkey deriving from fish consumption. Obviously the ADI set by WHO refers to the total amount of a pesticide that is ingested through all kind of food and not only through fish consumption. There is a difference between MRL and ADI. MRLs are important for commercial purposes while ADIs represent guidelines for the consumer For example a fish sample with one pesticide below the MRL may lead to an intake over the ADI if consumed in large quantities and viceversa a fish sample with one pesticide over the MRL may lead to an intake below the ADI if consumed only in small quantities.

Estimated daily intakes (EDI) of Dieldrin, Endrin, Heptachlor, DDTsthrough sea food by human (average body wt. 70 kg) forTurkey were calculated (Table 5.7).

$$EDI\left(\frac{\frac{ng}{day}}{kg}\right) = \frac{Daily\ fish\ consumption\left(\frac{g}{day}\right) \times OCP\ concentration\left(\frac{ng}{g}\ wet\ weight\right)}{Human\ body\ weight\ (kg)}$$

As shown in Tables 5.7 the estimated daily intake deriving from the estimated daily fish consumption in Turkey is very much below the ADI. This is valid for all OCPs, at least in the areas investigated. This represents a good indication for Turkish fish consumers.

Table 5.7 Estimated daily intakes (EDI) of dieldrin, endrin, heptachlor, DDTs through sea food by human (average body wt. 70 kg) in Turkey

EDI (ng day^{-1} kg^{-1})		Dieldrin	Endrin	Heptachlor	∑DDTs
Dalyan	Sea bream	0.14	0.23	0.09	1.25
	Gray mullet	0.20	0.32	0.11	1.81
	Blue crab (F)	0.06	0.08	0.01	0.71
	Blue crab (M)	0.30	0.06	0.00	0.97
Fethiye	Sea bream	0.19	0.23	0.00	0.85
	Gray mullet	0.21	0.19	0.15	1.57
	Blue crab(F+M)	0.09	0.06	0.00	0.34
Antalya	Sea bream	0.11	0.06	0.00	1.26
	Gray mullet	0.20	0.07	0.31	2.25
	Blue crab(F)	0.08	0.16	0.00	1.03
	Blue crab (M)	0.06	0.08	0.02	0.23
Adana	Sea bream	0.16	0.14	0.00	1.21
	Gray mullet	0.22	0.18	0.95	1.28
	Blue crab (F)	0.06	0.04	0.00	0.22
	Blue crab (M)	0.08	0.01	0.01	0.31
Iskenderun	Sea bream	0.07	0.19	0.07	0.65
	Gray mullet	0.12	0.22	0.09	0.68
	Blue crab (F)	0.17	0.05	0.00	0.27
	Blue crab (M)	0.16	0.02	0.00	0.38
Mersin	Sea bream	0.13	0.11	0.01	0.92
	Gray mullet	0.11	0.14	0.05	0.53
	Blue crab (F)	0.08	0.05	0.00	0.91
	Blue crab (M)	0.02	0.01	0.00	0.05
ADI ng kg^{-1} bw					
FAO/WHO*		100	200	500	2000

EDI: Estimated Daily Intake
ADI: Acceptable Daily Intake
*FAO/WHO, 2003

Table 5.8 shows the recommended monthly fish consumption limits for PCB for fish consumers based on EPA's default values for risk assessment parameters. Consumption limits have been calculated as the number of allowable fish meals per month, based on the ranges of PCBs in the consumed fish tissue. In this case the limits depend upon (a) the amount consumed; (b) contaminant concentrations; and (c) risk of concern (for example, non-cancer versus cancer endpoints).

Table 5.8 Monthly fish consumption limits of PCBs (United State enviromental protection agency, 1999)

Risk-based consumption limit	Non-cancer health endpoints	Cancer health endpoints
Fish meals/month	Fish tissue concentrations (ppm, w/w)	Cancer health endpoints (ppm, w/w)
16	>0.006–0.012	>0.0015–0.003
12	>0.012–0.016	>0.003–0.004
8	>0.016–0.024	>0.004–0.006
4	>0.024–0.048	>0.006–0.012
3	>0.048–0.064	>0.012–0.016
2	>0.064–0.097	>0.016–0.024
1	>0.097–0.19	>0.024–0.048
0.5	>0.19–0.39	>0.048–0.097
None (<0.5)[a]	>0.39	>0.97

[a]None=noconsumption is recommended.

Average PCBs levels in fish tissue are 0.026 ppm for sea bream 0.030 ppm for gray mullet and 0.020 ppm for blue crab in wet weight. Four fish meals (average fish meal size 0.227 kg) per month for sea bream and gray mullet based on the cancer health endpoint can safely be consumed. However eight crab meals per month can safely be consumed. EPA recommends using the more conservative of the two limits, for PCBs, this is the consumption limit based on the cancer endpoint.

5.4 Cluster Analysis

Cluster analysis, (hierarchical clustering, Bray Curtis), was utilized to appraise the complete linkage between groups on the transformed data (Table 5.3) collected from a number of different stations for blue crab (Figure 5.12). Two main groups, (G1 and

G2), are joined to each other at the similarity level of 95%. Group G1, comprising stations Adana Fethiye Iskenderun. G2 contains Mersin Dalyan Antalya. Two subgroups: stations Fethiye Iskenderun are different from the Mersin Dalyan Antalya subgroup stations. These subgroups are linked to each other with more than 98% similarity.

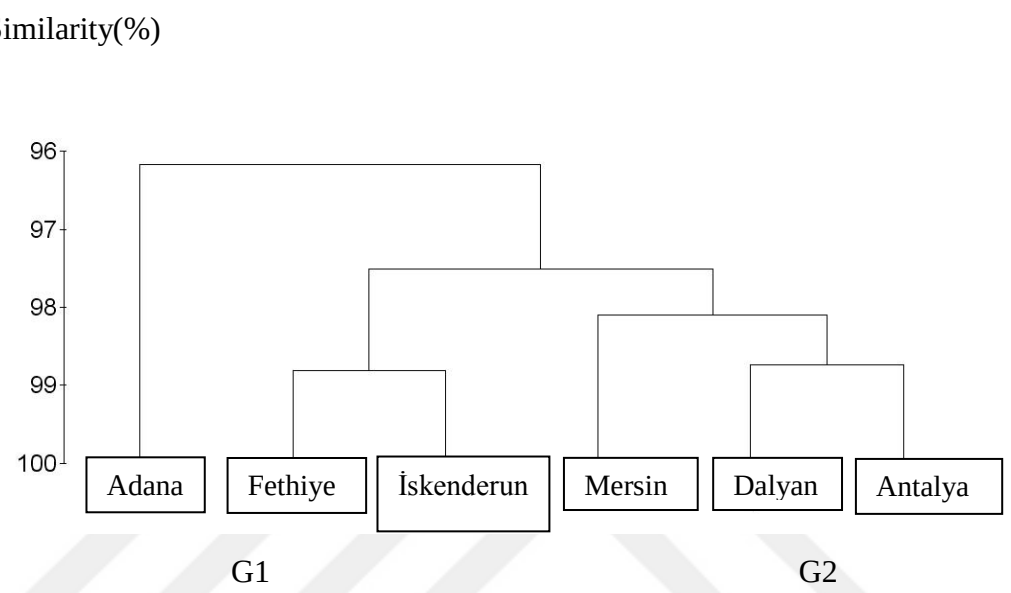


Figure 5.12 Dendogram of OCPs data classification for blue crab showing corresponding location

Cluster analysis, (hierarchical clustering, Bray Curtis), was utilized to appraise the complete linkage between groups on the transformed data (Table 5.3) collected from a number of different stations for sea bream (Figure 5.13). Two main groups, (G1 and G2), are joined to each other at the similarity level of 95%. Group G1, comprising stations Mersin Dalyan Antalya. G2 contains Adana Fethiye Iskenderun.

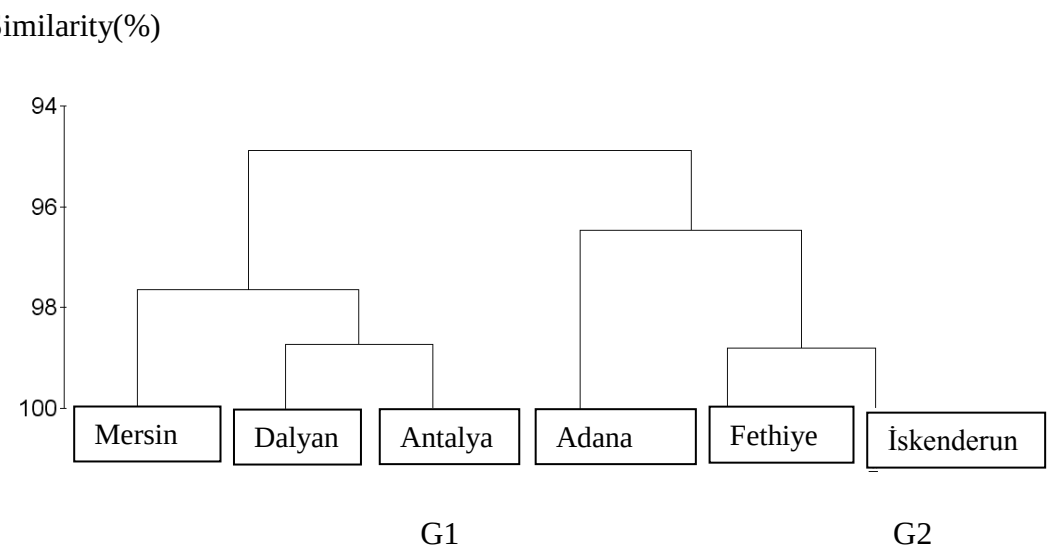


Figure 5.13 Dendogram of OCPs data classification for sea bream showing corresponding location

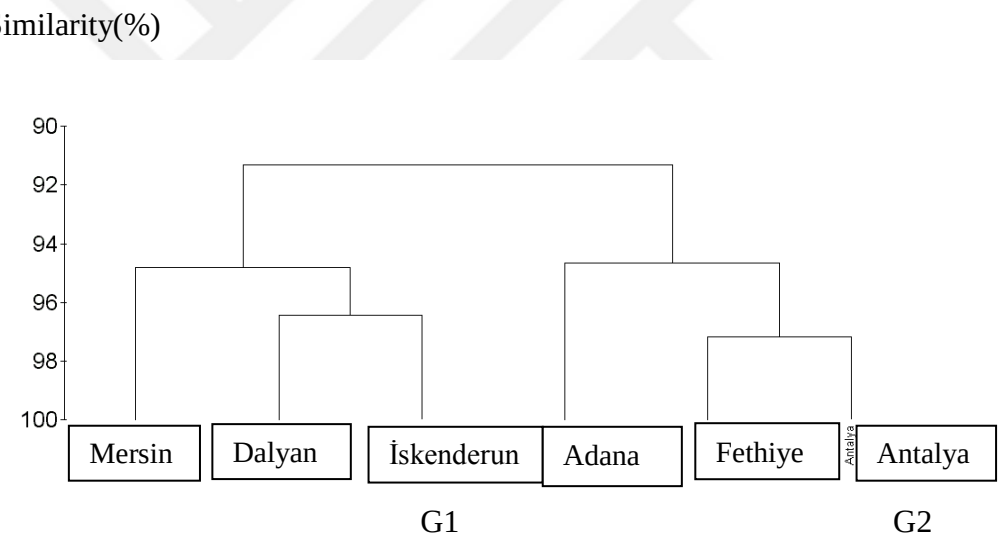


Figure 5.14 Dendogram of OCPs data classification for gray mullet showing corresponding location

Cluster analysis, (hierarchical clustering, Bray Curtis) was utilized to appraise the complete linkage between groups on the transformed data (Table 5.3) collected from a number of different stations for gray mullet (Figure 5.14). Two main groups, (G1 and G2), are joined to each other at the similarity level of 91%. Group G1, comprising stations Mersin, Dalyan, Iskenderun. G2 contains Adana, Fethiye, Antalya.

CHAPTER SIX
CONCLUSIONS

The thesis represents the first detailed study of determination of OCPs and PCBs in blue crab, gray mullet and sea bream from the Aegean and Mediterranean coast of Turkey. Analysis of biota samples showed that the maximum concentration of ΣOCPs (33.15 ng g^{-1}) was found in gray mullet samples collected from Antalya due to dense agricultural activities in the surroundings of Beymelek Lagoon (Antalya). The minimum concentration of ΣOCPs (0.87 ng g^{-1}) was found in male blue crab samples collected from Mersin. It is expected that minimum value was found in Goksu Delta (Mersin) is classified as a Wetland of International Importance according to the Ramsar Convention on Wetland.

The contamination levels of OCPs and PCBs in fish and crabs from the Aegean and Mediterranean coast of Turkey is low as compared to the other areas. The contamination levels of ΣPCB and ΣDDT in sea food samples from the Aegean and Mediterranean coast of Turkey ranging from 43-226 and 0.6-20.2 ng/g wet weight respectively.

The highest ΣDDTs concentrations were found in gray mullet samples in Antalya. Lowest ΣDDTs concentrations were found in male blue crab samples in Mersin similar to lowest ΣOCPs. The result of DDD/DDE ratios indicates in biota samples were lower than 1, indicating relatively aerobic conditions for Aegean and Eastern Mediterranean coast of Turkey.

The highest concentrations of HCB (8.71 ng g-1) and lindane (0.23 ng g-1 dry wt) were found in sea bream samples in Dalyan because OCPs were used in agriculture in the surrounding area of Dalyan. HCB and lindane were only observed below detection limit in blue crab samples in Adana and Mersin.

The highest concentration of ΣPCBs (226 ng g^{-1}) was found in samples collected in sea bream in Dalyan. The minimum concentration of ΣPCBs was found in sea bream samples in Antalya (43 ng g^{-1} dry wt).

In this study, health risk assesments were analyzed about OCPs and PCBs due to consumed sea food. The estimated daily intake deriving from the estimated daily fish consumption in Turkey is very much below the ADI. This is valid for all organochlorine pesticides, at least in the areas investigated.This represents a good indication for Turkish fish consumers.

MRL, tolerances and guidance levels established by the FDA is 5000 for ΣDDT and 2000 ng g^{-1}wet wt for PCB for all fish. Concentrations of ΣDDT and ΣPCB in sea food samples from the Aegean and Mediterranean coast of Turkey lower than the action level established by the FDA.

Average PCBs levels in fish tissue are 0.026 ppm for sea bream 0.030 ppm for gray mullet and 0.020 ppm for blue crab in wet weight. Four fish meals (average fish meal size 0.227 kg) per month for sea bream and gray mullet based on the cancer health endpoint can safely be consumed. However eight crab meals per month can safely be consumed. EPA recommends using the more conservative of the two limits, for PCBs, this is the consumption limit based on the cancer endpoint.

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