DOKUZ EYLUL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVESTIGATION OF CONTAMINANT CHARGES INTO İZMİR INNER BAY BY SURFACE WATERS

by
Sanem KELEŞ

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İZMİR

INVESTIGATION OF CONTAMINANT CHARGES INTO İZMİR INNER BAY BY SURFACE WATERS

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İZMİR

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"INVESTIGATION OFCONTAMINANT CHARGES INTO İZMİR INNER BAY BY SURFACE WATERS"** completed by **SANEM KELEŞ** under supervision of **ASSIST.PROF.DR.GÖRKEM AKINCI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Assist. Prof. Dr. Görkem AKINCI

Supervisor

Assoc.Prof.Dr. Erol KAYA

(Jury Member)

Assoc.Prof Dr. Nurdan BÜYÜKKAMACI

(Jury Member)

Prof.Dr. Mustafa SABUNCU
Director
Graduate School of Natural and Applied Sciences

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INVESTIGATION OF CONTAMINANT CHARGES INTO İZMİR INNER BAY BY SURFACE WATERS

ABSTRACT

The total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), and heavy metals concentrations and pH levels in the waters and in the sediments of the rivers feeding Izmir middle and inner Bay were investigated in the content of this thesis. Additionally, total solids and suspended solids concentrations in water samples are detected and settable solids concentrations are determined. Furthermore, the contaminant loads discharged into the Bay from each river was determined.

According to the findings; i) the river water pH values vary between 5.86 and 9.4 where sediment pHs express a slight alkali to alkali levels and vary between 7.8-8.8, ii) explain it before TSM concentrations are very high in the river waters, and the 98% of the solid material carried to the Bay by the rivers is settlable. This amount of settlable solids result with 4 cm of average annual sediment accumulation in the bottom of the inner Bay. The height of accumulation will be higher in the regions close to the shore, where the water circulation is poor and the water depth is short. This is an important issue for Izmir, since inner Bay is an international and commercially active harbour, which is previously dredged to remove the sediment that accumulated in the docking line of the ships, iii) the water TPH concentrations vary between 120-4000 mg/L and the water TPH concentrations are higher in the rivers having large catchment areas and high annual flows, the annual TPHs discharge to the Bay is 170.000 tons, and if the volume of the inner Bay is considered, TPHs concentration in inner Bay waters will be as high as 41.7 mg/L, iv) the total water PAHs levels vary between 2.4 and 16.9 mg/L, and the contribution of total PAHs concentration to TPHs concentration varies between 0.5 to 2.0 % for sampled waters, v) it is observed that 3 Ring PAHs contribution to total PAHs has a portion is the highest and it is between 22.43-84.47 %, iv) Chrysene has 4 benzene rings and its concentration is much higher than the other 4 ring structured PAHs, since it is emitted during the combustion of coal and fuel oil, vii) most of the

detected heavy metal concentrations in the rivers are above Class I water standards and express low quality water properties, viii) the annual total heavy metal load enters to the Bay is found as 55.75 tons/year, ix) Organic matter content of the dry sediment varies between 4.51% and 31.33%. Elevated organic matter levels are measured in the sediments of Bornova and Manda rivers that receive water from urban and small industry areas, x) TPHs levels in the sediments vary between 3563 mg/kg and 13998 mg/kg, xi) the minimum and maximum PAHs concentrations in the river sediments are measured as 44.22 mg/kg and 193.71 mg/kg, respectively, and it was stated that 1.2-1.4% of sediment TPHs are originated from PAHs, especially the groups with 3 and 4 benzene rings, xii) the maximum allowable limit for PAHs is 5 mg/kg for the clean soils according to the Turkish Soil Contamination Control Regulation (TSCCR, 2001). When the sediment PAHs concentrations are considered, it is seen that the river sediments are seriously polluted, xiii) most of the heavy metal concentrations in the river sediments exceed the limits given in TSCCR, xiv) the levels of TPHs are found higher in the largest and the smallest sediment fractions than the medium size fractions, xv) it is recognized that water and sediment PAHs concentrations are strongly correlated for all of the rivers in Summer and Winter seasons, xvi) there is an indication of a possible adsorption of PAHs in water on to the sediment particles, or on to the settlable solids in the water, annually 317.18 tonnes of PAHs are discharged into the inner Bay, which may create 0.78 mg/L PAHs concentration, xvii) If the amount of contaminant load collected from unit basin area is considered, the investigated rivers can be ranked in descending order as follows:

Melez > Manda > Old Gediz > Bostanlı > Sepetçi > Bornova > Harmandalı

Keywords: sediment, Izmir Bay, heavy metals, total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs).

İZMİR İÇ KÖRFEZE YÜZEYSEL SULAR VASITASIYLA TAŞINAN KİRLETİCİLERİN ARAŞTIRILMASI

ÖZ

İzmir iç ve orta körfezlerini besleyen derelerin Toplam Petrol Hidrokarbonları (TPH), Polisiklik Aromatik Hidrokarbonları (PAH), ağır metal konsantrasyonları, su ve sedimentteki pH seviyeleri bu tezin içeriğinde incelenmiştir. Ek olarak, su örneklerinde toplam katı maddeler, askıda katı maddeler ve çöken katı madde konsantrasyonları tespit edilmiştir. Ayrıca, her dereden körfeze deşarj olan kirletici madde yükleri belirlenmiştir.

Bulgulara göre; i) dere suyu pH değerleri 5,86 ve 9,4 arasında değişmektedir, sediment pH'larının hafif alkali ve alkali seviyelerinde 7,8-8,8 aralığında değişmektedir, ii) TKM konsantrasyonları dere sularında çok yüksektir ve derelerden körfeze taşınan katı maddelerin %98'i çökelebilir. İç körfez tabanında bu miktardaki çökelebilir katı madde yıllık ortalama 4 cm kadar sediment birikimine yol açması beklenmektedir. Birikimin yüksekliği kıyıya yakın yani su sirkülâsyonunun zayıf ve derinliğin az olduğu bölgelerde daha fazla olacaktır. Bu İzmir için önemli bir sorundur çünkü iç körfez uluslararası ve ticari olarak aktif bir limandır ve daha önceden gemilerin yanaşma hattında birikmiş sedimentler temizlemek amacı ile taranmıştır, iii) suda TPH konsantrasyonları 120-4000 mg/L arasında değişmekte ve havza alanları geniş olan ve yıllık akışı yüksek olan derelerde TPH konsantrasyonları daha yüksek olmaktadır, körfeze deşarj edilen yıllık TPH miktarı 170.000 tondur ve iç körfezin hacmi dikkate alındığında , iç körfez sularındaki TPH konsantrasyonları 41,7 mg/L gibi yüksek bir miktar olacaktır, iv) örnek sularda toplam PAH seviyeleri 2,4 ve 16,9 mg/L arasında değişmekte ve toplam PAH konsantrasyonunun TPH konsantrasyonuna katkısı %0,5 ile %2.0 arasındadır, v) toplam PAH içinde 3 halkalı PAH'ların payı en büyüktür ve %22,43- %84,47 aralığındadır, vi) Chrysene 4 benzen halkasına sahiptir ve konsantrasyonu diğer 4 halkalı PAH bileşiklerinden daha yüksektir, bunun nedeni kömür ve fuel oil gibi yakıtların yanması sırasında açığa çıkmaktadır, vii) derelerde tespit edilen ağır metal konsantrasyonların 1.sınıf su sınır değerlerinden yüksektir ve bu nedenle düşük

kaliteli su özelliklerini göstermektedir, viii) körfeze giren yıllık toplam ağır metal yükü 55,74 ton/yıl olarak belirlenmiştir, ix) kuru sedimentte organik madde içeriği %4,51 ve %31,33 arasında değişmektedir. Suyu kentsel ve küçük sanayi bölgelerinden toplayan Bornova ve Manda derelerindeki sedimentlerde yüksek seviyede organik madde ölçülmüştür, x) sedimentlerdeki TPH seviyeleri 3563 mg/kg ve 13998 mg/kg arasında değişmektedir, xi) dere sedimentlerindeki minimum ve maksimum PAH konsantrasyonları sırasıyla 44,22 mg/kg ve 193,71 olarak ölçülmüştür ve %1,2-%1,4'lük bir kısmı 3 ve 4 benzen halkalılar baskın olmak üzere PAH kaynaklıdır, xii) Türk Toprak Kirliliği Kontrol Yönetmeliğine (TTKKY) göre; temiz toprakta kabul edilebilen PAH miktarı 5 mg/kg la sınırlıdır. Sediment PAH konsantrasyonları düşünüldüğünde, dere sedimentlerinin ciddi seviyede kirli olduğu görülmektedir. xiii) bir çok dere sedimentlerindeki ağır metal konsantrasyonlarıTTKKY'nin belirttiği sınırı aşmaktadır. xiv) TPH seviyeleri büyük ve küçük tanecikli sediment fraksiyonlarında, orta büyüklükteki taneciklere göre daha yüksek, seviyede bulunmuştur, xv) su ve sediment PAH konsantrasyonlarının bütün derelerde yaz ve kış mevsimlerinde güçlü bir şekilde ilişkili olduğu görülmektedir, xvi) sudaki PAH'ın sediment parçalarına veya olası sudaki çökebilir katılara adsorpsiyonuna dair bulgular mevcuttur, yıllık olarak ortalama 0,78 mg/L PAH konsantrasyonu oluşturabilecek seviyede olan 317,18 ton PAH iç körfeze deşarj edilmektedir, xvii) birim havza alanından toplanan kirletici yüklerin miktarı dikkate alındığında incelenen dereler büyükten küçüğe doğru aşağıdaki gibi sıralanmaktadır:

Melez > Manda > Old Gediz > Bostanlı > Sepetçi > Bornova > Harmandalı

Anahtar Kelime: sediment, Izmir Körfezi, ağır metal, Toplam Petrol Hidrokarbonları (TPH), Polisiklik Aromatik Hidrokarbonları (PAH).

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CHAPTER ONE
INTRODUCTION

In Turkey, at the beginning of 1970's, the event of environment pollution became the current issue. In those years, water, air and land pollution began. In recent years, rapid development of industry, unsupervised, unplanned and rapid settlements, wrong parceling and excessive population growth caused increase of pollution in Turkey. Water pollution problems firstly appeared around Halic, which is an estuary in Istanbul, and 1940's first scientific measurements had been made. After Halic, in the middle of 1960's, pollution began in Izmir and Izmit Bays and in 1970's Mersin, Iskenderun and Edremit Bays, increasingly (Deniz kirliliği, 2010) .

Rapid population growth, reduction of capitation area, spread of industry, mechanization of agriculture cause to pollution of environment by implication of water. Above all of them, people are not aware enough of the importance of the environmental conditions for life. In Turkey domestic, industrial, agricultural activities are not kept under control for many reasons. That's why today, many of the pollution in the watershed are known to reach significant size (Mansuroğlu, 2004; Nas *et al*., 2004). In Turkey, there is a little number of industry organizations with treatment plant, even most of them don't have treatment plants or existing treatment plants are not used actively, so surface water pollution is increasing rapidly (Burak *et al*., 1997; Yıldırım *et al*., 2004; Akman *et al*., 2004). In addition, rapid increase of unplanned settlement, sewage systems and polluted water streams that came from the area of waste storage land, are the considerable reasons of the pollution of underground water (Mansuroğlu, 2004; Yüksel *et al*., 1997).

Excessive pollution is determined in some of the present surface and ground waters in Turkey due to reasons such as rapid population growth, industrial activities, increase of fertilizer and herbicide use in agriculture and environmental unconsciousness. So that, some of the surface waters of basins have been polluted in serious levels. Aegean is one of the seven geographical regions in Turkey. When the water basin pollution is reviewed it can be seen that the region faces with a certain

pollution rate as a result of Bakır Stream, soma lignite and oil production facilities activities. Load of sewage water depends on the population density. In the Aegean Region, Gediz is in a highly polluted surface water condition. Domestic waste, industrial waste and as a result of agricultural activities nitrogen, organic matter and heavy metals cause the river to have IV. class water quality. Büyük Menderes and Küçük Menderes rivers have III. and IV. class pollution levels (Akın *et al*., 2007*).* Depending on the environment Act 1988, published in the Water Pollution Control Regulations (SKKY), comprehensive water quality management regulations were introduced. According to this regulation, surface water divided into 4 classes by their quality. Water Quality Class Definition**:** I- high quality water, II- low quality water, III-dirty water, IV-very polluted water (Burak *et al*., 1997; Dağlı, 2005).

Another type of pollution involves the disruption of sediments (fine-grained powders) that flow from rivers into the sea. Contaminated sediments are crucial indicators of pollution in aquatic environments and can be defined as soils, sand, organic matter, or minerals accumulated at the bottom of a water body (USEPA, 1998). Contaminants contained in sediments can be released to overlying waters and sediments can be important sources of contaminants in waters (Allen, 1995 ; Güven & Akıncı, 2008). Many of the sediments in seas, rivers, lakes, and oceans have been contaminated by pollutants. These pollutants are directly discharged by industrial plants and municipal sewage treatment plants, others come from polluted runoff in urban and agricultural areas, and some are the result of historical contamination (Begum *et al*., 2009; Pempkowiak *et al*., 1999).

There are various water pollutants in the environment grouped as organics and inorganics. Organic pollutants consume dissolved oxygen in the water and cause to pollution. Examples are: Hydrocarbons, PCB, DDT, Detergents, Polycyclic Aromatic Hydrocarbons (PAHs), total petroleum hydrocarbons (TPHs)...etc. Among these pollutants, PAHs and TPHs are the ones that will be handled in this study. On the other hand, Inorganic wastes are also polluting the water systems significantly. These are salts, metals, acidic mineral and minerals (Su kirlenmesi, 2010). In this study heavy metals such as Cr, Cu, Pb, Zn, Cd, Ni, and Al will be observed in detail.

Izmir Bay has been polluted by urban and industrial wastewater discharges for several years. Continued discharges have caused a serious pollution of organics and heavy metals in the sediments in this area. In past, partial dredging of the sediments was done and the dredged material was dumped in a natural ditch in the Outer Bay (Aksu 1998; Atgın*et al*., 2000; Cihangir & Küçüksezgin, 2003). The streams and hundreds of small domestic discharge outlets, flow to the bay. The main industries in the region include food processing, beverage manufacturing and bottling, tanneries, oil, soap and paint production, chemical industries, paper and pulp factories, textile industries, metal processing and timber processing (UNEP, 1993).

Izmir Bay has a highly disturbed environment due to the rapid increase of the population and development of industry. Untreated domestic and industrial wastes, atmospheric and agricultural pollution, shipping, dredging activities in the harbor and the disposal of the dredged material to the outer bay are the major sources of pollution. Among these, domestic and industrial wastes including heavy metal contamination are the most important sources of pollution (Atgın *et al*., 2000). Prevalent industries with heavy metal content in their wastewaters are: textile (Manda and Sepetci Creeks), chemicals (Melez and Sepetci Creeks), metal (Manda, Melez, Ilica, and Bostanlı Creeks), automotive (Manda Creek) industries, the tanneries (on Manda and Melez Creeks), and the industrial zones (Melez and Old Gediz 1 Creeks) (IZTO, 1995).

The presented study aims to investigate the level loads of the organic and inorganic contaminant discharges in to the Izmir inner Bay by surface water. To achieve this, seasonal water and sediment samples collected from 7 rivers discharging in to the Bay (Old Gediz Harmandalı, Bostanlı, Sepetçi, Bornova, Manda, Melez) were analyzed for their TPH (Total Petroleum Hydrocarbons) heavy metal (Cr, Cu, Pb, Zn, Cd, Ni, Al) and PAH (Polycyclic Aromatic Hydrocarbons) concentrations in order to make a proper assessment of contaminant load entering the Bay.

CHAPTER TWO
BACKGROUND INFORMATION AND LITERATURE SURVEY

2.1 Sources of Water Pollution

Surface waters and ground waters are the water resources under the effect of various pollutants. There are also two different ways in which pollution can occur. If pollution comes from a single location, such as a discharge pipe attached to a factory, it is known as point-source pollution. Other examples of point source pollution include an oil spill from a tanker, a discharge from a smoke stack (factory chimney), or someone pouring oil from their car down a drain. A great deal of water pollution happens not from one single source but from many different scattered sources. This is called non-point-source pollution. When point-source pollution enters the environment, the place most affected is usually the area immediately around the source. For example, when a tanker accident occurs, the oil slick is concentrated around the tanker itself and, in the right ocean conditions, the pollution disperses the further away from the tanker you go. This is less likely to happen with non-point source pollution which, by definition, enters the environment from many different places at once (Woodford, 2006).

Sometimes pollution that enters the environment in one place has an effect hundreds or even thousands of miles away. This is known as transboundary pollution.

Pollution is also caused when silt and other suspended solids, such as soil, wash off plowed fields, construction and logging sites, urban areas, and eroded river banks when it rains. Under natural conditions, lakes, rivers, and other water bodies undergo Eutrophication, an aging process that slowly fills in the water body with sediment and organic matter. When these sediments enter various bodies of water, fish respiration becomes impaired, plant productivity and water depth become reduced, and aquatic organisms and their environments become suffocated.

Pollution in the form of organic material enters waterways in many different forms as sewage, as leaves and grass clippings, or as runoff from livestock feedlots and pastures. When natural bacteria and protozoan in the water break down this organic material, they begin to use up the oxygen dissolved in the water. Many types of fish and bottom-dwelling animals cannot survive when levels of dissolved oxygen drop below two to five parts per million. When this occurs, it kills aquatic organisms in large numbers which leads to disruptions in the food chain (Krantz *et al*., n.d.).

Another type of pollution involves the disruption of sediments (fine-grained powders) that flow from rivers into the sea. Dams built for hydroelectric power or water reservoirs can reduce the sediment flow. This reduces the formation of beaches, increases coastal erosion (the natural destruction of cliffs by the sea), and reduces the flow of nutrients from rivers into seas (potentially reducing coastal fish stocks). Increased sediments can also present a problem. During construction work, soil, rock, and other fine powders sometimes enter nearby rivers in large quantities, causing it to become turbid (muddy or silted). The extra sediment can block the gills of fish, effectively suffocating them. Construction firms often now take precations to prevent this kind of pollution from happening (Woodford, 2006).

2.2 Pollutants in Surface Water

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources (Anonymous, 2007).

Most water pollution doesn't begin in the water itself. In the oceans, around 80 percent of ocean pollution enters our seas from the land. Virtually any human activity can have an effect on the quality of our water environment. When farmers fertilize the fields, the chemicals they use are gradually washed by rain into the

groundwater or surface waters nearby. Sometimes the causes of water pollution are quite surprising. Chemicals released by smokestacks (chimneys) can enter the atmosphere and then fall back to earth as rain, entering seas, rivers, and lakes and causing water pollution. Water pollution has many different causes and this is one of the reasons why it is such a difficult problem to solve (Woodford, 2006). In developed countries, sewage, nutrients, waste water, chemical waste, oil pollution, plastics and other forms of pollution often causes problems. Many causes of pollution including sewage and fertilizers contain nutrients such as nitrates and phosphates. In excess levels, nutrients over stimulate the growth of aquatic plants and algae. Excessive growth of these types of organisms consequently clogs our waterways, use up dissolved oxygen as they decompose and block light to deeper waters. This, in turn, proves very harmful to aquatic organisms as it affects the respiration ability or fish and other invertebrate that reside in water (Woodford, 2006) .

Sewage contains all kinds of other chemicals, from the pharmaceutical drugs people take to the paper, plastic, and other wastes they flush down their toilets. When people are sick with viruses, the sewage they produce carries those viruses into the environment. It is possible to catch illnesses such as hepatitis, typhoid, and cholera from river and sea water. Sewage discharged into coastal waters can wash up on beaches and cause a health hazard. People who bathe or surf in the water can fall ill if they swallow polluted water yet sewage can have other harmful effects too. It can poison shellfish (such as cockles and mussels) that grow near the shore. People who eat poisoned shellfish risk suffering from an acute and sometimes fatal illness called paralytic shellfish poisoning. Shellfish is no longer caught along many shores because it is simply too polluted with sewage or toxic chemical wastes that have discharged from the land nearby (Woodford, 2006). When nutrients are suitably treated and used in moderate quantities, sewage can be a fertilizer. It returns important nutrients to the environment, such as nitrogen and phosphorus, which plants and animals need for growth. The trouble is that sewage is often released in much greater quantities than the natural environment can cope with. Chemical fertilizers used by farmers also add nutrients to the soil, which drain into rivers and

seas and add to the fertilizing effect of the sewage. Together, sewage and fertilizers can cause a massive increase in the growth of algae or plankton that overwhelms huge areas of oceans, lakes, or rivers (Woodford, 2006)

Chemical waste includes chemical both by products of large manufacturing facilities and laboratories, as well as the smaller-scale solvents and other chemicals disposed of by households. Chemical waste may fall under the classification of hazardous waste depending on the nature of the chemicals – for example, chemicals such as ethanol and glycerol don't require special disposal procedures. Health and safety legislation varies internationally, and dictates the manner in which chemical waste must be handled and disposed of (What is chemical waste, 2010*).* Industrial and agricultural work involves the use of many different chemicals that can run-off into water and pollute it.

Metals and solvents from industrial work can pollute rivers and lakes. These are poisonous to many forms of aquatic life and may slow their development, make them infertile or even result in death. Pesticides are used in farming to control weeds, insects and fungi. Run-offs of these pesticides can cause water pollution and poison aquatic life. Subsequently, birds, humans and other animals may be poisoned if they eat infected fish. Petroleum is another form of chemical pollutant that usually contaminates water through oil spills when a ship ruptures. Oil spills usually have only a localized affect on wildlife but can spread for miles. The oil can cause the death of many fish and stick to the feathers of seabirds causing them to lose the ability to fly (The causes of water pollution, n.d).

Oil spills make up about 12% of the oil that enters the oceans comes from tanker accidents; over 70% of oil pollution at sea comes from routine shipping and from the oil people pour down drains on land the rest come from shipping travel, drains and dumping. However, what makes tanker spills so destructive is the sheer quantity of oil they release at once — in other words, the concentration of oil they produce in one very localized part of the marine environment (Woodford, 2006).

Plastic is far and away the most common substance that washes up with the waves. There are three reasons for this: plastic is one of the most common materials, used for making virtually every kind of manufactured object from clothing to automobile parts; plastic is light and floats easily so it can travel enormous distances across the oceans; most plastics are not biodegradable (they do not break down naturally in the environment), which means that things like plastic bottle tops can survive in the marine environment for a long time. (A plastic bottle can survive an estimated 450 years in the ocean and plastic fishing line can last up to 600 years). While plastics are not toxic in quite the same way as poisonous chemicals, they nevertheless present a major hazard to seabirds, fish, and other marine creatures (Woodford, 2006).

Pathogens are another type of pollution that proves very harmful. They can cause many illnesses that range from typhoid and dysentery to minor respiratory and skin diseases. Pathogens include such organisms as bacteria, viruses, and protozoan. These pollutants enter waterways through untreated sewage, storm drains, septic tanks, runoff from farms, and particularly boats that dump sewage. Though microscopic, these pollutants have a tremendous effect evidenced by their ability to cause sickness (Krantz *et al*.,n.d.).

Other forms of pollution; these are the most common forms of pollution. Factories and power plants cause heat of thermal pollution. This pollution causes problems in the rivers. Raising temperature reduces the amount of dissolved oxygen in the water and also reduces the level of aquatic life that the river can support.

Chemical pollution, occur in water with organic and inorganic substances. The most common organic pollution types are proteins, fats, food and hydrocarbons (Bükülmez, 2009). In this section, heavy metals of chromium(Cr) , copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni), aluminum(Al) as an inorganic pollutants and also total petroleum hydrocarbons (TPH) and Polycyclic Aromatic Hydrocarbons (PAH) as an organic pollutants will be mentioned in detail.

2.2.1 Heavy Metals

Environmental pollution with toxic metals is becoming a global phenomenon. As a result of the increasing concern with the potential effects of the metallic contaminants on human health and the environment, the research on fundamental, applied and health aspects of trace metals in the environment is increasing (Vernet ,1991).

The term heavy metal is often used to cover diverse range of elements which constitute an important class of pollutants. Heavy metals enter into the environment mainly via three routes: **(i)** deposition of atmospheric particulates, **(ii)** disposal of metal enriched sewage sludge's and sewage effluents and **(iii)** by-products from metal mining processes (Shrivastav, 2001).

Metals are natural constituents of rocks, soils, sediments, and water. However, over the 200 years following the beginning of industrialization huge changes in the global budget of critical chemicals at the earth's surface have occurred, challenging those regulatory systems which took millions of years to evolve (Wood & Wang , 1983).

The estimation of metal input into environment from the two latter sources is relatively easy to measure. However, atmospheric input is difficult to quantify accurately mainly due to atmospheric mixing of metal-bearing particulates and the diversity of metals and metal-emitting sources which contribute to the overall atmospheric metal pool (Wood & Wang, 1983).

The heavy metal content of sediments comes from natural sources (rock weathering, soil erosion, dissolution of water-soluble salts) as well as anthropogenic sources such as municipal wastewater-treatment plants, manufacturing industries, and agricultural activities etc. (Güven & Akıncı, 2008).

Heavy metals occur naturally as they are components of the lithosphere and are released into the environment through volcanism and weathering of rocks (Fergusson, 1990). However, large-scale release of heavy metals to the aquatic environment is often a result of human intervention (Mance, 1987; Denton *et al*., 1997). Coastal regions are some of the most sensitive environments and yet they are subject to growing human pressures (David, 2003) because of increasing urbanization, industrial development, and recreational activities. Therefore, pollution levels are often elevated in the coast because of nearby land based pollution sources (Fergusson , 1990 ; Wang *et al*., 2007).

The metals must be both abundant in nature and readily available as soluble species. Abundance generally restricts the available metals to those of atomic numbers below 40, some of which are virtually unavailable due to the low solubility of their hydroxides. Viewed from the standpoint of environmental pollution, metals may be classified according to three criteria (Wood, 1974);

(i) Non-critical (Na, Mg, Fe, K, Ca, Al, Sr, Li, Rb),

(ii) Toxic but very insoluble or very rare (Ti, Hf, Zr, W, Ta, Ga, La, Os, Ir, Ru, Ba,Rh), and

(iii) Very toxic and relatively accessible (Be, Co, Ni, Cu, Zn, Sn, Cr, As, Se, Te, Ag, Cd, Hg, Tl, Pb, Sb, Bi).

Industrial processes that release a variety of metals into waterways include mining, smelting and refining. Almost all industrial processes that produce waste discharges are potential sources of heavy metals to the aquatic environment (Denton *et al*., 2001).

Domestic wastewater, sewage sludge, urban runoff, and leachate from solid waste disposal sites are also obvious sources of heavy metals into rivers, estuaries and coastal waters (Mance, 1987). A proportion of the total anthropogenic metal input in

the sediments in near shore waters, adjacent to urban and industrial growth centers comes from the combustion of fossil fuels. Other potential sources include ports, harbors, marinas and mooring sites, also subjected to heavy metal inputs associated with recreational, commercial and occasionally, military, boating and shipping activities (Denton *et al*., 1997).

Typical pollutants generated from these activities are lead (Pb), zinc (Zn), chromium (Cr), copper (Cu), cadmium (Cd), mercury (Hg), aluminum (Al), iron (Fe), manganese (Mn), and nickel (Ni) which are considered as the most frequently found metals in sediments. Heavy metals such as cadmium (Cd), mercury (Hg), lead (Pb), copper (Cu), and zinc (Zn) are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains (Förtsner & Wittman, 1983). Among them; cadmium, lead and mercury are highly toxic at relatively low concentrations because they can accumulate in body tissues over long periods of time (Garbarino *et al*., 1995). The fate and transport of a metal in soil or aquatic environment depends significantly on the chemical form and speciation of the metal (Allen & Torres, 1991).

2.2.1.1 Chromium (Cr)

Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 mg/kg. Chromium compounds are found in the environment, due to erosion of chromium containing rocks and can be distributed by volcanic eruptions. The concentrations range in soil is between 1 and 3000 mg/kg, in sea water 5 to 800 µg/L and in rivers and lakes 26 µg/L to 5.2 mg/L. Chromium like zinc, is one of the most abundant heavy metals in the lithosphere with an average concentration of about 69 µg/g and mercury content in carbonate sediments is reported to be 0.03 µg/g (Callender, 2003).

Chromium is moderately toxic to aquatic organisms. Major coastal marine contributors of chromium are dominated by input from rivers, urban runoff, domestic and industrial wastewaters and sewage sludge (Denton *et al*., 1997). Also other main

sources in the aquatic environment include the waste stream from electroplating and metal finishing industry (Callender, 2003; Finkelman, 2005).

Levels of chromium in marine sediments range from 2.4 μg/g at unpolluted sites to 749 μg/g at grossly contaminated sites (Denton *et al*., 1997). Chromium is carcinogenic to humans and long term exposure has been associated with lung cancer in workers exposed to levels in air that in the order of 100 to 1000 times higher than usually found in the environment (Finkelman, 2005).

Cr (VI) is the dominant form of chromium in water bodies where aerobic conditions exist. Major Cr (VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations (especially Ba^{2+},Pb^{2+}, and Ag^{+}). Cr (III) is the dominant form of chromium at low pH (<4). Cr^{3+} forms solution complexes with NH_3, OH^-, Cl^-, F^-, CN^-, $SO4^{2-}$-, and soluble organic ligands. Cr (VI) is the more toxic form of chromium and is also more mobile (Chrotowski et al., 1991). Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Most of chromium released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Smith *et al*., 1995).

2.2.1.2 Copper (Cu)

Copper is a moderately abundant heavy metal with mean concentration in the lithosphere about 39 μg/g. It is an essential trace element for the growth of most aquatic organisms however it becomes toxic to aquatic organisms at levels as low as 10 μg/g (Callender, 2003). Heavily polluted sediments have been reported to exceed 200 μg/g. Inputs of copper into the natural waters come from various source including mining, smelting, domestic and industrial wastewaters, steam electrical production, incinerator emissions, and the dumping of sewage sludge (Denton *et al*., 1997).

Algaecides and antifouling paints are identified as major contributors of copper to harbor areas whereas coastal waters are generally receiving inputs from rivers and atmospheric sources (Denton *et al*., 997).

Copper is essential for good health. However, exposure to higher doses can be fatal. Long term exposure of copper results in nose irritation, mouth, and eyes, and cause headache, and diarrhea (Finkelman, 2005).

In aerobic, sufficiently alkaline systems, $CuCO_3$ is the dominant soluble copper species. The cupric ion, Cu^{2+}+, and hydroxide complexes, $CuOH^+$ and $Cu(OH)_2$ are also commonly present. Copper forms strong solution complexes with humic acids. Copper mobility is decreased by sorption to mineral surfaces. Cu^{2+} sorbs strongly to mineral surfaces over a wide range of pH values (Dzombak & Morel, 1990). The cupric ion (Cu^{2+}+) is the most toxic species of copper. Copper toxicity has also been demonstrated for $CuOH^+$ and $Cu_2(OH)_2^{2+}$ (Evanko & Dzombak, 1997).

2.2.1.3 Lead (Pb)

The major sources of Pb in natural waters include manufacturing processes, atmospheric deposition. Other sources include domestic wastewaters, sewage and sewage sludge (Denton *et al*., 1997).

Lead is reported to be in the 15 - 50 μg/g range for coastal and estuarine sediments around the world (Denton *et al*., 1997) with < 25 μg/g in clean coastal sediments.

Lead is toxic and a major hazard to human and animals. Lead has two quite distinct toxic effects on human beings, physiological and neurological. The relatively immediate effects of acute lead poisoning are ill defined symptoms, which include nausea, vomiting, abdominal pains, anorexia, constipation, insomnia, anemia, irritability, mood disturbances and coordination loss. In more severe situations

neurological effects such as restlessness, hyperactivity, confusion and impairment of memory can result as well as coma and death (Ansari *et al*., 2004).

Lead occurs most commonly with an oxidation state of 0 or +II. Pb(II) is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides. Under most conditions Pb^{2+} and lead-hydroxy complexes are the most stable forms of lead. In water bodies, a significant fraction of lead is undissolved and occurs as precipitates ($PbCO_3$, Pb_2O, $Pb(OH)_2$, $PbSO_4$), sorbed ions or surface coatings on minerals, or as suspended organic matter. Lead carbonate solids form above pH 6 and PbS is the most stable solid when high sulfide concentrations are present under reducing conditions. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater (Evanko & Dzombak, 1997).

2.2.1.4 Zinc (Zn)

Zinc is a very common environmental contaminant and usually outranks all other metals considered (Denton *et al*., 1997; Finkelman, 2005). Major sources of Zinc to the aquatic environment include the discharge of domestic wastewaters, coal-burning power plants, manufacturing processes involving metals and atmospheric fallout (Denton, et al., 2001). Approximately one third of all atmospheric zinc emissions are from natural sources, the rest come from nonferrous metals, burning of fossil fuels and municipal wastes and from fertilizer and cement production (Denton *et al*., 2001; Callender, 2003).

Sediments are known as major sinks for zinc in the aquatic environment and residues in excess of 3000 μg/g have been reported close to mines and smelters (Denton *et al*., 2001). The highest sedimentary zinc levels are found to be from enclosed harbors reaching as high as 5700 μg/g. This is mainly due to restricted water circulation and also particularly prone to zinc contamination from a variety of

localized sources including brass and galvanized fittings on boats, wharves and piers, zinc-based anti-corrosion and anti-fouling paints (Denton *et al*., 1997).

The average zinc content of the lithosphere is approximately 80 μg/g (Callender, 2003). Sediments from uncontaminated waters typically contain zinc concentration in the order of 5-50 μg/g. Ingesting high levels of zinc for several months may cause anemia, damage to pancreas and decrease levels of high-density lipoprotein (HDL) cholesterol (Finkelman, 2005).

Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. Zinc usually occurs in the +II oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zn may precipitate as $Zn(OH)_2(s)$, $ZnCO_3(s)$, ZnS(s), or $Zn(CN)_2(s)$. Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic matter, is the primary fate of zinc in aquatic environments (Evanko & Dzombak, 1997).

2.2.1.5 Cadmium (Cd)

Cadmium is a common impurity as complex oxides, sulfides, and carbonates in zinc, lead and copper ores, and it is most often isolated during the production of zinc. Some zinc ores concentrates from sulfidic zinc ores contain up to 1.4 % of cadmium (Finkelman, 2005). Cadmium is extremely toxic to most plants and animal species particularly in the form of free cadmium ions (Denton *et al*., 1997). The major sources of cadmium include metallurgical industries, municipal effluents, sewage sludge and mine wastes, fossil fuels and some phosphorus containing fertilizers.

In sediments, cadmium does not appear to be absorbed to colloidal material, but organic matter, appear to be the main sorption material for the metal. Cadmium levels tend to increase with decrease in size and increase in density in terms of partition of sediment samples by size and density. The sorption of cadmium by sediments and the clay content increases with pH. The release of cadmium from the

sediment is influenced by a number of factors including acidity, redox conditions and complexing agents in the water. Cadmium is less mobile under alkaline conditions (Fergusson, 1990).

The average concentration of cadmium in the lithosphere is ~0.1μg/g and it is strongly chalcophilic (Callender, 2003). Concentrations in pristine areas are <0.2 μg/g with levels exceeding 100 μg/g at severely contaminated sites (Naidu and Morrison, 1994). The major effects of cadmium poisoning are experienced in the lungs, kidneys and bones. Acute effects of inhalation are bronchitis and toxemia in the liver. Chronic inhalation of cadmium compounds as fumes or dust produce pulmonary emphysema, where the small air sacs of the lungs become distended and eventually destroyed reducing lung capacity (Ansari *et al*., 2004).

The most common forms of cadmium include Cd^{2+}, cadmium-cyanide complexes, or Cd(OH)2 solid sludge (Smith et al., 1995). Hydroxide ($Cd(OH)_2$) and carbonate ($CdCO_3$) solids dominate at high pH . Under reducing conditions when sulfur is present, the stable solid CdS(s) is formed. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions. Under acidic conditions, Cd may form complexes with chloride and sulfate (Evanko & Dzombak, 1997).

2.2.1.6 Nickel (Ni)

Nickel is moderately toxic to most species of aquatic plants, though it is one of the least toxic inorganic agents to invertebrates and fish. The major source of discharge to natural waters is municipal wastewater followed by smelting and the refining of nonferrous metals (Denton *et al*., 2001). Also mine drainage effluents are known to be major contributors due to high concentrations of nickel found in the discharges (Finkelman, 2005). Typically, nickel residues in sediments can be up to 100 μg/g or higher but may fall below 1 μg/g in some clean coastal waters (Denton *et al*., 1997) with the average concentration of nickel in the lithosphere of 55 μg/g (Callender, 2003).

In the bottom sediments of estuaries in which anaerobic conditions often occur, sulfide tends to control the mobility of nickel. However, under aerobic conditions, the solubility of nickel is mainly controlled by either the co-precipitate Ni(OH)2(s) (Callender, 2003). Some of the most serious health effects due to exposure to nickel include reduced lung function some nickel compounds are reported to be carcinogenic to humans and metallic nickel may also be carcinogenic (Finkelman, 2005).

2.2.1.7 Aluminum (Al)

Aluminum naturally occurs in waters in very low concentrations. Higher concentrations derived from mining waste may negatively affect aquatic biocoenosis. Aluminum is toxic to fish in acidic, unbuffered waters starting at a concentration of 0.1 mg/L. Simultaneous electrolyte shortages influence gull permeability, and damage surface gull cells. Aluminum is mainly toxic to fish at pH values 5.0-5.5 (Lenntech, 2010).

The amount of aluminum in seawater varies between approximately 0.013 and 5 ppb. Aluminum metal rapidly develops a thin layer of aluminum oxide of a few millimeters that prevents the metal from reacting with water. When this layer is corroded a reaction develops, releasing highly flammable hydrogen gas. Aluminum chloride hydrolyses in water, and forms a mist when it comes in contact with air, because hydrochloric acid drops form when it reacts with water vapor (Lenntech, 2010).

The most abundant aluminum compounds are aluminum oxide and aluminum hydroxide, and these are water insoluble. Aluminum oxide may be present in water both in alkalic form ($2Al_2O_3$ (s) + $6H^+$ (aq) -> Al^{3+} (aq) + $3H_2O$ (l)) and in acidic form ($2Al_2O_3$ (s) + $2OH^-$ (aq) -> AlO_2^- (aq) + H_2O (l)). An example of a water soluble aluminum compound is aluminum sulphate with a water solubility of 370g/L(Lenntech,2010).

2.2.1.8 Heavy Metal Levels in Sediments and Surface Waters

In Table 2.1 heavy metal levels in the sediments of different countries are given. It is seen that the river sediment concentration of heavy metals can be detected in elevated levels in industrialized and contaminated regions, such as Spain.

Table 2.2 reports the data collected from the river waters present in the Black Sea Region of Turkey. It is seen that the heavy metal concentrations are generally show low quality water to dirt water characteristics according to the Turkish Water Pollution Control Regulation (TWPCR, 2004)

Table 2.1 Metals concentrations in sediments of the selected regions around the world literature. (mg kg^{-1})

Sampling sites	**Metals**							
	Cu	**Pb**	**Zn**	**Cr**	**Cd**	**Ni**	**Al**	**Reference**
Odiel River, Spain	2109.05	589.91	1153.71	nd	14.43	nd	nd	J.J.Vicente-Martorell et. al. , 2009
Tinto River, Spain	1897.18	495.95	1115.23	nd	8.42	nd	nd	
Bottom Sediments of Volga Delta, Russia	50	24	23	96	nd	<36	nd	Lychagin et al., 1995
Pre-Industrial sediments from Vagen, Germany	<9	<12	<33	<32	<10	<17	nd	Sivertsen, 2000
Pre-Industrial sediments from Norwegian fjords and coastal waters, Norway	<35	<30	<150	<70	<0,25	<30	nd	Sivertsen, 2000
Kızılırmak River, Turkey	140.48	875.63	36.35	96.10	58.93	679.1	4, 85	Arıman, S.,et. al.,2007
Subsamples from Izmir Bay, Turkey	17	8,5	65	175	0,03	nd	nd	Aksu et al., 1998
World Average	32	16	127	71.	0.2	nd	nd	Arıman, S., et. al.,2007

Table 2.2 Metals concentration in various river waters in Turkey. (μg L^{-1}).

Sampling sites	Metals							
	Cu	**Pb**	**Zn**	**Cr**	**Cd**	**Ni**	**Al**	**Reference**
Yeşilırmak River, Turkey	0.013	0.148	<0.05	<0.05	<0.01	0.089	0.069	Arıman.S. et.al.,2007
Abdal River .Turkey	009	0.237	<0.05	<0.05	0.006	0.108	0.064	
Mert River Turkey	0.009	0.675	<0.05	<0.05	0.006	0.112	0.060	
Kürtün River ,Turkey	0.070	0.171	<0.05	0.018	<0.01	0.253	0.076	
Engiz River, Turkey	0.428	0.130	<0.05	0.091	0.025	0.725	0.137	
Kızılırmak River, Turkey	0.085	0.357	<0.05	0.011	0.006	0.450	0.065	

2.2.2 Total petroleum hydrocarbons (TPH)

Total petroleum hydrocarbons (TPH) are a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. Crude oil is used to make petroleum products, which can contaminate the environment. Because there are so many different chemicals in crude oil and in other petroleum products, it is not practical to measure each one separately. However, it is useful to measure the total amount of TPH at site (G. De Luca *et al*., 2005).

TPH is mixture of chemicals, but they are all made mainly from hydrogen and carbon, called hydrocarbons. Scientists divide TPH into groups of petroleum hydrocarbon fractions. Each fraction contains many individual chemicals (G. De Luca *et al*., 2005).

Some chemicals that may be found in TPH are hexane, jet fuels, mineral oil, benzene, toluene, xylenes, naphthalene, as well as other petroleum products and gasoline components. However, it is likely that sample of TPH will contain only some, or a mixture, of these chemicals (G. De Luca *et al*., 2005).

TPH may enter the environment through accidents, from industrial releases, or as by products from commercial or private uses. TPH may be released directly into water though spills or leaks. Some TPH fractions will float on the water and from surface films. Other TPH fractions will sink to the bottom sediments. Bacteria and microorganisms in the water may break down some of the TPH fractions. Some TPH fractions will move into the soil where they may stay for a long time.

2.2.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic compounds (PAHs) are the organic pollutants that may be originated from food, drink, leather, vegetable oil, soap, chemistry, waste of paint and textile industries. Polycyclic aromatic compounds include different groups of compounds which have two or more benzenoid groups in their structure and various

functional groups which may contain several elements. An important group of polycyclic aromatic compounds are the polycyclic aromatic hydrocarbons (PAHs) which have two or more fused benzonoid rings and no elements other than carbon and hydrogen (Henner *et al*., 1997). They may be eliminated or transformed to even more toxic compounds by chemical reactions such as sulfonation, nitration or photooxidation. For instance, in some conditions, traces of nitric acid can transform some PAHs into nitro-PAHs (Marce & Borrull, 2000).

The molecular structures of PAHs were shown in Figure 2.1. PAHs are relatively neutral and stable molecules. PAHs have low solubilities and low volatilities except small components like naphthalene. Solubility's of PAHs in water decreases with increasing molecular weight. Their liphophilicity is high, as measured by water – octanol partition coefficients (Kow). Due to their hydrophobic nature, the concentrations of dissolved PAHs in water are very low. PAHs show long half- lives in geological media. In anaerobic sediment, for example, half lives range from three weeks for naphthalene up to 300 weeks for benzo (a) pyrene. PAHs are regarded as persistent organic pollutants (POPs) in the environment. This persistence increases with ring number and condensation degree (Henner *et al*., 1997).

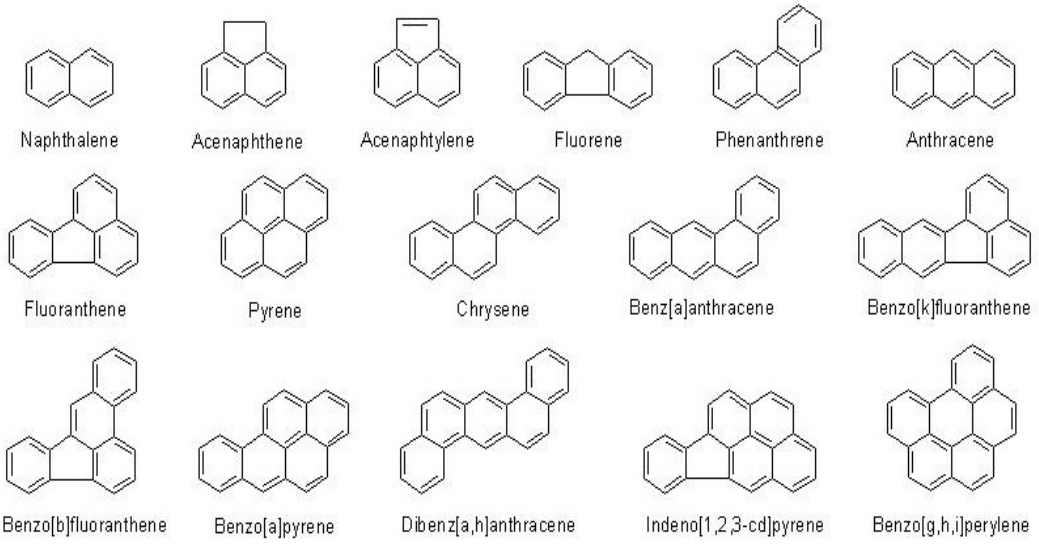

Figure 2.1 Molecular structures of PAHs

The induction of polycyclic aromatic hydrocarbons (PAHs) into natural waters is considered in terms of both point and non point source discharges to surface, ground and drinking water .The occurrence PAHs has been evaluated with regard to their concentrations in some aqueous samples and frequency of occurrence. In addition, an overview of the capabilities of the currently available analytical techniques is given along with requirements for achieving reliable analysis of PAHs in various environmental water samples (E. Manoli *et al*., 1999).

PAHs are introduced into the environment mainly by way of natural and anthropogenic combustion processes. As a consequence, their loadings to aquatic and terrestrial systems all have a component which is atmospheric in origin. Volcanic eruptions and forest and prairie fires are among the major natural sources of PAHs in the atmosphere. Important anthropogenic sources include combustion of fossil fuels, waste incineration, coke and asphalt production, oil refining, aluminum production and many other industrial activities (S.O. Beak *et al*., 1991). Despite their large source strength in urban /industrial sites, PAHs occur at relatively high concentrations in rural and remote areas due to their ability to be transported over long distances as gases or aerosols and their apparent resistance to degradation on atmospheric particulates. Thus, PAH emissions into urban /industrial atmospheres may significantly affect coastal and inland surface water. There are three kinds of sources and occurrence of PAHs in natural waters. They are surface waters, drinking waters and ground waters (E. Manoli *et al*., 1999).

In the Table 2.3 and 2.4, PAH concentrations in the sediments from the various regions of the world observed between the years of 1993 and 2008 are summarized (San Francisco Bay, Baltic in the Odra Estuary, Turkey).

Table 2.3 Total PAH concentrations (mg kg^{-1}) in San Francisco Bay and Baltic in the Odra Estuary sediment sampling stations for comparison to PAH sediment quality threshold.

Station	**PAHs**								
	1997-08	**1998–02**	**1998–07**	**1999–02**	**1999–07**	**2000–02**	**2000–07**	**2001–02**	**2001–08**
NE Napa River , San Francisco Bay	0.579	1,907	1.185	2.477	0.807	0.753	0.935	0.503	0.630
NE Davis Point , San Francisco Bay	0.099	0.120	0.125	0.088	0.060	0.054	0.156	0.056	0.137
NE San Pablo Bay , San Francisco Bay	2.136	2.591	4.202	3.471	1.135	2.185	1.090	1.247	1.344
EI Guadalupe River , San Francisco Bay	1.135	0.866	0.697	1.507	0.854	-	0.849	-	0.914
NE Napa River	0.579	1.907	1.185	2.477	0.807	0.753	0.935	0.503	0.630
CB Horseshoe Bay	0.585	1.816	1.772	2.722	2.351	-	2.433	-	1.706
CB Richardson Bay	1.415	1.278	1.738	1.833	1.677	-	1.682	-	2.144
SB Dumbarton Bridge	1.796	0.953	1.776	2.646	1.449	-	1.784	-	1.914
SB Alameda	2.351	1.857	2.609	2.911	2.222	-	3.511	-	2.218

Table 2.3 Continued

Station	PAHs								
	1997-08	**1998–02**	**1998–07**	**1999–02**	**1999–07**	**2000–02**	**2000–07**	**2001–02**	**2001–08**
SB South Bay	1.254	0.999	1.126	1.682	1.383	-	1262	-	1.349
CB Point Isabel	1.531	1.069	1.506	1.868	1.007	-	1.682	-	2.144
Alaska-Prince William Sound,(natural seepages) , Odra Estuary	-	-	-	-	-	-	0.875–6.687	-	-
Tokyo Bay	-	-	-	-	-	-	-	1.350 - 2.010	-
San Francisco BayCalifornia,USA (Pacific),Odra Estuary coast	-	-	-	-	-	-	-	0.955, 3.884 (21PAHs)	-
Eastern (of the shore), Odra Estuary	-	-	-	-	-	0.0146 –01585	-	-	-
Yellow Sea	-	-	-	-	-	-	-		0.370–3.800

2.2.3.1 PAHs in Surface Waters

PAHs enter surface waters mainly via atmospheric fallout, urban run off, municipal effluents, industrial effluents and oil spillage or leakage. Crude oil content high levels of PAHs, but the relative concentrations of each compound depend largely on the type and origin of oil. Variability in PAH content is also found in refined petroleum products (E. Manoli *et al*., 1999).

In general, industries that use oil or coal as raw material or fuel produce effluents with high concentrations of PAHs (A.Terashi *et al*., 1993). Municipal wastewaters are another source of PAHs in surface waters. Concentrations of total PAHs in raw municipal wastewaters have been found to vary significantly, depending on the amount of industrial effluents possible co-treated with domestic wastewaters. Atmospheric fall out includes wet and deposition of particle and vapors. PAHs, as Semi-volatile organic compounds, exist in both the gaseous and the particulate phase in air, and are subject to both vapor and particle washout from the atmosphere during precipitation. A significant amount of PAHs carried to surface waters by sewers derives from urban run-off. Urban run-off consists of the storm water from impervious areas, such as roads, motorways, paved parking lots, roofs, sidewalks, etc. and pervious areas (for example, garden unpaved parking areas, construction sites, etc.). As a consequence, urban run-off contains PAHs deposited on surfaces, as well as mobile related PAHs from gasoline and oil drips or spill, exhaust products, tire particles and bitumen from road surfaces (M.T. Bomboi *et al*., 1991). Higher concentrations of PAHs in urban run off were found during autumn and winter (M.T. Bomboi *et al*., 1991).

PAH high concentrations in Mersin, Antalya and Iskenderun domestic wastewaters observed between the years of 2003 and 2006 are given in Table 2.4

Table 2.4 Annual PAH concentrations in Mersin, Antalya and Iskenderun domestic waste waters (μg L^{-1}).

Station	PAHs				
	2003	**2004**	**2005**	**2006**	**Reference**
Mersin Wastewater	0.66	11.5	4.87	121	Tuğrul, S *et al*., 2006
Antalya Wastewater	3.38	8.70	0.83	2.09	
Iskenderun Wastewater	nd	1.75	2.31	1.23	

2.2.3.2 PAHs in Groundwater

PAHs in groundwater may originate from polluted surface water bodies, agricultural irrigation with effluents, leachates from solid waste disposal sites or contaminated soil. However, the movement and transport of PAHs in systems as well as their penetration mechanisms into groundwater remain unclear (A.Terashi *et al*., 1993).

2.2.3.3 PAHs Drinking Water

The presence of PAHs in drinking water may be due to the surface or groundwater used as raw water sources, or to the use of coal tar-coated pipes in public water supply systems, as is permitted in certain countries (H.Shiraishi *et al*.,1985).

It has been reported that higher PAHs levels must be expected in potable water from sources such as water treatment plants and rainwater collecting basins (K. Kveseth *et al*., 1982).Regarding the chlorination of drinking Water, it has been found that this disinfection technique may lead to formation of oxygenated and chlorinated PAHs, i.e. compounds that are more toxic than the parent PAHs (H.Shiraishi *et al*.,1985)

2.2.4 Izmir Bay

Izmir Bay (western Turkey) is one of the great natural bays of the Mediterranean. The main urban conurbation around the bay is the Izmir Metropolitan Municipality, covering 88,000 ha. Izmir is an important industrial and commercial centre and a cultural focal point. The bay has a total surface area of over 500 km^2, water capacity of 11.5 billion m^3, a total length of 64 km and opens in the Aegean Sea. The depth of water in the outer bay is about 70 m and decreases towards to the Inner Bay. The bay has been divided into three sections (outer, middle and inner) according to the physical characteristics of the different water masses (Figure 2.2). The middle bay is separated from the inner bay by a 13 m deep sill the Yenikale Strait. The Gediz River, which flows to the northern part of the bay, is the second biggest river along the eastern Aegean coast. Gediz River is densely populated and includes extensive agricultural lands and numerous manufacturing, food and chemical industries (F. Kucuksezgin *et al.*, 2005).

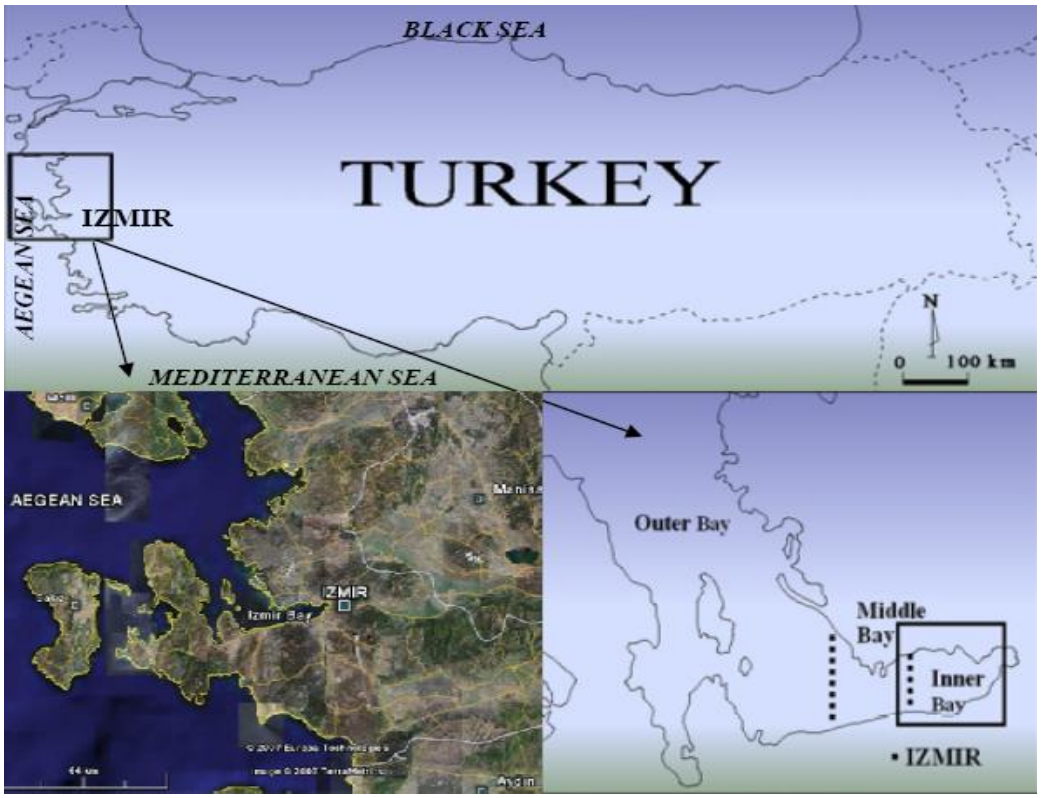

Figure 2.2 Location of Izmir Bay in Turkey.

The water circulation in ˙Izmir Bay is predominantly controlled by the prevailing winds in the region: semidiurnal tides of 20–40 cm have negligible effect (Akyarlı *et.al.*, 1988). During the summer and autumn, surface water is driven towards the southeast by the prevailing northwester lies with speeds of _40 cm s^{-1}. During the winter northerlies and northeaster lies drive the surface waters towards the south-southwest with speeds of <30 cm s^{-1}. There is no dominant surface current direction in the spring and measurements show significant reduction in current speeds to 6–20 cm s^{-1}. Although surface Water moves with the prevailing winds, there is little water exchange between the Inner and Central ˙Izmir Bays (Akyarlı *et al*., 1988).

There are various creeks flowing into the Izmir Bay. These creeks are Old Gediz, Harmandalı, Bostanlı and Sepetçi. These creeks are feeding the Bay from the north, and Bornova, Manda, and Melez Creeks feeding the Bay from the east (Figure 2.3). Creeks coordinates of the sampling stations are given with Table 2.5, and also the hydrological properties of these creeks are given with Table 2.6

Table 2.5 Creeks coordinates of the sampling stations. (Google Earth, 2010).

The Creek Name	Coordinates
Harmandalı	38^0 29' 10.40'' N 26^0 58' 24. 59'' E
Old Gediz	38^0 28' 48. 02'' N 27^0 02' 35. 39'' E
Bostanlı	38^0 28' 08. 73'' N 27^0 04' 47. 94'' E
Sepetçi	38^0 27' 54. 57'' N 27^0 07' 47. 77'' E
Bornova	38^0 27' 40. 02'' N 27^0 10' 05. 40'' E
Manda	38^0 26' 48. 94'' N 27^0 10' 42. 20'' E
Melez	38^0 26' 10. 18'' N 27^0 10' 21. 18'' E

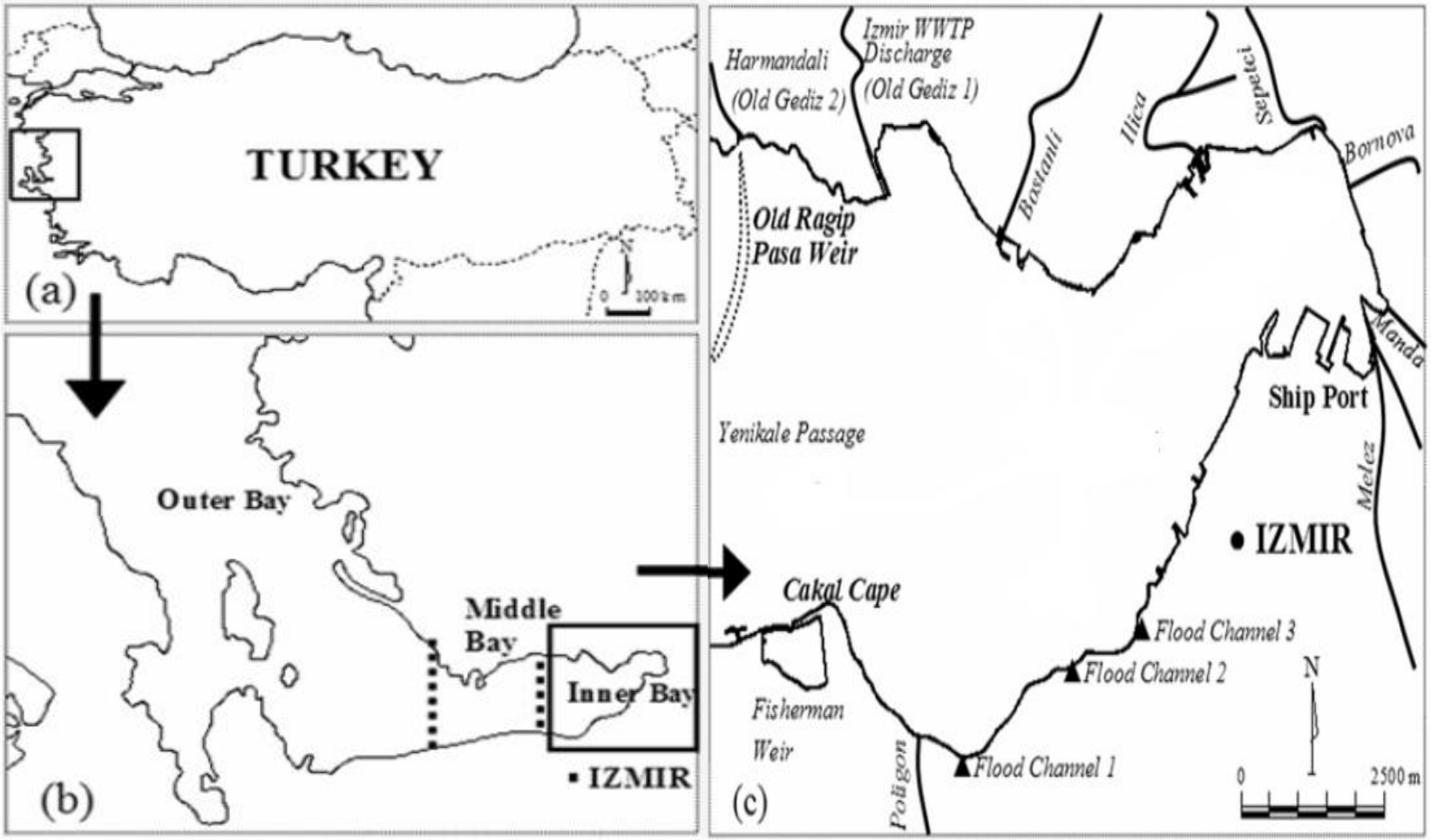

Figure 2.3 (a) Location of Izmir Bay in Turkey (b) Divisions of the Bay (c) Creeks and coastal structures around the inner Bay and the locations of the sampling points (Güven , 2006).

Table 2.6 Hydrological properties of creeks which are discharge in and central bay (Küçükgül, 1994).

The Creek Name	Hydrological properties of creeks		
	Basin Area (10^6 m^2)	**Discharge Area**	**Flow (10^6 m^3/year)**
Melez Creek	123.4	Inner Bay	29.98
Manda Creek	107.5	Inner Bay	30.59
Laka and Bornova Rivers	49.3	Inner Bay	13.18
Turan Area	7.3	Inner Bay	1.67
Izmir (Public Square)	10.3	Inner Bay	1.84
Poligon River	11.7	Inner Bay	2.48
Balçova River	10.5	Inner Bay	2.31
Ilıca River (Balçova)	41.6	Inner Bay	13.19
Ilıca River (Karşıyaka)	23	Inner Bay	5.90
Bostanlı River	36.5	Inner Bay	9.68
Çiğli and Old Gediz (East)	148.1	Inner Bay	27.50
Narlıdere	21.7	Central Bay	6.89
Abdullahağa Basin	17.2	Central Bay	5.16
Yağ River	14.8	Central Bay	5.12
Kaklıç Basin and Old Gediz(west)	53.5	Central Bay	8.29
Total	726.6	Inner+Central Bay	181.94

Between the years of 1960 and 1992 years, high population growth, migration, unplanned urbanization, rapid industrialization has occurred in the city. Returning domestic, industrial and agricultural irrigation wastewater spilled into bay waters. So Izmir bay, particularly the inner bay, concentration of pollution gradually speed up. In addition to that pollutants, bay reaching streams, rain brought loads to urban area and that falls to bay catchments, loads that occur in the catchments of bays' water collection as a result of agricultural activities, loads that caused by port, marina activities and maritime traffic, loads that pass from sediment to water column and material exchange with open sea, are among the most important reasons (Erden & Sayın, 2001). Rapid increase in the city population and as a result of industrial sectors intensive activities, various chemical wastes without treatment and uncontrolled way discharged and still is to be continued. The importance of the streams for the bays is containing pollutant loads more than brought freshwater inputs. Especially while passing from the Izmir metropolitan area, as a result of wastewater discharge, contaminates in extraordinary degree. Besides this pollution loads, moved from catchments area to bay has great importance. Especially streams that discharges to inner bay of Izmir basically cause to be shallower of the bay (Anonymous, 1995).

In 2001, the Big Channel Project by Izmir Metropolitan Municipality was completed and a sewage network was connected to a major collector followed by an urban wastewater treatment plant for the city. But the sediment layer at the bottom of the inner Bay still has organic and inorganic contaminants and creates potential hazard (Aksu *et al*., 1998; Atgın *et al*., 2000; Cihangir & Küçüksezgin, 2003). Domestic and industrial wastes including organic and heavy metal contamination are the most important sources of pollution (Atgın *et al*., 2000). Prevalent industries with heavy metal content in their wastewaters are: textile (Manda and Sepetci Creeks), chemicals (Melez and Sepetci Creeks), metal (Manda, Melez, Ilica, and Bostanli Creeks), automotive (Manda Creek) industries, the tanneries (on Manda and Melez Creeks), and the industrial zones (Melez and Old Gediz 1 Creeks) (IZTO, 1995).

In the past, various studies were conducted to determine the heavy metals pollution in the sediments of Izmir Bay. As can be seen in Table 2.7, the highest Cr concentration in the inner Bay was measured in 1997 as 600 mg kg^{-1} (Aksu *et al*., 1998). In the same study, the highest Zn concentration found in the sediments of inner Bay was 350 mg kg–1. The highest Cu and Pb values were determined as 121 mg kg^{-1} and 110 mg kg^{-1}, respectively by Cihangir and Küçüksezgin, 2003 (Güven, 2006).

Table 2.7 Heavy metal concentrations in the sediment of Izmir bay,. (mg kg^{-1}, dry mass).

Metals	**Izmir Inner Bay, 1997 (min-max)**	**Izmir Inner Bay, 1999 (mean ± sd)**	**Izmir Inner and Middle Bay, 2001 (min-max)**	**This work Izmir Inner Bay (min-max)**
Cr	250-600	300±100	171-295	404 - 1563
Cu	20-80	70±38	32-121	66 - 993
Pb	20-60	62±29	61-110	18 - 203
Zn	50-350	nd	86-286	217 - 1031
Ref.	Aksu *et al*., 1998	Atgın *et al*., 2000	Cihangir & Küçüksezgin, 2003.	Güven ,2006.

As mentioned above Izmir Bay has been polluted by urban and industrial wastewater discharges for several years. Continued discharges have caused a serious pollution of organics and heavy metals in the sediments in this area. It was reported that for the removal of contaminated sediments in the Bay, partial dredging of the sediments were done between the years of 1976 and 1990.

The dredging was done mainly along the centre line (from east to west) of the Inner Bay. The dredged material was dumped in a natural ditch in the Outer Bay. In

2001, as a part of a project of Izmir Metropolitan Municipality, the creeks entering the Bay were taken under control and the sewage network was connected to a major collector followed by urban wastewater treatment plant for the city. But still, there are some direct or indirect illegal discharges into the bay which cannot be prevented. As a result, the sediment layer at the bottom of the Inner Bay still has organic and inorganic contaminants (Guven & Akıncı, 2008).

Previous studies mention about high concentrations of heavy metals and organic pollutants in the sediments of Izmir inner Bay (Aksu *et al*., 1998; Atgin *et al*., 2000; Cihangir & Küçüksezgin, 2003). According to a study done in the past about PAH concentrations, which is one of the organic pollutants, Total PAH Concentrations are highest in Izmir Bay (9.27 μg/g or ppm), dramatically decreasing to 1.25 μg/g at the Yenikale Entrance and to 0.42 μg/g in Central ˙Izmir Bay (Aksu *et al*., 1998) . Table 2.8 gives brief information about the increasing concentrations of heavy metals in sediments of Izmir Bay and its two big tributaries; Büyük Menderes and Gediz Rivers.

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Table 2.8 Heavy metal concentrations in sediments of Büyük Menderes River ,Gediz River and Izmir Bay (mg kg $^{-1}$)

	Büyük Menderes River, 2003	**Gediz River, 2003**	**Izmir Outer Bay, 97 (min-max**	**Izmir Inner Bay, 97 (min-max)**	**Izmir Inner Bay, 99 (mean ± sd)**	**Izmir Outer Bay, 99 (mean ± sd)**	**Izmir Outer Bay, 99 (mean ± sd)**	**Izmir Outer Bay, 2001 (min-max)**
Cr	165±7	200±6	150–300	250–600	300±100	210±64	171–295	38–199
Cu	137±5	140±3	15–40	20–80	70±38	34±24	32–121	4,1–31
Fe	18500±1000	25500±1000	nd	nd	46000±5300	44400±13000	nd	nd
Mn	388,5±15	510±25	nd	nd	454±80	479±137	nd	nd
Ni	315±15	106±10	nd	nd	125±32	148±39	nd	nd
Pb	54±8	128±15	15–30	20–60	62±29	41±14	61–110	25–73
Zn	120±10	160±10	50–150	50–350	260±100	99±37	nd	nd
Ag	nd	nd	0,2–0,5	0,2–1	nd	nd	nd	nd
Cd	nd	nd	0,1–0,6	0,2–0,8	0,42±0,22	0,26±0,16	0,051–0,545	0,027-0,054
As	nd	nd	20–50	30–60	nd	nd	nd	nd
Hg	nd	nd	0,2–0,6	0,2–1,5	nd	nd	0,38–0,82	0,41–0,62
Zn	nd	nd	50–150	50–350	nd	nd	86–286	20–94
Reference	Akçay et al., 2003		Aksu et al., 1998		Atgın et al., 2000		Cihangir & Küçüksezgin, 2003	

CHAPTER THREE
MATERIALS AND METHODS

3.1 Sampling

Seasonal sediment and water samples were taken from 7 creeks flowing into the Inner and Middle Bay. These creeks are Old Gediz, Harmandalı, Bostanlı and Sepetçi Creeks feeding the Bay from the north, and Bornova, Manda and Melez Creeks feeding the Bay from the east (Figure 3.1). Sediment samples could not be taken from Bostanlı and Melez Creeks since the water levels were high and it was impossible to take sediment samples.

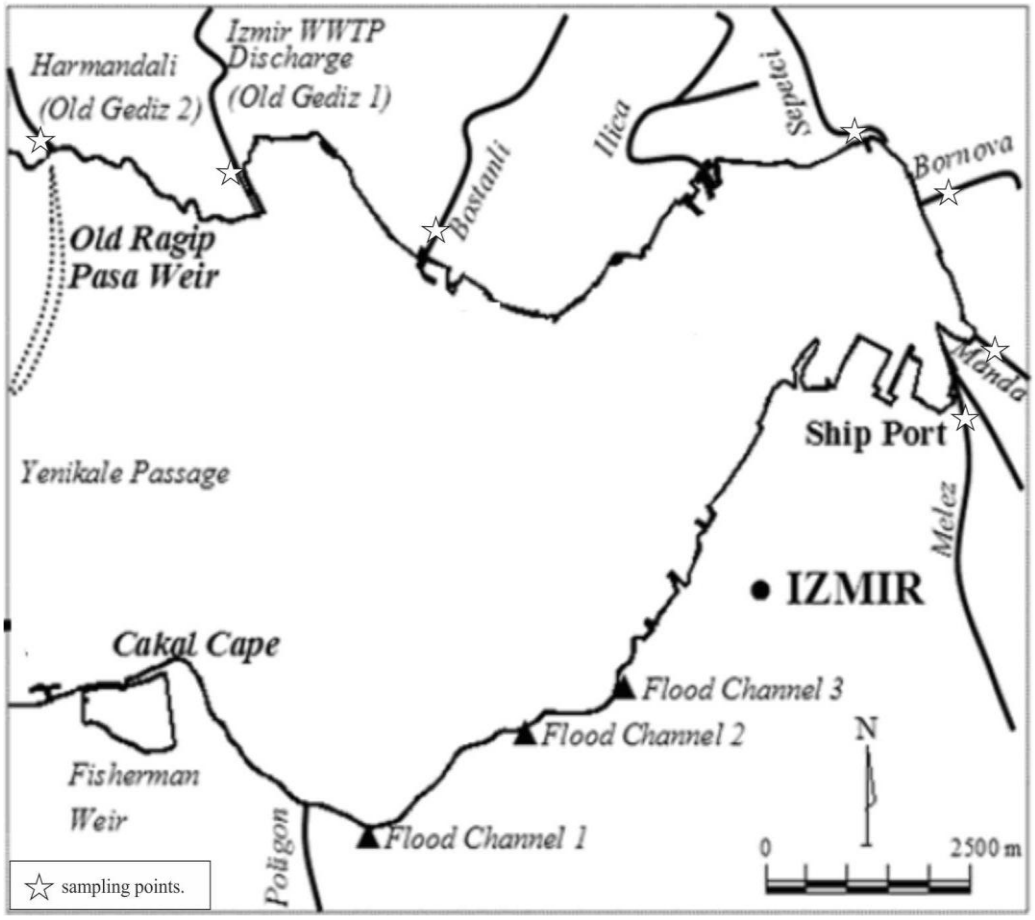

Figure 3.1 Creeks and coastal structures around the inner Bay and the locations of the sampling points.

Spring, summer, autumn, and winter samples were taken on the last months of each season (May 2009 - August 2009 - November 2009 - February 2010), at least 3 days after the last rainy day. Sediment and water samples were taken by manual sampling with the help of a shovel. The sediment samples were collected from the top 10 cm of the surface and deposited into plastic bags. Water samples were taken into plastic bottles; pH was measured on site (a). Nitric acid was added to the water samples to prevent the degradation of the samples and keep the metals solubilized for further heavy metal analysis. The water and sediment samples collected from the rivers were taken to the laboratory and stored at 4^0C until processing and analysis. (b) shows the general appearance of wet and dry sediment samples.

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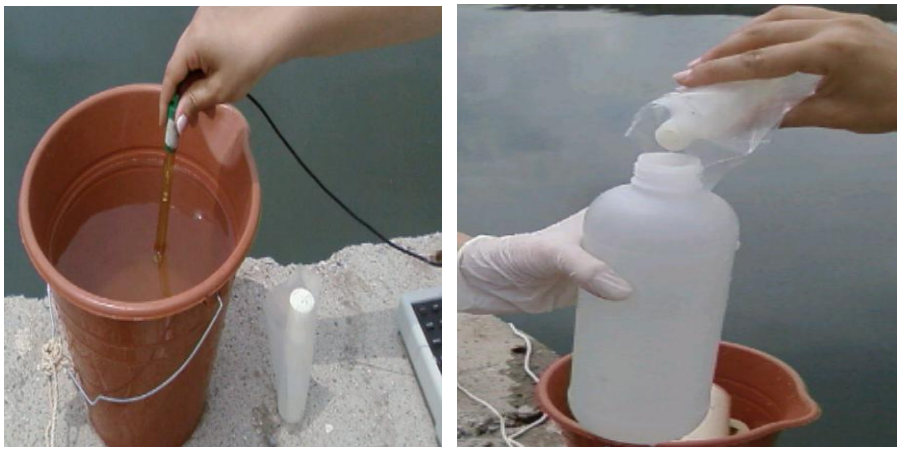

(a)

(b)

Figure 3.2 Onsite pH measurement and acid addition to the water samples (a), and the view of wet and dry sediment samples (b)

3.2 Characterization Studies

The sediment and water samples were analyzed for the following physical and chemical parameters; water content, organic matter content, grain size distribution (for sediment samples); pH, total petroleum hydrocarbons (TPHs), heavy metals (Cd, Cr, Cu, Pb, Zn, Ni, Al) and polyaromatic hydrocarbons (PAHs) for sediment and water samples.

3.2.1 pH

3.2.1.1 Water pH

pH of the water samples were measured during sampling by using HANNAH HI 8314 pH meter.

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3.2.1.2 Sediment pH

The pH values of the sediment samples were determined by using wet samples according to the EPA Method 9045 C (USEPA, 1995). 20 g of sediment sample was vigorously mixed with 20 ml of distilled water for 5 minutes and centrifuged at 4000 rpm for 10 minutes. Then, the pH value of the supernatant was measured. NUVE NF 815 centrifuge and HANNAH HI 8314 pH meter is used for the experiments

3.2.2 Solid Matter

Total solid matter (TSM) and suspended solid matter (SSM) were determined by gravimetric method due to the Standard Methods (APHA, AWWA, WEF, 2005). Settalable solid fraction (SF) is determined by subtracting the SSM concentrations from TSM concentration.

3.2.3 Sediment Water Content

Sediment water content was determined via gravimetric analysis by drying the wet sediment samples overnight at 105^0C. MEMMERT Loading Modell 100-800 drying oven is used for this process. The moisture content of the sample is determined gravimetrically by using the difference between the weight of wet and dry samples.

3.2.4 Sediment Organic Matter Content

The determination of organic matter content of the sediment samples were conducted according to the Standard Methods (AWWA 1981). The dried samples were combusted at 550°C for 2 hours and differences between the initial and final weights are used to determine the organic matter content of dry portion. MEMMERT LM 100–800 furnace is used for the experiments.

3.2.5 Sediment Grain Size Distribution

The grain size distribution of the sediment samples were determined by wet sieving using 4 sieves with different hole sizes. Particles larger than 2000 μm were eliminated since they are counted as rock and gravels. Slurry sediment samples were poured on the top of the sieve and rocked to collect the fractions under the tap water (pH 7.8 -8.2). Particles accumulated on the sieves were air dried and sediment samples with different size fractions were obtained on the sieves. Dry sediments samples on the sieves were then swept and weighed. The humidity of the sediment size fractions are considered in the following analysis.The detected size fractions are given with Table 3.1

Table 3.1 Fractions used to determine grain size distribution.

Fraction	Soil Type
2000µm > F_A >600 µm	Sand
600µm > F_B >300 µm	Sand
300 µm > F_C >90 µm	Sand
90 µm > F_D > 45 µm	Sand +silt
45 µm > F_E µm	Silt +clay

3.2.6 Heavy Metals

3.2.6.1 Heavy Metals in Water

The acidified water samples were filtered through 0.45 µm filter paper and prepared for the analysis without any dilution.

3.2.6.2 Heavy Metals in Sediment

Total heavy metal content of the sediment samples were determined by using microwave acid digestion system with a closed extraction system. The Questron MicroPrep Q20 Microwave Digestion System with four digestion vessels was used for the extraction (Figure 3.2). The system includes a microwave oven, four high pressure digestion vessels and a vessel module. The maximum microwave power the system can reach is 1000 watts. Samples were placed in liners (TFM Teflon, softening point 250°C) which are mounted in ultem caps. The vessels support an operating pressure of 350 psi and a maximum temperature of 260°C and they are resistant to HF (Questron Technologies, 2005). Rupture disks were placed in the Over Pressure Valve Stems in the vessels to become a pressure control device in the digester. The system allows the digestion of four samples at the same time and different programmes can be operated by using the control panel.

Figure 3.3 The Questron microwave digestion system (a) microwave oven (b) digestion vessels.

0.1 g of each sample was placed in the digestion vessels. A combination of nitric acid (3 ml of%65 HNO3- used for easily oxidizable material) and hydrofluoric acid (1 ml of %40 HF- used for extraction of inorganic matrixes) and hydrochloric acid (1 ml of 37% HCl) were added to each of the digestion vessels. An improved heating programme was used for the digestion of the sediment samples (Güven & Akıncı, 2008). The details of the heating program are given in Table 3.2. In order to determine the accuracy of the extraction procedure, a standard reference material (SRM-1646-A Estuarine sediment obtained from National Institute of Standards and Technology) was digested using the same method. For precision, all extractions with SRM and the samples were duplicated and the mean values were reported. The digestate obtained were then filtered through 0.45 μm membrane paper, diluted to 50 ml for storage and further analyses.

Table 3.2 Microwave heating procedure used for the digestion of the samples

Sample weight (g)	**Reactives and Consumptions (ml)**	**Programme step**	**Applied Power (W)**	**Time (min)**
0.1	% 65 HNO_3(3 ml) % 40 HF(1 ml) %37 HCI(1ml)	1	200	8
		2	400	6
		3	600	2
		4	0	10

The analysis of Cr, Cu, Pb, Zn, Cd, Ni, and Al in the water samples and the acid extracts were done by using an inductively coupled plasma emission spectrometer (ICP ES) (Varian 710-ES). The wavelengths used in the analyses were 231.604 for Ni, 396.152 for Al, 214.439 for Cd, 267.716 for Cr, 327.395 for Cu, 220.353 for Pb, and 213.857 for Zn.

3.2.7 Total Petroleum Hydrocarbons (TPHs)

3.2.7.1 Water TPHs

The total petroleum hydrocarbons (TPH) in water samples were determined according to the Oil Grease Analysis in Standard Methods (5-41)

3.2.7.2 Sediment TPHs

Sample is extracted with hexane in an ultrasonic extractor according to EPA 3550B. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. Here, the described procedure is simplified to allow fast measurements. A 5 g of sample was mixed with 5 g of Na_2SO_4, and extracted with 20 ml of hexane in an ultrasonic bath (84 Watt) for 10 minutes at 20°C.After the extraction, 10 mL extract is transferred into a crucible and evaporated under fume hood. The TPHs is determined gravimetrically by using initial and final weights of the crucible. The recovery rate of the method is 97% (Bilgin, 2010). EIA CP102 ultrasonic extractor is used for the experiments.

3.2.8 ***Polycyclic Aromatic Hydrocarbons Analysis (PAHs)***

For GC-MS analysis of PAHs, soil extractions are completed according to the EPA Method 3550A- Ultrasonic Extraction. 1 g of soil is placed into a 40 mL vial and 25 mL 1:1 acetone: hexane mixture was added. Prior to extraction, all samples were spiked with PAH internal surrogate standards to monitor analytical recovery efficiencies. 0.5 mL PAH internal standard (Accustandard-8000 mg/L each:

Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12) was added into the vial and retained overnight. The vial, then, has extracted in ultrasonic extractor for 30 min with 380 Watt, filtered from glass wool and transferred to another vial.

The samples were cleaned up on an alumina- silicic acid column containing 3 g of silicic acid (3% water) and 2 g of alumina (6 % water) (EPA Method 3610B). The column was pre-washed with 20 mL of DCM followed by 20 mL of petroleum ether. Then , 20 mL DCM was added to the column and the strain containing PAHs was collected in another 40 mL vial. This strain was transferred into the Kuderna-Danish Apparatus (water temperature 65 ^{0}C, DCM boiling point :40 ^{0}C) and the volume of the extract reduced to 10 mL. 10 mL hexane was added to system once more and the volume was reduced to 5 mL final volume by arranging it to 95 ^{0}C (Hexane boling point: 69 ^{0}C) for hexane collection. 1 mL of final volume was placed in a 1.5 mL glass vial and used for GC-MS analysis (Bilgin, 2010).

All extracts were analyzed for 16 PAHs including acenaphthylene, acenaphthene (ACT), fluorine (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fuoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benz[b]Fluoranthene (BbF), benz[k]Fluoranthene (BkF), benz[a]pyrene (BaP), indeno [1, 2, 3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), and benzo[g,h,I]perylene (BahiP) with a gas chromatograph (GC) (Agilent 7890A) equipped with a mass selective detector (Agilent 5975C inert MSD). A capillary column (HP5-ms, 30 m, 0.25 mm, 0.25 μm) was used .The initial oven temperature was held at 50 ^{0}C for 1 min, was raised to 200 ^{0}C at 25 ^{0}C min^{-1} and from 200 to 300 ^{0}C at 8 ^{0}C min $^{-1}$, and was held for 5.5 min. The injector, ion source, and quadrupole temperatures were 295, 300, and 180 ^{0}C, respectively. High purity helium was used as the carrier gas at constant flow mode (1.5 mL min $^{-1}$, 45cm s^{-1} linear velocity). The MSD was run in selected ionmonitoring mode. Compounds were identified on the basis of their retention times, target and qualifier ions quantified using the internal calibration procedure.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Water Samples

4.1.1 pH

The pH values of the water samples measured on site are given in Table 4.1. As can be seen from the table, the pH values vary between 5.86 (Melez, Winter) and 9.4 (Bornova, Summer). Depending on the temperature, the dissolution of air CO_2 in the water increases in winter and causes relatively low pH levels, while higher pH values have seen in other seasons. Lower pH levels observed in Summer and Autumn (in Sepetçi, Harmandalı, and Melez) may be caused by the acidic compounds which were released from the degraded organic fraction present in the bottom sediment.

Table 4.1 pH levels in river waters

River	pH			
	Spring	Summer	Autumn	Winter
Harmandalı	8,3	7,8	7,5	6,42
Old. Gediz	8,5	8	8,4	6,4
Bostanlı	nd	8,1	8	7,41
Sepetçi	nd	7,9	8,3	6,71
Bornova	8,1	9,4	8,8	7,07
Manda	8,1	8	8	6,31
Melez	7,7	7,4	7,8	5,86

4.1.2 Total Solid Matter and Suspended Solid Matter

Total solid matter (TSM) and suspended solid matter (SSM) are measured in the laboratory and settable solid fraction (SF) was determined by taking the difference between TSM and SSM. Figures 4.1, 4.2., and 4.3 give the results for TSM, SSM, and SF, respectively, according to the seasons.

The analysis showed that TSM concentrations are very high in the rivers, especially the ones with larger catchment area, namely: Old Gediz, Manda, Melez and Bornova (Table 2.6), while SSM has a small portion of TSM (< 2%). The 98% of the solid material carried to the Bay by the rivers is settlable.

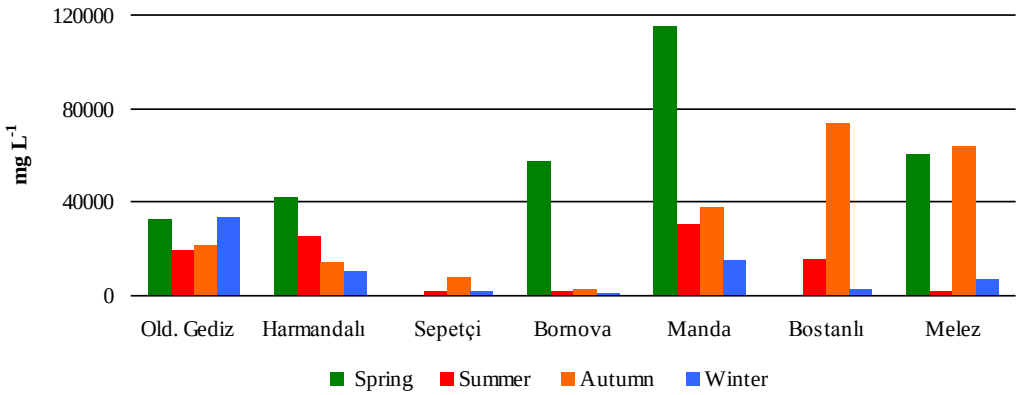


Figure 4.1 Total solid matter (TSM)

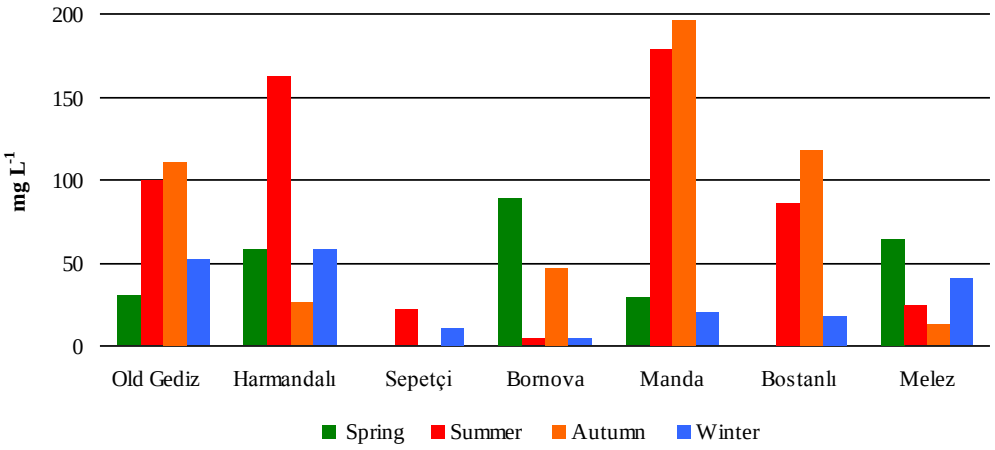


Figure 4.2 Suspended solid matter (SSM)

TSM is usually higher in Spring season, and the concentration of the particles that can precipitate (SF) are in high concentration during Summer and Autumn seasons.

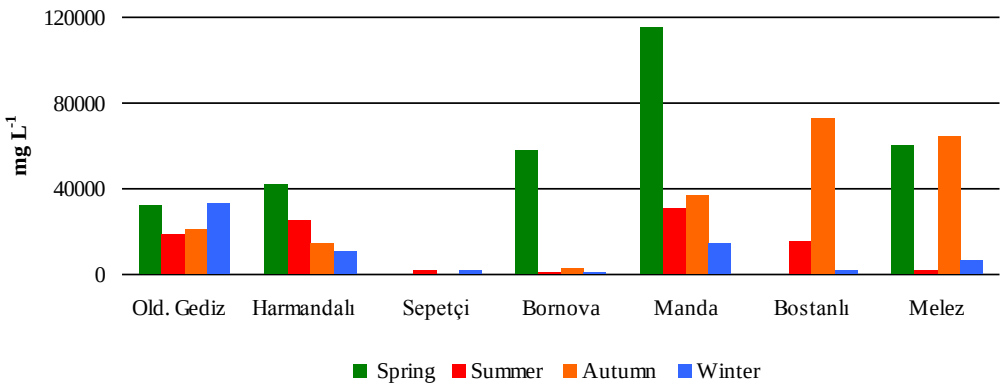


Figure 4.3 Settlable solid fraction (SF)

4.1.3 Total Petroleum Hydrocarbons (TPHs) and Polycyclic Aromatic Hydrocarbons (PAHs)

4.1.3.1 Total Petroleum Hydrocarbons (TPHs)

TPHs concentrations found in sampled river waters according to the seasons are given in Figure 4.4.

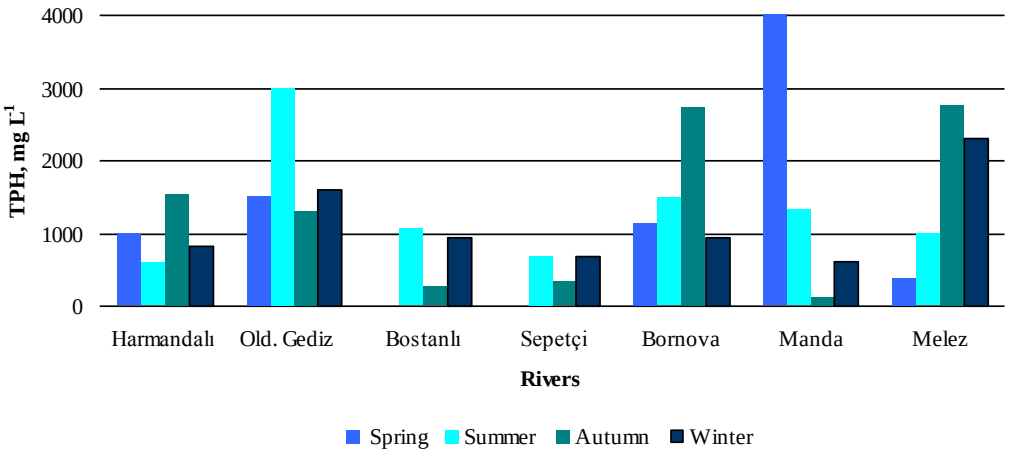


Figure 4.4 Total Petroleum Hydrocarbons (TPHs) in water

The TPH concentrations vary between 120-4000 mg/L. Similar with the results obtained for TSM, water TPH concentrations are higher in the rivers having large catchment areas and high annual flows. In the data for these rivers, Spring, Autumn and Winter TPH concentrations are higher. An exception for Old Gediz has seen in Summer season, which can be explained by a illegal discharges.

4.1.3.2 Polycyclic Aromatic Hydrocarbons Analysis (PAHs)

PAHs concentrations in water samples are also measured and the findings are given in Figure 4.5. The total PAHs levels vary between 2.4 and 16.9 mg/L. Higher concentrations have seen in Bornova, Manda, and Bostanlı rivers, which have moderate annual flows. It is also seen that PAHs concentrations are higher in Autumn and Winter seasons.

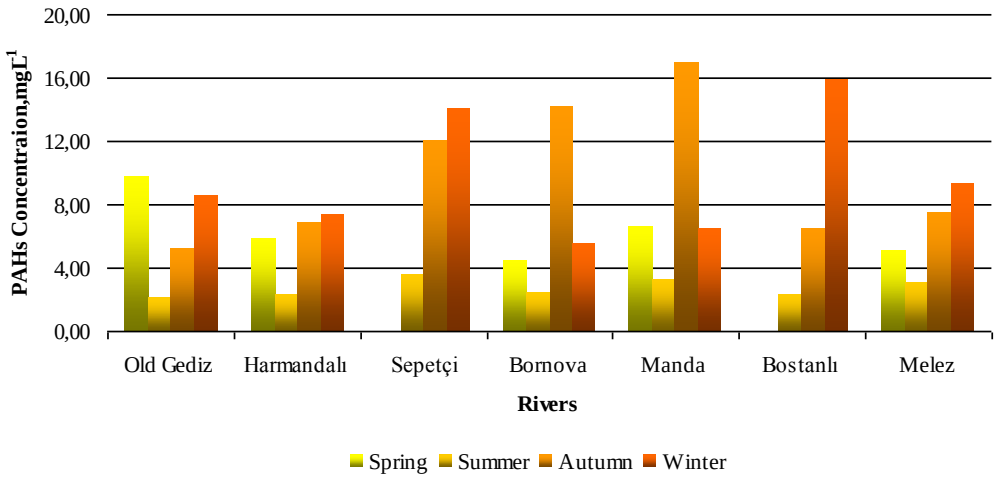
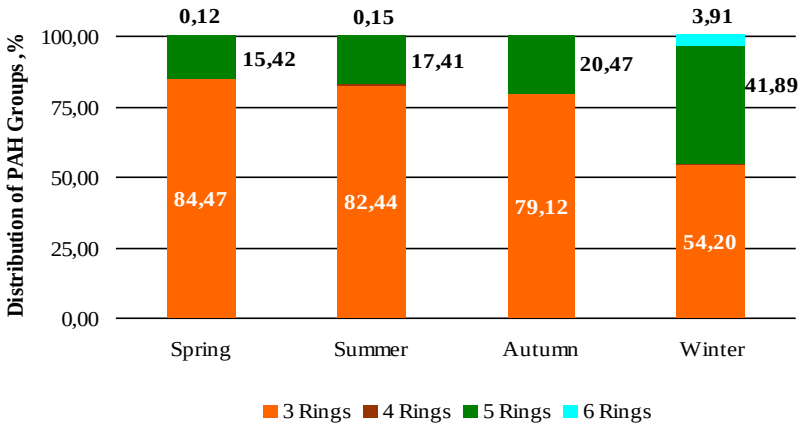


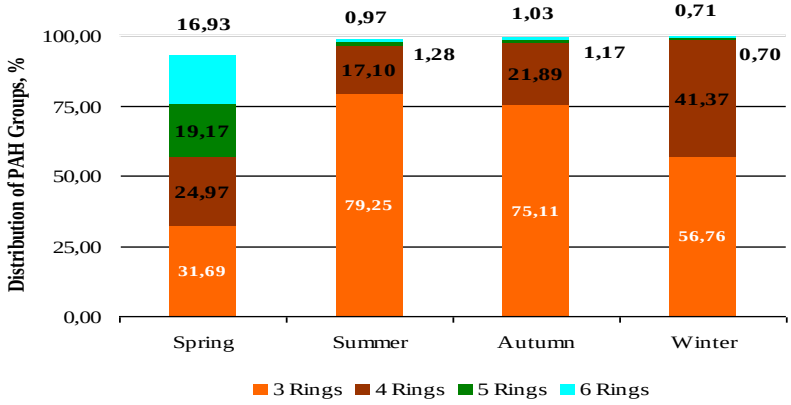
Figure 4.5 PAHs total concentrations in river waters.

Additionally, the concentrations of the detected 16 PAHs are investigated according to the benzene rings in their chemical structure. As the PAHs with 3 benzene rings are; Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, and Carbazole, PAHs with 4 benzene rings are; Fluoranthene, Pyrene, Benz (a) anthrancene, and Chrysene, PAHs with 5 benzene rings are; Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, and Dibenz (a,h)anthrancene, and PAHs with 6 benzene rings are; Benzo (g,h,i) perylene, Indeno (1,2,3-cd)pyrene, the distributions of total

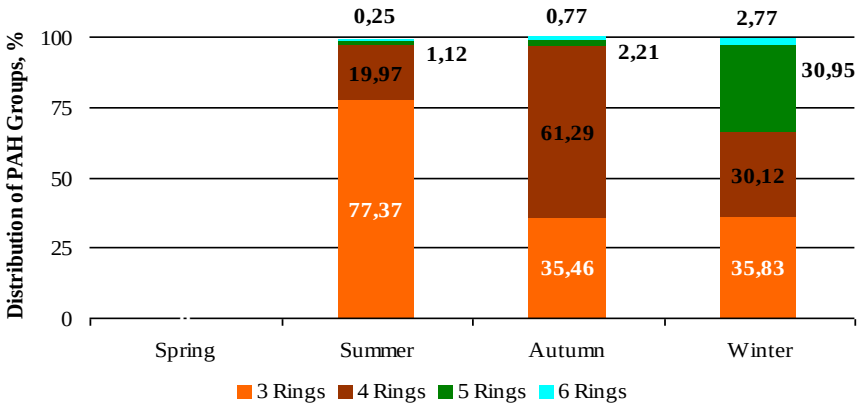
concentrations obtained by these groups in total PAHs concentrations are determined and given in Figure 4.6 for each river.



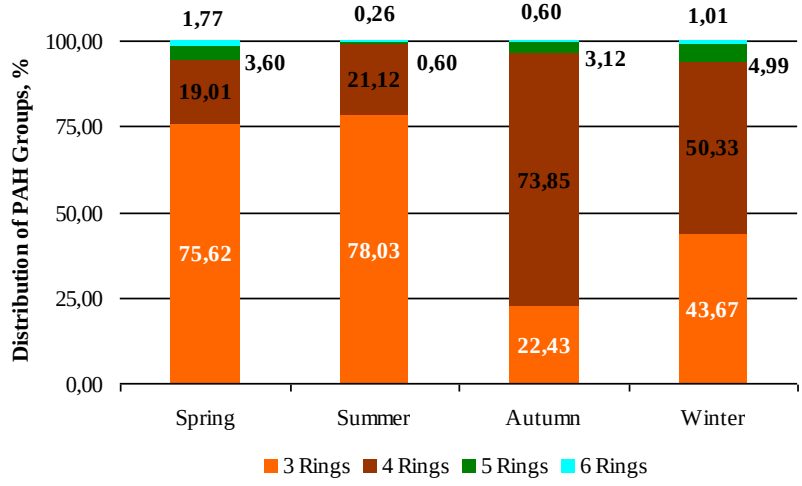
a) Harmandalı



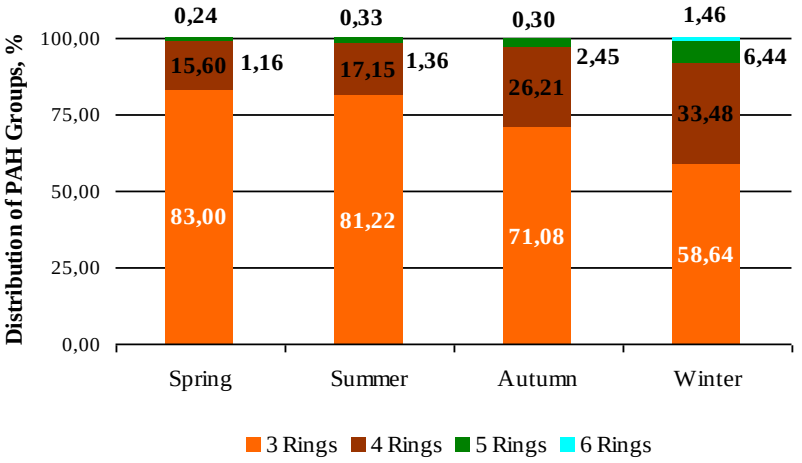
b) Old Gediz



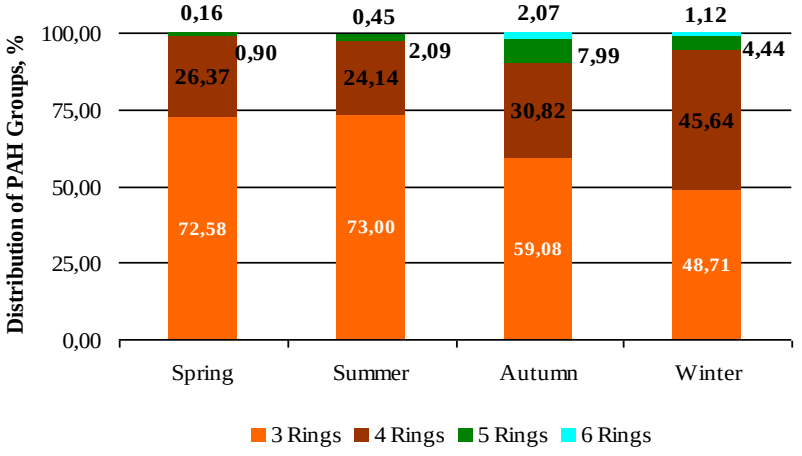
c) Sepetçi



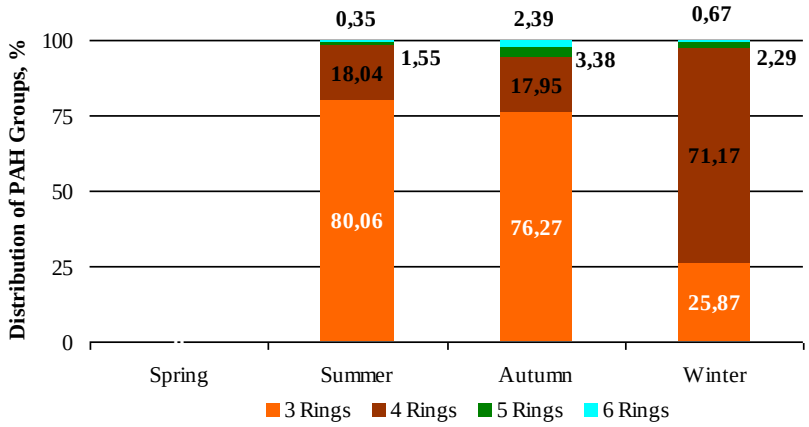
d) Bornova



e) Manda



f) Melez



g) Bostanlı

Figure 4.6 Distribution of PAHs according to the number of benzene rings

The contribution of total PAHs concentration to TPHs concentration varies between 0.5 to 2.0 %. It is observed that 3 Ring PAHs contributes to total PAHs as a portion between 22.43-84.47 %, where 4 Ring PAHs contributes between 0.05-73.85 %. 5 Ring PAHs has a portion of 0.6-41.89 %, and 6 Ring PAHs has a share between 0.12-16.93%. These data show that 3 and 4 Ring PAHs has a big share in the total PAHs concentrations. Chrysene has 4 benzene rings and its concentration is much higher than the other 4 ring structured PAHs (Appendix 1). As Chrysene is emitted during the combustion of coal and fuel oil, it is expected to detect in increasing levels when high population is considered. It is known that molecular weight and boiling point of PAH compounds increase with increasing benzene rings while their solubility decreases. According to these knowledge, it is expected to find higher levels PAHs consisting 3 and 4 benzene rings, in river waters.

Raw data obtained for each of the 16 PAHs for the river waters are given in Appendix 1-A.

4.1.4 Heavy Metals

Ni, Al, Cd, Cr, Cu, Pb and Zn are detected in river waters seasonally (Table 4.2.). The evaluation of the heavy metals concentrations detected in river waters is completed according to the Turkish Water Quality Criteria for Inland Waters

(TWPCR, 2004). In TWPCR, inland waters are divided into four groups according to the quality parameters. As it is emphasized in Table 4.2, most of the detected Al and Cr concentrations in the rivers are above Class I water standards and express low quality water properties.

Table 4.2 Heavy metal levels detected in river waters

River	Season	Heavy Metals (µg l^{-1})						
		Ni	Al	Cd	Cr	Cu	Pb	Zn
Old Gediz	Spring	30,111	499,604	0,000	5,002	32,124	0,000	134,612
	Summer	17,000	148,000	0,000	3,000	12,000	4,000	115,000
	Autumn	22,000	201,500	0,000	4,500	14,500	7,000	199,500
	Winter	28,000	221,000	0,000	3,500	23,000	9,000	586,000
Harmandalı	Spring	10,963	0,000	0,000	1,849	1,896	0,000	41,919
	Summer	11,468	0,000	0,000	3,384	0,461	0,000	55,950
	Autumn	34,629	240,850	0,000	15,590	23,007	7,483	252,463
	Winter	30,448	140,662	0,000	9,253	9,591	3,801	114,467
Sepetçi	Spring							
	Summer	13,667	16,192	0,000	2,071	1,462	0,000	39,488
	Autumn	16,706	2398,610	0,400	8,309	37,599	13,551	248,404
	Winter	14,811	154,958	0,000	2,831	15,302	0,000	99,330
Bornova	Spring	17,320	122,334	0,117	1,970	14,106	0,000	122,201
	Summer	14,111	310,620	0,121	3,677	11,965	7,103	136,187
	Autumn	6,228	200,547	0,055	2,993	21,681	4,270	93,887
	Winter	8,141	144,873	0,237	3,202	7,058	3,543	59,692
Manda	Spring	19,333	432,911	0,117	5,665	88,704	6,158	174,357
	Summer	32,804	167,662	0,000	5,968	6,170	3,333	193,147
	Autumn	8,872	449,789	0,000	4,200	12,290	4,881	85,877
	Winter	8,014	227,232	0,000	4,342	7,002	6,249	41,026
Melez	Spring	20,799	284,969	0,085	4,635	24,968	2,279	127,499
	Summer	6,305	7,159	0,000	2,213	0,000	0,000	32,728
	Autumn	19,391	179,116	0,201	3,097	11,181	10,193	162,828
	Winter	12,610	2,036	0,420	3,085	0,251	0,444	51,754
Bostanlı	Spring	nd	nd	nd	nd	nd	nd	nd
	Summer	19,041	160,091	0,196	2,598	23,889	5,392	212,603
	Autumn	13,266	1538,870	0,176	5,418	19,825	10,247	197,645
	Winter	17,231	151,973	0,000	2,575	4,310	0,000	136,019

TWP CR Criteria, µg l^{-1}	**Class I**							
	Class II	20	**0,3**	3	**BDL***	20	10	200
		50	**0,3**	5	**20**	50	20	500
	Class III	200	**1**	10	**50**	200	50	2000
	Class IV	>200	**>1**	>10	**>50**	>200	>50	>2000

Bolded: Low Quality(Class II)

Bolded and Underlined: Dirty (Class III)

BDL*: below detection Limits

Ni concentrations are found above the Class I quality limit (20 µg l^{-1}) in the waters of Old Gediz and Harmandalı in Autumn and Winter. Cu concentrations are also detected above the Class I limit (20 µg l^{-1}) in the rivers, at least once and Manda river Cu level is evaluated as Class III (dirty water) during Spring season. Cd concentrations express Class I water quality, where Pb concentrations is above Class I limits in Autumn at the waters of Sepetçi, Melez and Bostanlı. In Winter season, Zn concentration of Old Gediz was significantly high and should be evaluated as Class III water.

The correlations between water heavy metal concentrations are also investigated, but any relations between the metal levels could not be found.

4.2 Sediment Samples

4.2.1 pH

The pH values of the sediment samples measured in the laboratory due to EPA Method 9045 C are given in Table 4.3.

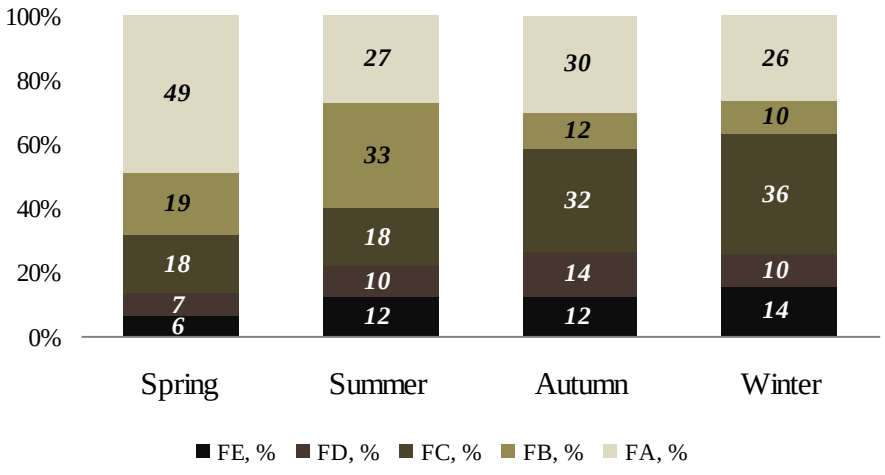
Table 4.3 Sediment pH

Station	*Sediment pH*			
	Spring	**Summer**	**Autumn**	**Winter**
Harmandalı	8,4	8,6	8,3	8,7
Old. Gediz	8,5	8,8	8,7	8,3
Sepetçi	nd	8,8	8,3	8,2
Bornova	8,6	8,3	8,5	7,8
Manda	8,1	8,5	8,3	7,9

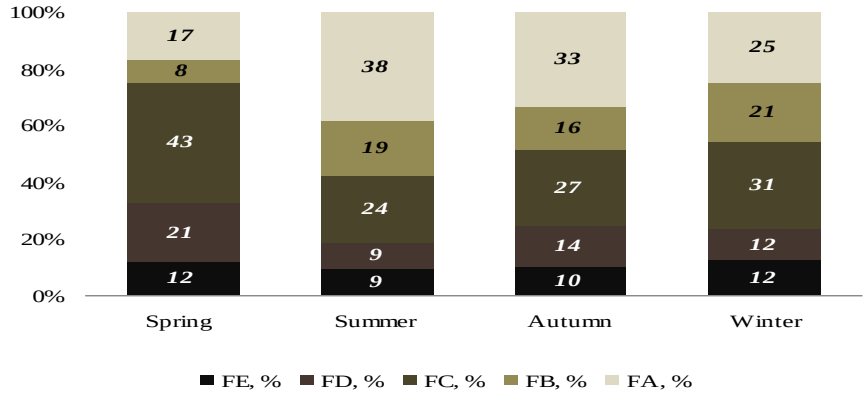
Sediment pHs express a slight alkali to alkali levels and vary between 7.8-8.8. Lower pH levels are detected in Winter season in most of the river sediments.

4.2.2 Sediment Grain Size Distribution

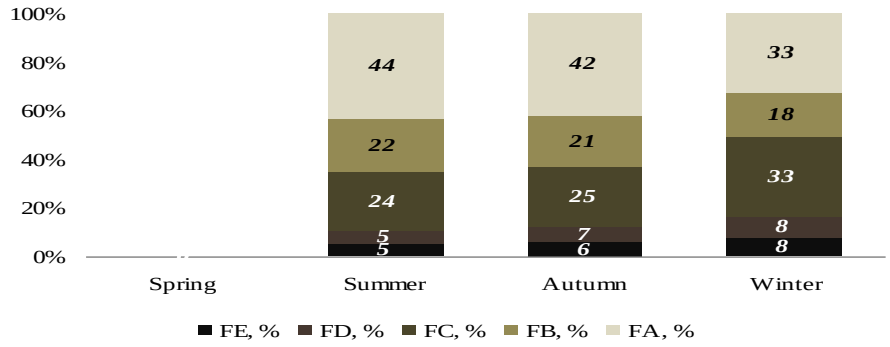
Sediments grain size distributions are determined in seasonal samples and the results are given in Figure 4.7.



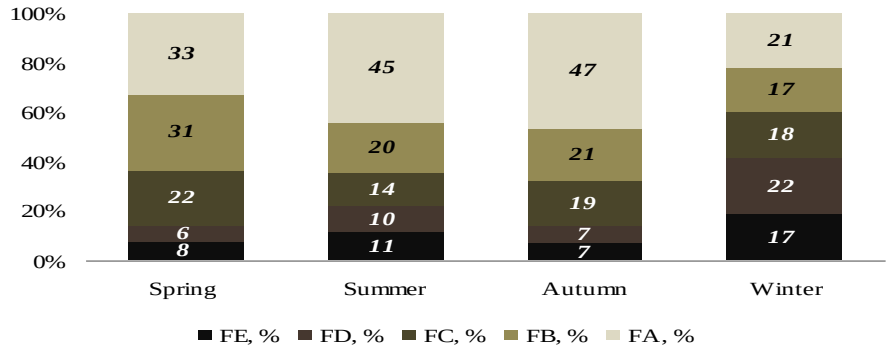
a) Harmandalı



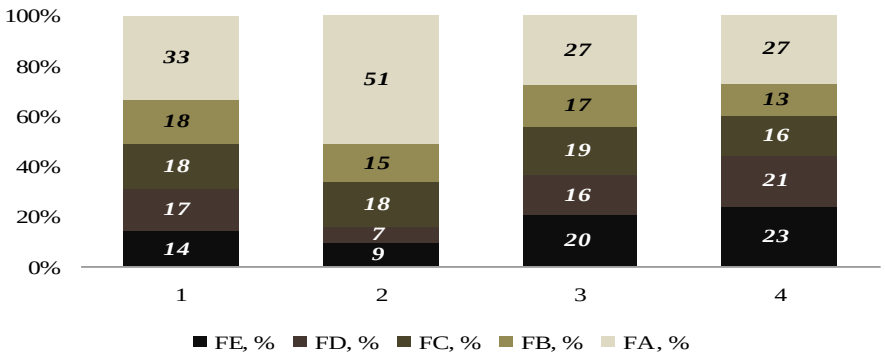
b) Old Gediz



c) Sepetçi



d) Bornova



e) Manda

Figure 4.7 Grain size distribution for the sediment samples according to the seasons

In Harmandalı river sediment, the larger particles dominantly present, especially in Spring season, and tend to decrease through the end of the year. In Old Gediz sediment medium size particles are dominant, as it flows through agricultural areas. In Sepetçi river, the presence of smaller particles is significantly low, since this water flow through the city and receives urban rainwater. Bornova river sediment has high amount of larger particles, which flows through agricultural, industrial and urban areas. In the sediment of Manda river, even though the large particles are in higher portion, medium and small size particles are also in considerable amounts, since the river passes through urban and small size industry areas.

4.2.3 Sediment Water Content and Organic Matter Content

Water content and organic matter content of the sediment samples are determined and the results are presented in Table 4.4. and Table 4.5., respectively.

Table 4.4 Sediment water content

Station	Sediment Water Content (% w)			
	Spring	**Summer**	**Autumn**	**Winter**
Harmandalı	33,48	38,89	33,77	23,77
Old. Gediz	23,66	34,15	26,10	23,07
Sepetçi	nd	25,05	30,55	32,42
Bornova	28,73	47,18	32,67	39,21
Manda	47,82	48,35	48,51	33,57

As it is recognized, water content of the sediment samples vary between 23.07% and 48.51%. Organic matter content of the dry sediment varies between 4.51% and 31.33%. Elevated organic matter levels are measured in the sediments of Bornova and Manda rivers that receive water from urban and small industry areas.

Table 4.5 Sediment organic matter content

Station	Sediment Organic Matter Content (% dry matter)			
	Spring	**Summer**	**Autumn**	**Winter**
Harmandalı	5,52	4,97	8,6	7,79
Old. Gediz	4,99	7,25	4,65	7,37
Sepetçi	nd	5,52	7	9,2
Bornova	4,51	31,33	4,94	14,06
Manda	16,84	19,02	16	26,49

4.2.4 Total Petroleum Hydrocarbons (TPHs) and Polycyclic Aromatic Hydrocarbons (PAHs)

TPHs and PAHs levels in sediment samples were determined and the results are given in below part.

4.2.4.1 Total Petroleum Hydrocarbons (TPHs)

TPHs levels in the sediments vary between 3563 mg/kg (Bornova, Spring season) and 13998 mg/kg (Manda, Winter season) (Figure 4.8). It is also observed that TPHs levels are higher in Winter season, especially in the sediments of the rivers with large catchment areas.

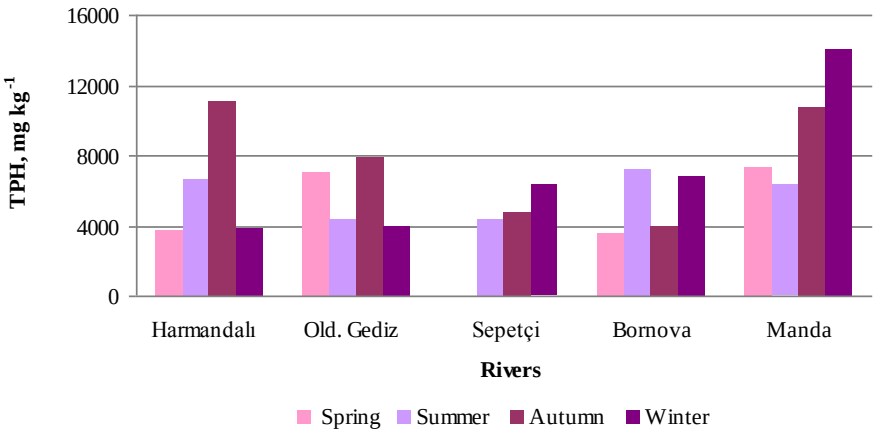


Figure 4.8 TPHs in sediments

4.2.4.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs levels in sediments are also measured and the total values are given in Figure 4.9 according to the seasons. The minimum and maximum PAHs concentrations in the river sediments are measured as 44.22 mg/kg (Old Gediz, Summer season) and 193.71 mg/kg (Bornova, Spring season), respectively. It is seen that lower concentrations are obtained in Winter season.

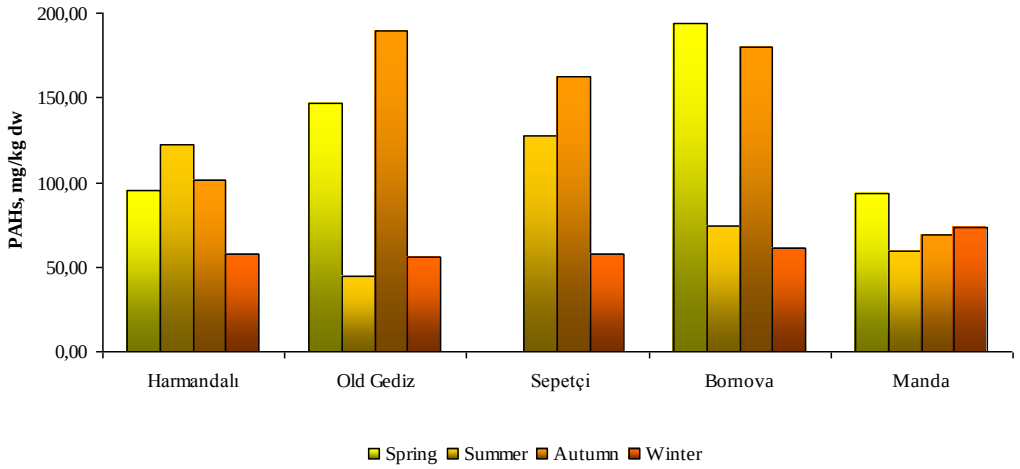
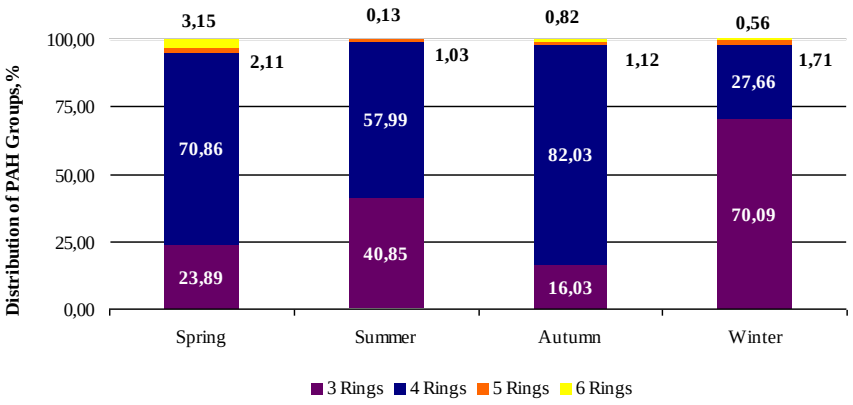


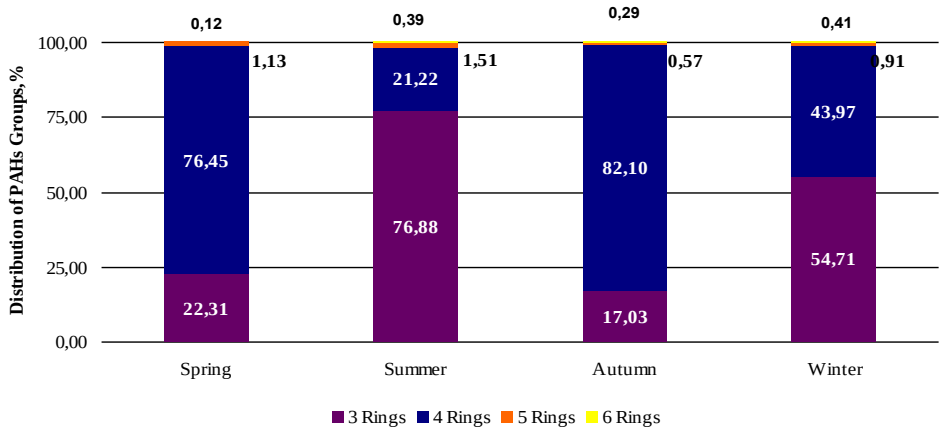
Figure 4.9 Total PAHs in river sediments

It was stated that 1.2-1.4% of sediment TPHs are originated from PAHs. Sediment PAHs are also evaluated according to the number of benzene rings in their structure as it was defined previously in section 4.1.3.2 (Figure 4.10).

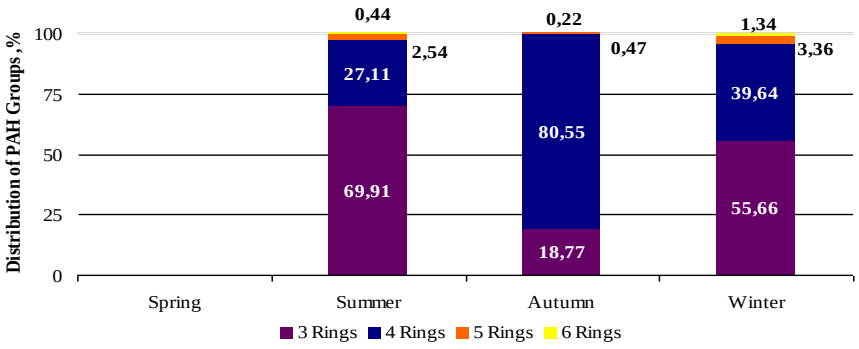
The distributions of PAHs groups show that 3 and 4 ringed PAH compounds are dominantly present in the sediments. The total concentration of PAHs present in these two groups consist 80% to 97% of the total PAHs investigated. The only considerable data related with other PAHs groups are recorded in Manda river sediment on Spring season with the 17.5% of 6 ring PAHs.



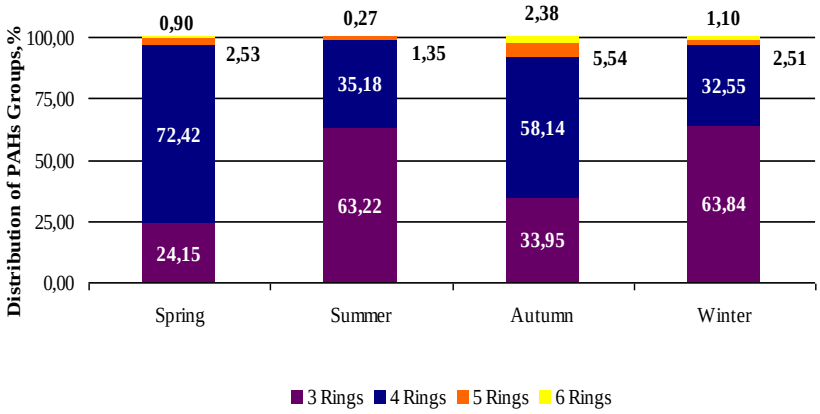
a) Harmandalı



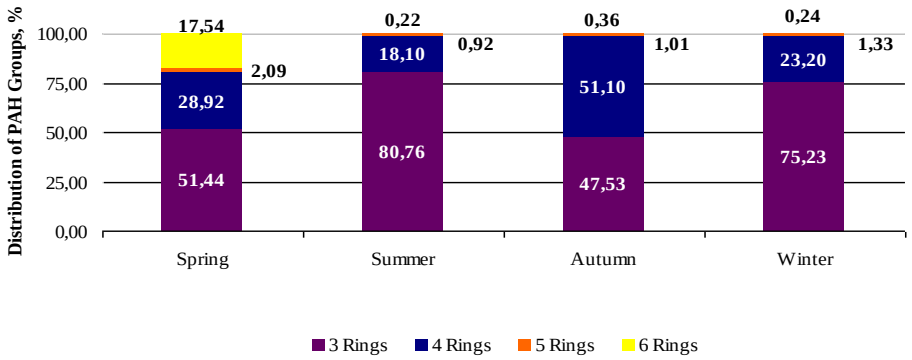
b) Old Gediz



c) Sepetçi



d) Bornova



e) Manda

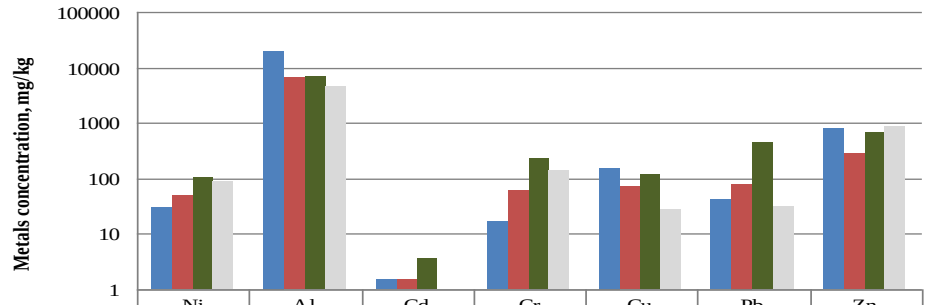
Figure 4.10 PAHs distribution in the sediment according to the number benzene rings they include

It should be noted that there is not a sediment quality standard in Turkey, but the maximum allowable limit for PAHs is 5 mg/kg for the clean soils according to the Turkish Soil Contamination Control Regulation (TSCCR, 2001). When the sediment PAHs concentrations are considered, it is seen that the river sediments are seriously polluted.

Raw data obtained for each of the 16 PAHs for the river sediments are given in Appendix 1-B.

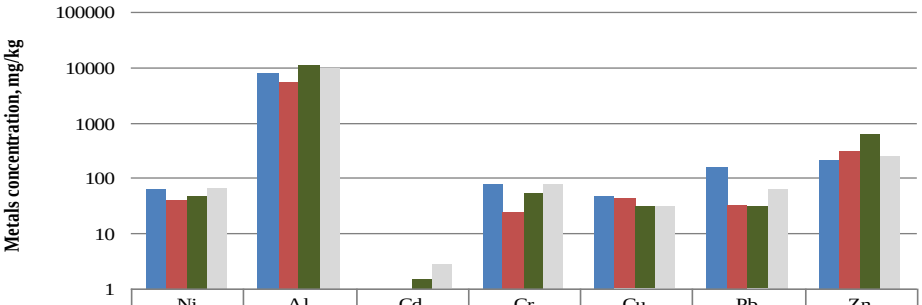
4.2.5 Heavy Metals

Heavy metal levels in river sediment are investigated and the results are evaluated by comparing the values with the maximum allowable limits for clean soils defined in Turkish Soil Contamination Control Regulation (TSCCR, 2001). The heavy metal concentrations in river sediments are given in Figure 4.11 with their seasonal variation.



	Ni	Al	Cd	Cr	Cu	Pb	Zn
Spring	29	19627	2	17	154	42	792
Summer	47	6530	2	60	71	78	281
Autumn	104	6935	4	222	115	430	677
Winter	91	4509	1	142	28	32	834

a) Harmandalı

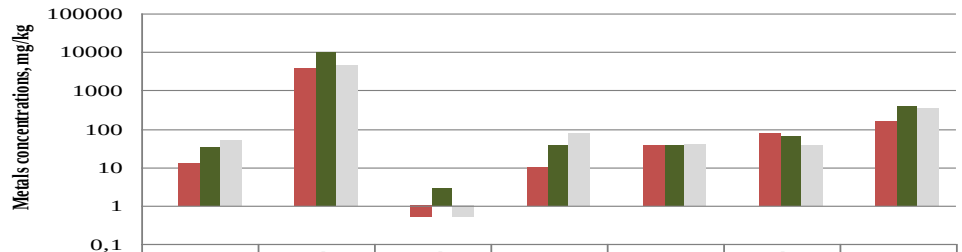


	Ni	Al	Cd	Cr	Cu	Pb	Zn
Spring	63	7770	1	79	49	157	210
Summer	40	5317	1	25	42	32	306
Autumn	48	10897	1,5	53	30	31	613
Winter	65	9770	2,75	78	31	63	252

b) Old Gediz

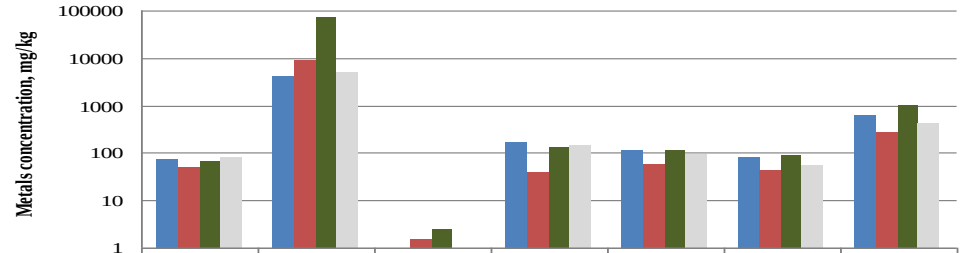
	Ni	Al	Cd	Cr	Cu	Pb	Zn
Spring	0	0	0	0	0	0	0
Summer	13	3967	0,5	10	37	81,5	158
Autumn	34	10404	3	39	38	67	389
Winter	50	4379	0,5	82	40	37	355

c) Sepetçi



	Ni	Al	Cd	Cr	Cu	Pb	Zn
Spring	0	0	0	0	0	0	0
Summer	13	3967	0,5	10	37	81,5	158
Autumn	34	10404	3	39	38	67	389
Winter	50	4379	0,5	82	40	37	355

d) Bornova



	Ni	Al	Cd	Cr	Cu	Pb	Zn
Spring	75	4303	0	170	113	83	607
Summer	49	9339	2	40	57	44	280
Autumn	70	74567	3	132	112	92	1057
Winter	81	4953	1	144	99	56	427

e) Manda

Figure 4.11 Heavy metal levels in river sediments

The maximum allowable limits for heavy metals in soils (with pH> 6) are defined in TSCCR as follows; Pb: 300 ppm dw, Cd: 3 ppm dw, Cr: 100 ppm dw, Cu: 140 ppm dw, Ni: 75 ppm dw, and Zn:300 ppm dw. There is no defined limit for Al, which is also detected.

According to the above mentioned limits;

- In Harmandalı river sediment Ni, Cd, Cr, Pb, and Zn concentrations exceed the limits on Autumn, Ni, Cr, and Zn concentrations exceed the limits on Winter, and Cu and Zn concentrations exceed the limits on Spring.
- In Old Gediz river sediment Zn limits was exceeded on Autumn.
- In Sepetçi river sediment Zn concentration exceed the limits on Autumn and Winter.

- In Bornova river sediment Zn concentration exceed the limits on Autumn and Winter.
- In Manda river sediment Cr and Zn concentrations exceed the limits on Autumn, Ni, Cr, and Zn concentrations exceed the limits on Winter, and Ni, Cr, and Zn concentrations exceed the limits on Spring seasons.
- None of the heavy metals in the sediments collected in Summer season exceed the limit values.

The correlations between water and sediment heavy metal concentrations are also investigated in the content of the study. However, since any linear relation with a correlation coefficient (R^2) greater than 0.4 could not be found, the results are not presented here.

4.2.6 Organic Matter Content and TPHs levels in Sediment Grain Sizes

Organic matter content and TPH levels in sediment grain sizes are also determined and the weighted average of the data obtained in size fractions is calculated by using the percentage of the size fractions which is given in section 4.2.2.

The findings for organic matter and TPHs are given in Table 4.6 for organic matter content and in Table 4.7 for TPHs. The measured values in bulk sediment samples are also presented in the tables. It was seen that weighted average values and bulk levels are compatible with each other both for organic matter content and TPHs.

Table 4.6 Organic matter content in size fractions of sediment samples (% dw)

River	Season	2000µm > FA >600 µm	600µm > FB >300 µm	300 µm > FC >90 µm	90 µm > FD > 45 µm	45 µm > FE µm	Total (Weighted average)	Bulk
Old Gediz	Spring	5,95	7,18	3,48	5,34	8,29	5,14	4,99
	Summer	9,35	7,38	5,43	10,80	9,10	8,13	7,25
	Autumn	6,51	5,54	4,16	6,75	6,47	5,76	4,65
	Winter	8,5	5,9	6,44	9,71	10,5	7,70	7,37
Harmandalı	Spring	4,12	4,7	5,22	10	11,63	5,33	5,52
	Summer	7,45	7,26	2,13	4,69	3,71	5,71	4,97
	Autumn	9,06	9,69	5,85	7,79	10	8,05	8,60
	Winter	7	6,34	6,05	5,7	10,73	6,72	7,79
Sepetçi	Spring	nd	nd	nd	nd	nd	nd	nd
	Summer	5,59	6,18	7,24	7,68	9,46	6,42	5,52
	Autumn	6,88	6,15	5,77	10,58	12,76	7,04	7,0
	Winter	7,97	8,45	7,26	11,06	11,09	8,31	9,2
Bornova	Spring	6,29	3,1	3,35	6	11,91	5,06	4,51
	Summer	37,76	35,88	27,78	3,87	12,26	29,55	31,33
	Autumn	5	2,45	4,91	10,11	12,66	5,35	4,94
	Winter	15,65	15,97	11,88	12,1	12,83	13,57	14,06
Manda	Spring	15,99	16,53	17,48	13,58	14,26	15,71	16,84
	Summer	24,41	24,18	17,52	14,38	14,79	21,61	19,02
	Autumn	21,22	15,13	21,19	16,15	16,47	18,37	16
	Winter	23,49	24	23,37	18,65	21,11	21,98	26,49

It was seen that organic matter content of larger sediment particles are relatively high in most of the samples. Significantly high values are obtained in the largest fraction of the sediments of Bornova and Manda rivers in Summer season. The results are evaluated according to the sediment TPHs levels in size fractions. For the larger grain sizes (FA and FB) it is recognized that TPHs levels are quite high in the

sediment of Harmandalı, Sepetçi and Manda rivers, higher TPHs concentrations are found in FC fractions of Manda, Sepetçi and Bornova sediments. For the fraction FD, high TPHs concentrations are found in the sediments of Manda, Harmandalı and Sepetçi rivers, while the elevated concentrations are found in FE in the sediments of Manda and Bornova rivers.

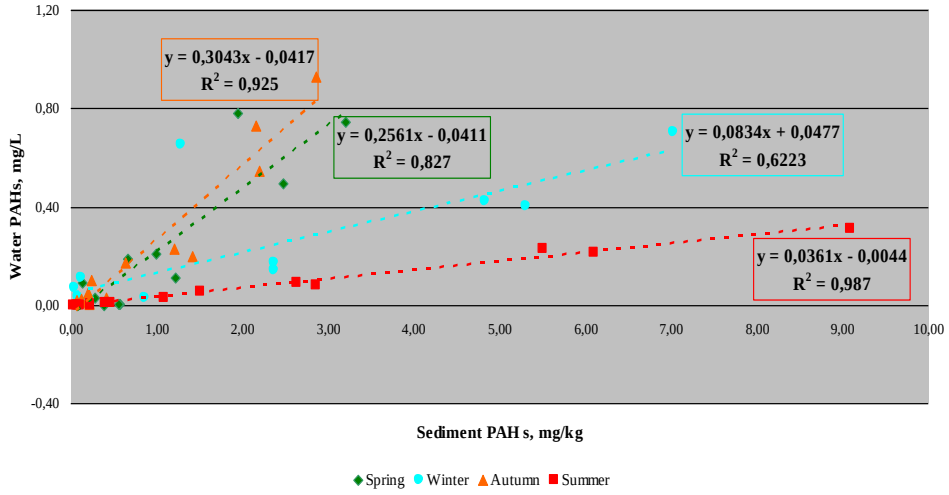
Additionally, the levels of TPHs are found higher in the largest (FA) and the smallest (FE) fractions than the medium size fractions generally.

Table 4.7 TPHs content in size fractions of sediment samples (mg/kg dw)

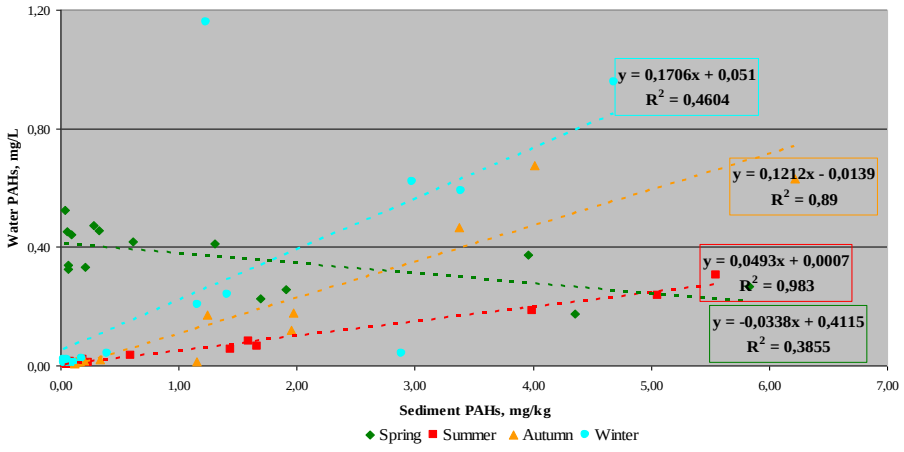
Station		2000µm > FA >600 µm	600µm > FB >300 µm	300 µm > FC >90 µm	90 µm > FD > 45 µm	45 µm > FE µm	Weighted average	Bulk
Old Gediz	Spring	7488,34	4423,11	8274,3	9265,39	9732,51	8220,59	7021,20
	Summer	4302,57	2597,44	5475,35	2050,49	4050,39	4028,61	4392,30
	Autumn	9131,67	6604,95	8170,05	10385,05	5276,25	8274,01	7930,17
	Winter	7156,76	3528,72	3947,87	1470,35	7388,5	4779,89	3970,80
Harmandalı	Spring	3291,64	9004,21	2171,38	2351,77	1149,13	3994,50	3728,20
	Summer	9861,24	4520,33	5117,12	12917,94	10054,83	7592,18	6639,30
	Autumn	41265,7	640,8	527,9	888,7	962,3	12906,28	11020,50
	Winter	1076,1	1096,3	5045,9	8918,6	7839,9	4226,24	3884,50
Sepetçi	Spring	nd	nd	nd	nd	nd	nd	3728,20
	Summer	7274,12	9954,44	7255,5	7682,45	9137,42	7965,31	6639,30
	Autumn	14589,9	10419,7	12105,8	12336,2	10744,4	12730,85	11020,50
	Winter	4082,7	978,1	7139,98	7601,1	955,9	4585,17	3884,50
Bornova	Spring	3995,09	1613,7	2771,26	7195,34	15446,81	4056,04	3563,00
	Summer	8113,71	7798,18	8040,89	9569,1	10479,74	8460,09	7194,20
	Autumn	3894,06	3784,3	4615,1	7997	10721,4	4766,59	3980,90
	Winter	8504,1	7529,8	8635,7	6687,1	9727,2	7813,78	6842,10
Manda	Spring	9540,82	5750,09	7854,35	7341,89	8011,12	7973,90	7282,50
	Summer	7067,76	6785,09	6616,65	8151,98	10907,65	7367,02	6273,00
	Autumn	11723,6	10578,2	11800,5	10944,3	19336,8	12965,68	10798,20
	Winter	12947,0	20726,7	20656,2	10993,98	13817,45	15005,23	13997,60

4.3 The Correlations Between Water and Sediment PAHs Concentrations

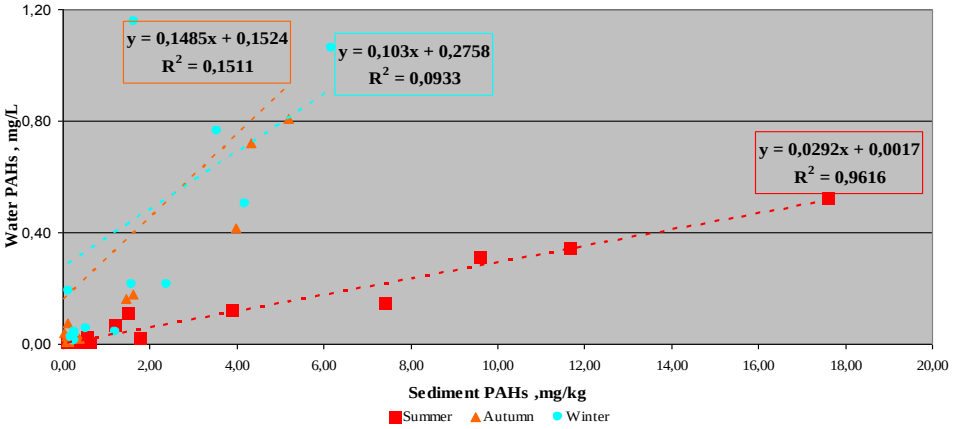
The possible correlations between water and sediment PAHs concentrations are investigated in the content of the thesis. The data are evaluated seasonally for each river and the findings are illustrated below in Figure 4.12.



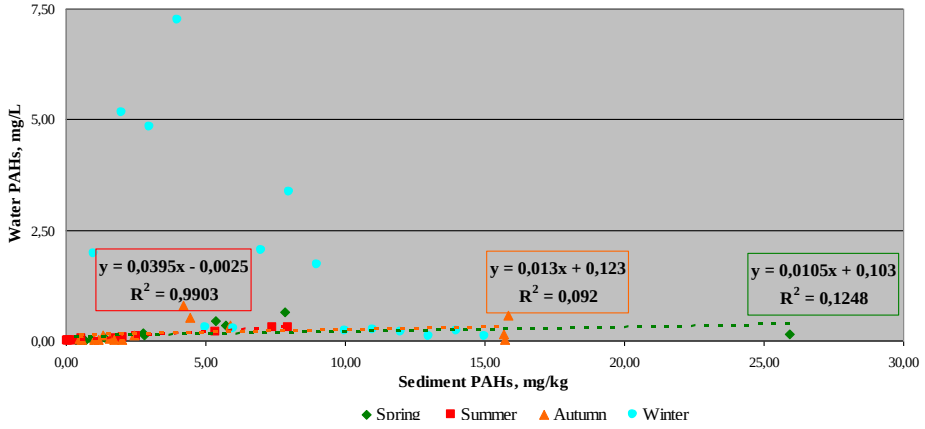
a)Harmandalı



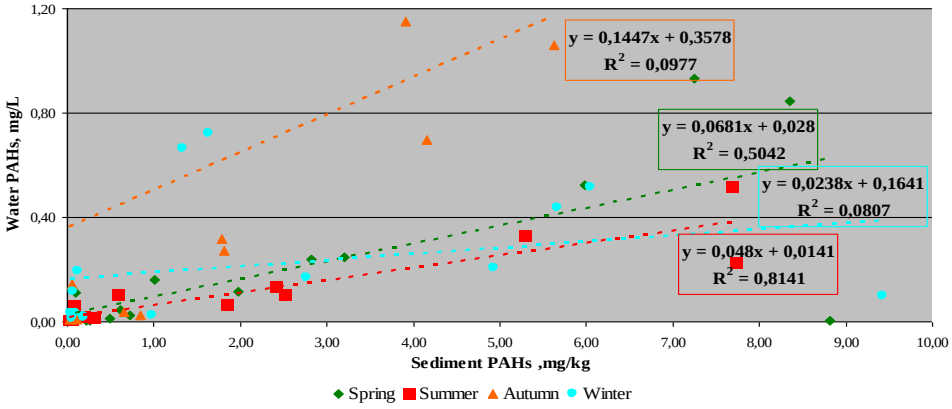
b) Old Gediz



c) Sepetçi



d) Bornova



e) Manda

Figure 4.12 The correlations between sediment and water PAHs levels in rivers.

It is recognized that water and sediment PAHs concentrations are strongly correlated for all of the rivers in Summer and Winter seasons. Additionally, the water PAHs levels are not raising in the same rate as the sediment concentrations. That is an indication of a possible adsorption of PAHs in water on to the sediment particles, or on to the settlable solids in the water.

4.4 Contaminant Loads Discharged into the Bay

The contaminant loads discharged into the Bay by the investigated rivers are calculated seasonally and the findings are presented in this section. The load calculations are completed depending on i) the percentage of the average precipitation observed for each season between the years of 1996-2006, ii) the flow of the corresponding river, and iii) the seasonal concentration of the contaminant (TPHs, PAHs, heavy metals, and settlable solids) in river water. Below equation (Eq. 4.1) was applied for the calculation of a river's contaminant load discharged in each season:

$$L_c = P_s * F_r * C_c * 10^{-6} \qquad \text{Eq. 4.1}$$

where L_c is the contaminant load discharged into the Bay from the corresponding river(tones), P_s is the amount of the seasonal precipitation as a percentage of annual rain (%), F_r is the annual flow of the corresponding river (m^3), and C_c is the seasonal contaminant concentration for the corresponding river (g/m^3).

The raw data related with the precipitation between the years of 1996 and 2006 (DMI, 2007) are given in Appendix II. The average seasonal precipitations and related percentages (P_s) are given below in Table 4.8.

Table 4.8 Average Seasonal Precipitation in Izmir and its Distribution

	Average Seasonal Precipitation, mm	**Distribution (P_s), %**
Spring	154,0	**22,4**
Summer	11,8	**1,7**
Autumn	103,9	**15,1**
Winter	418,7	**60,8**
Annual (Total)	**688,5**	**100,0**

As can be seen from the table, winter precipitation occurs 60.8% of the annual rain and summer precipitations is almost negligible (1.7%). Because of that fact, the major part of the contaminant load enters the Bay in winter season.

4.4.1 Total Petroleum Hydrocarbons (TPHs) Loads Entering the Bay

Calculated TPHs loads originated from the investigated rivers are presented in Figure 4.13. The maximum TPHs load is originated from Melez river, which has the largest catchment area of 123.4 $*10^6$ m^2 and the highest annual flow of 29.98 m^3. Even though Manda, Bornova and Old Gediz have similar water TPHs concentrations, extend of their catchment areas is narrower and this situation results with lower TPHs load to discharge into inner Bay.

Since the volume of Izmir Bay is approximately 10^{10} m^3 (Ka rsiyaka, 2010and the annual TPHs load discharged is 170.000 tons, the TPHs concentration in Izmir Bay can be calculated as 17 mg/L. If the volume of the inner Bay ($407.7*10^6$ m^3) (IZTO, 1995) is considered, TPHs level in inner Bay waters will be as high as 41.7 mg/L.

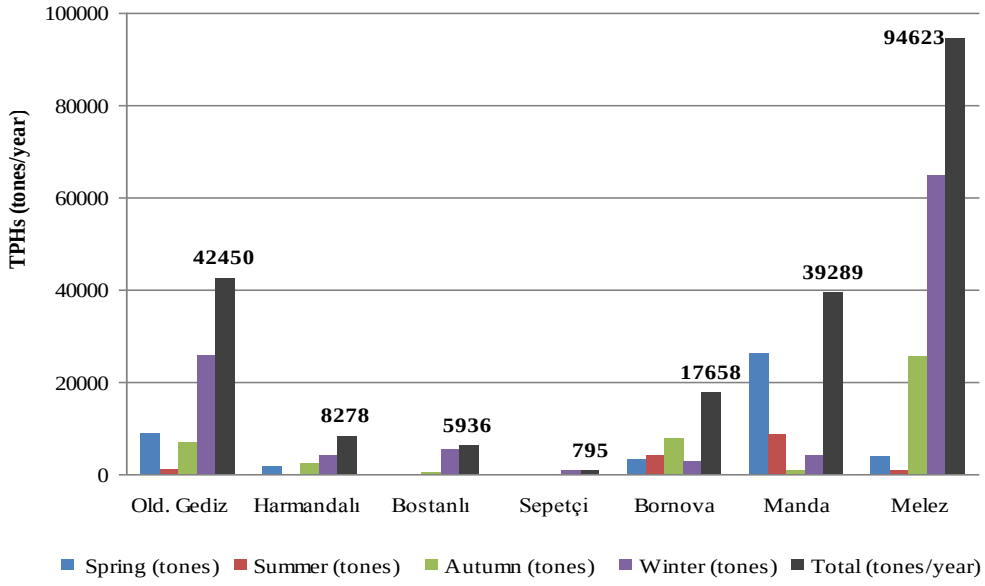
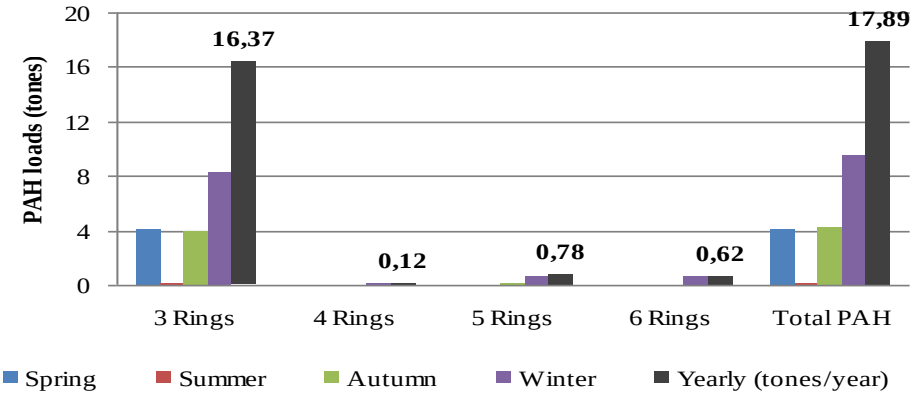


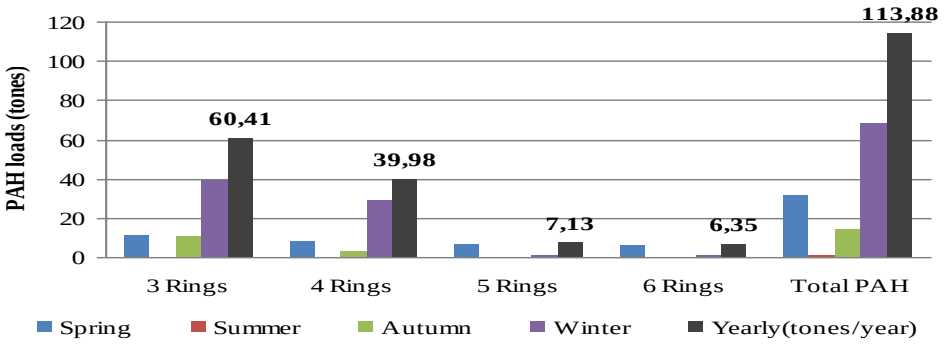
Figure 4.13 TPHs loads coming from the creek

4.4.2 PAHs Loads Entering the Bay

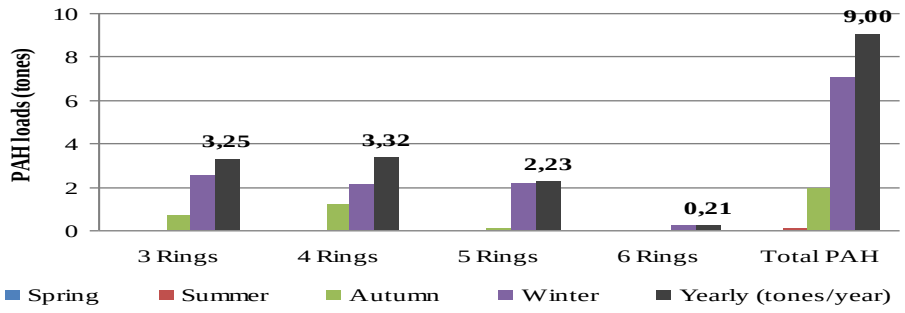
The major components of the PAHs are the 3 and 4 ringed compounds. High loads are generated in winter and autumn because of heavy precipitation. PAHs loads originated from Manda and Old Gediz are significantly high.



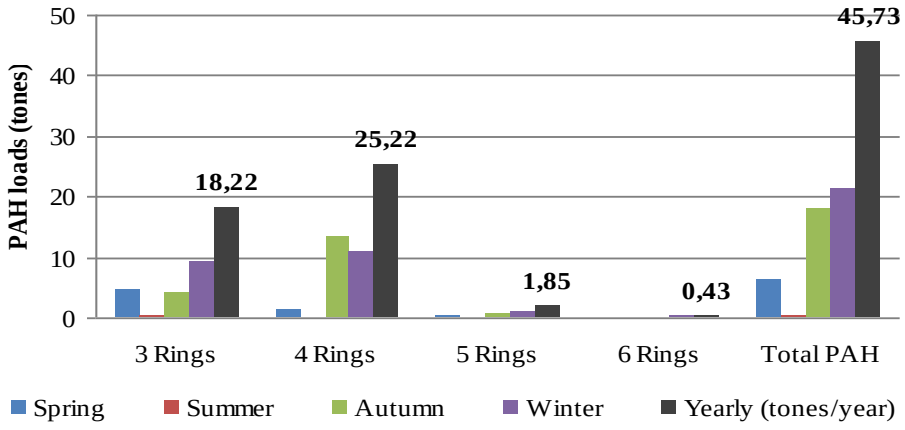
a) Harmandalı



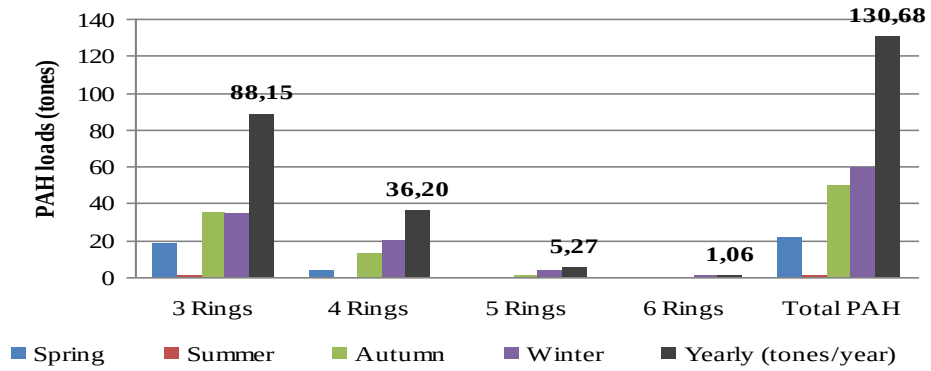
b) Old Gediz



c) Sepetçi



d) Bornova



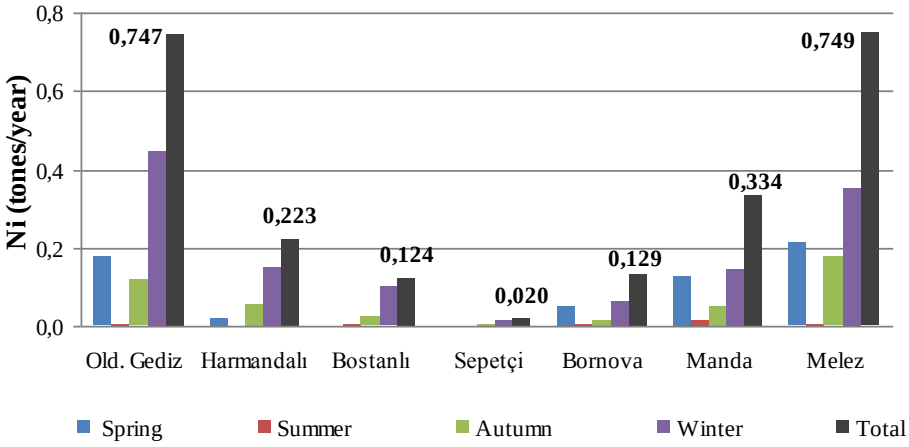
e) Manda

Figure 4.14 Seasonal TPHs loads enter the Bay according to the studied rivers

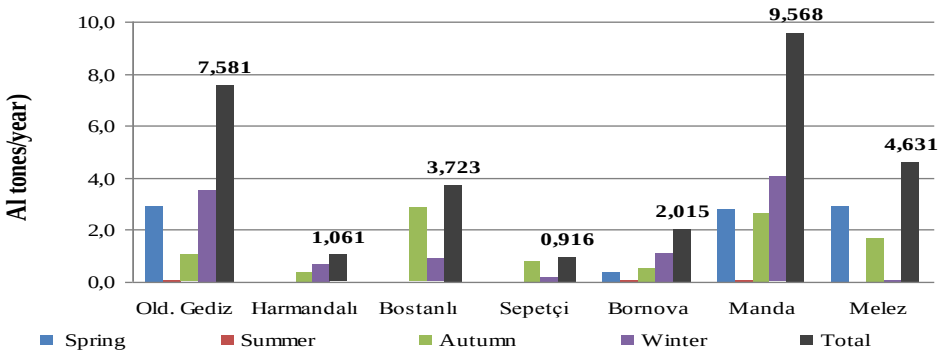
Annually 317.18 tonnes of PAHs are discharged into the inner Bay, which may create 0.78 mg/L PAHs concentration.

4.4.3 Heavy Metal Loads Entering the Bay

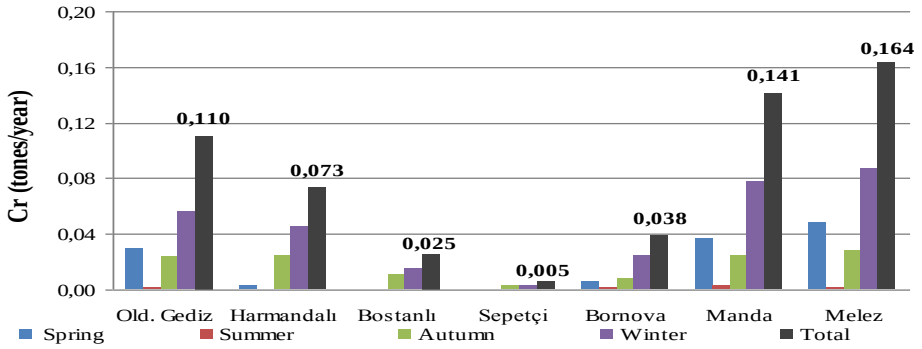
Determination of the heavy metal loads generated from the river waters and discharged to the Bay is also completed and the findings are illustrated in Figure 4.15 seasonally for each heavy metal studied.



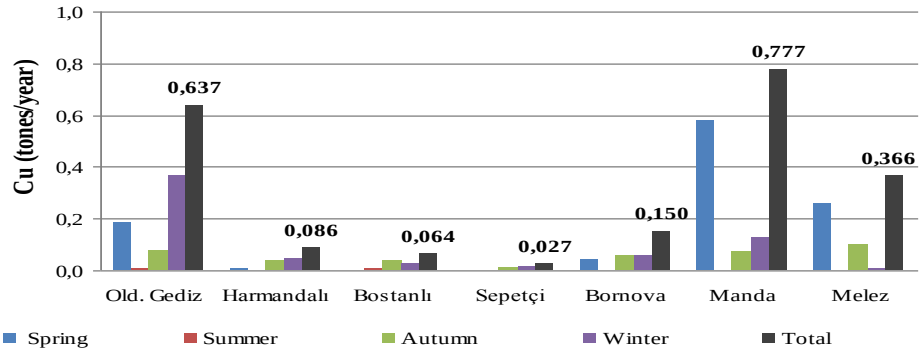
a) Ni load coming from the creeks



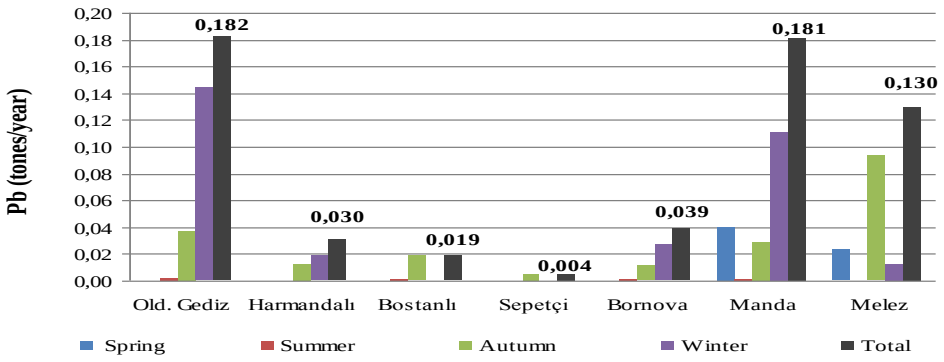
b) Al load coming from the creeks



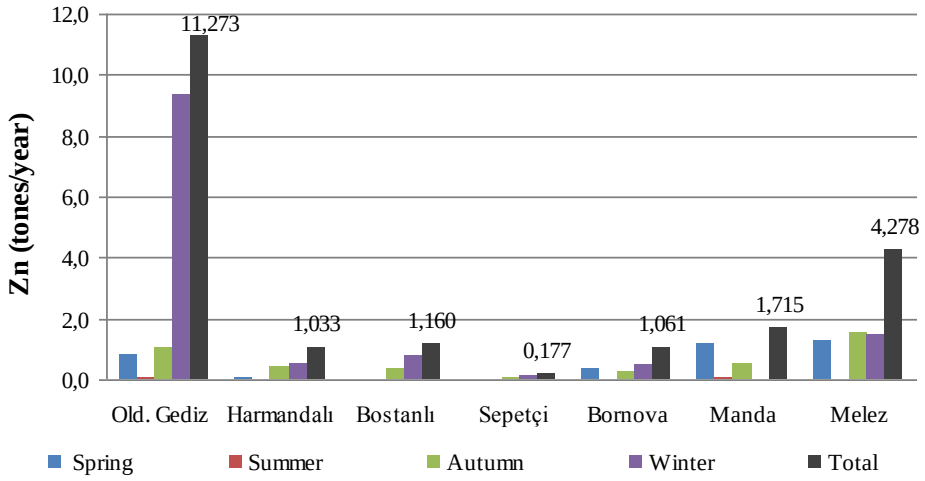
c) Cr load coming from the creeks



d) Cu load coming from the creeks



e) Pb load coming from the creeks



e) Zn load coming from the creeks

Figure 4.15 Ni, Al, Cr, Cu, Pb loads originated from the rivers

The major Ni sources are Melez, Old Gediz and Manda rivers, which carries high loads of Ni especially in winter and spring seasons. The annual Ni entrance into the inner Bay is 2.3 tons that may create 0.006 mg/L (6 µg/L)of Ni concentration.

Al discharge is generated by Manda and Old Gediz, dominantly and the total Al discharge is 29.5 tons annually. That amount may create Al concentration of 0.07 mg/L (70 µg/L) in inner Bay waters.

Melez, Manda and Old Gediz carry the major part of the total Cr into the Bay (0.56 ton/year). Expected Cr concentration in the inner Bay is 0.0014 mg/L (1.4 μg/L).

Copper load is mainly sourced Manda and Old Gediz. Annual discharge from the investigated rivers is 2.1 ton/year that may create 0.005 mg/L of Cu concentration (5 μg/L) in the inner Bay waters.

Old Gediz, Manda and Melez are the rivers that carry Pb dominantly. The total annual Pb discharge into the Bay is 0.59 ton, which may create 0.0012 mg/L (1.2 μg/L) of water concentration.

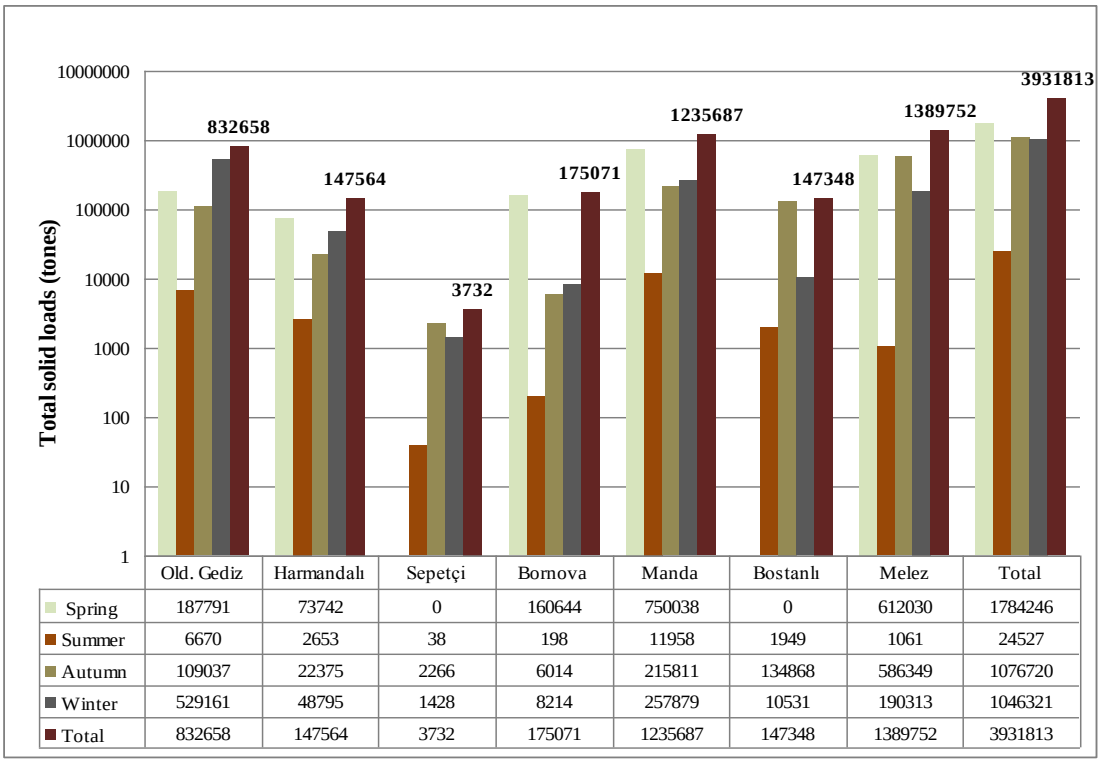
Zn load originated from Old Gediz is significantly high, and the total Zn amount carried into the Bay from the studied rivers is 20.7 tons/year. That amount may cause 0,05 mg/L Zn concentration (50 μg/L) in the inner Bay waters.

4.4.4 Settlable Solids Discharged into the Bay

The settable solid loads carried into the Bay are also calculated and the results are displayed in Figure 4.16. As can be seen from the figure; Melez, Manda and Old Gediz have considerable contributions of settlable solid material into the Bay.

The total settlable solid fraction discharged into the Bay in a year is 3.931.813 tonnes. The sediment density vary between 1.53-2.07 tons/m^3 (UW Technology, 2010) If sediment density is accepted as 1.75 tons/m^3, the settelable solid amount correspond to a volume of 2.247.000 m^3 of sediment. Since the area of inner Bay is 57 km^2 (IZTO, 1995)this amount of carried settlable solids result with 4 cm of average annual sediment accumulation in the bottom of the inner Bay. The heigt of accumulation will be higher in the regions close to the shore, where the water circulation is poor and the water depth is short. This is an important issue for Izmir, since inner Bay is an international and commercially active harbour, which is

previously dregged to remove the sediment that accumulated in the docking line of the ships.



	Old. Gediz	Harmandalı	Sepetçi	Bornova	Manda	Bostanlı	Melez	Total
Spring	187791	73742	0	160644	750038	0	612030	1784246
Summer	6670	2653	38	198	11958	1949	1061	24527
Autumn	109037	22375	2266	6014	215811	134868	586349	1076720
Winter	529161	48795	1428	8214	257879	10531	190313	1046321
Total	832658	147564	3732	175071	1235687	147348	1389752	3931813

Figure 4.16 The Loads for the Settlable Solid Fraction (SF) for the Rivers Studied

4.4.5 Contaminants Discharge from the Rivers' Unit Area of Catchment

The contaminant loads entering the Bay are calculated according to the data obtained in the laboratory, the precipitation data and the rivers flow data. For estimating the level of contamination collected from the unit catchment area of a river, the contaminant loads are divided to the area of collection for each of the rivers.

The findings are given in Table 4.9. It is seen that the rivers flowing through the inner city collect high loads of TPHs and/or PAHs from unit area, which are sourced from the burning of coal and fuel. Additionally, Manda and Melez rivers are washing considerable amount of heavy metals from their unit catchment area.

Higher Cr and Ni loads collected from unit area of Harmandalı basin may be sourced from the landfill area which is located at the springhead of this river.

Table 4.9 Contaminant Loads Collected from the Rivers Unit Catchment Area (tons/km^2)

River	Contaminant Load from Unit Area of Catchment (tons/km^2)								
	TPHs	**PAHs**	**Ni**	**Al**	**Cr**	**Cu**	**Pb**	**Zn**	**SF**
Old Gediz	286,6	0,77	**0,0050**	0,051	0,0007	**0,0043**	**0,0012**	**0,076**	5622
Harmandalı	154,7	0,33	**0,0042**	0,020	**0,0014**	0,0016	0,0006	0,019	2758
Bostanlı	162,6	**1,40**	0,0034	0,102	0,0007	0,0018	0,0005	0,032	4037
Sepetçi	108,9	**1,23**	0,0027	**0,126**	0,0007	0,0037	0,0006	0,024	511
Bornova	**358,2**	0,93	0,0026	0,041	0,0008	0,0031	0,0008	0,022	3551
Manda	**365,5**	1,22	0,0031	**0,089**	**0,0013**	**0,0072**	**0,0017**	0,016	**11495**
Melez	**766,8**	**1,57**	**0,0061**	0,038	**0,0013**	0,0030	0,0010	0,035	**11262**

Old Gediz passes through an industrial zone and because of that Cu, Pb and Zn loads are higher. Settlable solids load from unit basin area are also high in Manda and Melez rivers. According to the amount of contaminant load collected from unit basin area, the investigated rivers can be ranked in descending order as follows:

Melez > Manda > Old Gediz > Bostanlı > Sepetçi > Bornova > Harmandalı

CHAPTER FIVE
CONCLUSIONS

The total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), and heavy metals concentrations and pH levels in the waters and in the sediments of the rivers feeding Izmir middle and inner Bay were investigated in the content of this thesis. Additionally, total solids and suspended solids concentrations in water samples are detected and settable solids concentrations are determined.

According to the annual and seasonal precipitation data, flow data of the investigated rivers, and the contaminant levels detected, the contaminant loads discharged into the Bay from each river was determined.

Additionally, the contaminant loads generated by unit catchment area of each river are calculated to exhibit the contamination potential of the rivers.

The findings of the study can be given as follows:

- The river water pH values vary between 5.86 (Melez, Winter) and 9.4 (Bornova, Summer).

- TSM concentrations are very high in the river waters, especially the ones with larger catchment area, namely: Old Gediz, Manda, Melez and Bornova, while SSM has a small portion of TSM (< 2%). The 98% of the solid material carried to the Bay by the rivers is settlable.

- The water TPH concentrations vary between 120-4000 mg/L. Similar with the results obtained for TSM, water TPH concentrations are higher in the rivers having large catchment areas and high annual flows.

- The total water PAHs levels vary between 2.4 and 16.9 mg/L. Higher concentrations have seen in Bornova, Manda, and Bostanlı rivers, which have moderate annual flows. It is also seen that PAHs concentrations are higher in Autumn and Winter seasons.

- The contribution of total PAHs concentration to TPHs concentration varies between 0.5 to 2.0 % for sampled waters.

- It is observed that 3 Ring PAHs contributes to total PAHs as a portion between 22.43-84.47 %, where 4 Ring PAHs contributes between 0.05-73.85 %. 5 Ring PAHs has a portion of 0.6-41.89 %, and 6 Ring PAHs has a share between 0.12-16.93% in river waters.

- Chrysene has 4 benzene rings and its concentration is much higher than the other 4 ring structured PAHs. As Chrysene is emitted during the combustion of coal and fuel oil, it is expected to detect in increasing levels when heavy population density is considered. It is known that molecular weight and boiling point of PAH compounds increase with increasing benzene rings while their solubility decreases. According to these knowledge, it is expected to find higher levels PAHs consisting 3 and 4 benzene rings, in river waters.

- Most of the detected Al and Cr concentrations in the rivers are above Class I water standards and express low quality water properties.

- Ni concentrations are found above the Class I quality limit (20 μg l^{-1}) in the waters of Old Gediz and Harmandalı in Autumn and Winter. Cu concentrations are also detected above the Class I limit (20 μg l^{-1}) in the rivers, at least once and Manda river Cu level is evaluated as Class III (dirty water) during Spring season. Cd concentrations express Class I water quality, where Pb concentrations is above Class I limits in Autumn at the waters of Sepetçi, Melez and Bostanlı. In Winter season, Zn concentration of Old Gediz was significantly high and should be evaluated as Class III water.

- Sediment pHs express a slight alkali to alkali levels and vary between 7.8-8.8. Lower pH levels are detected in Winter season in most of the river sediments.

- In Harmandalı river sediment, the larger particles dominantly present, especially in Spring season, and tend to decrease through the end of the year. In Old Gediz sediment medium size particles are dominant, as it flows through agricultural areas. In Sepetçi river, the presence of smaller particles is significantly low, since this water flow through the city and receives urban rainwater. Bornova river sediment has high amount of larger particles, which flows through agricultural, industrial and urban areas. In the sediment of Manda river, even though the large particles are in higher portion, medium and small size particles are also in considerable amounts, since the river passes through urban and small size industry areas.

- As it is recognized, water content of the sediment samples vary between 23.07% and 48.51%. Organic matter content of the dry sediment varies between 4.51% and 31.33%. Elevated organic matter levels are measured in the sediments of Bornova and Manda rivers that receive water from urban and small industry areas.

- TPHs levels in the sediments vary between 3563 mg/kg (Bornova, Spring season) and 13998 mg/kg (Manda, Winter season).

- The minimum and maximum PAHs concentrations in the river sediments are measured as 44.22 mg/kg (Old Gediz, Summer season) and 193.71 mg/kg (Bornova, Spring season), respectively. It is seen that lower concentrations are obtained in Winter season.

- It was stated that 1.2-1.4% of sediment TPHs are originated from PAHs. The distributions of PAHs groups show that 3 and 4 ringed PAH compounds are dominantly present in the sediments (80% to 97%).

- It should be noted that there is not a sediment quality standard in Turkey, but the maximum allowable limit for PAHs is 5 mg/kg for the clean soils according to the Turkish Soil Contamination Control Regulation (TSCCR, 2001). When the sediment PAHs concentrations are considered, it is seen that the river sediments are seriously polluted.

- In Harmandalı river sediment Ni, Cd, Cr, Pb, and Zn concentrations exceed the limits on Autumn, Ni, Cr, and Zn concentrations exceed the limits on Winter, and Cu and Zn concentrations exceed the limits on Spring. In Old Gediz river sediment Zn limits was exceeded on Autumn. In Sepetçi river sediment Zn concentration exceed the limits on Autumn and Winter. In Bornova river sediment Zn concentration exceed the limits on Autumn and Winter. In Manda river sediment Cr and Zn concentrations exceed the limits on Autumn, Ni, Cr, and Zn concentrations exceed the limits on Winter, and Ni, Cr, and Zn concentrations exceed the limits on Spring seasons.

- None of the heavy metals in the sediments collected in Summer season exceed the limit values.

- It was seen that organic matter content of larger sediment particles are relatively high in most of the samples. Significantly high values are obtained in the largest fraction of the sediments of Bornova and Manda rivers in Summer season.

- The levels of TPHs are found higher in the largest (FA) and the smallest (FE) sediment fractions than the medium size fractions generally

- It is recognized that water and sediment PAHs concentrations are strongly correlated for all of the rivers in Summer and Winter seasons. Additionally, the water PAHs levels are not raising in the same rate as the sediment concentrations. That is an indication of a possible adsorption of PAHs in water on to the sediment particles, or on to the settlable solids in the water.

- Since the volume of Izmir Bay is approximately 10^{10} m^3 and the annual TPHs load discharged is 170.000 tons, the TPHs concentration in Izmir Bay can be calculated as 17 mg/L. If the volume of the inner Bay ($407.7*10^6$ m^3) is considered, TPHs level in inner Bay waters will be as high as 41.7 mg/L.

- The major components of the PAHs are the 3 and 4 ringed compounds. High loads are generated in winter and autumn because of heavy precipitation. PAHs loads originated from Manda and Old Gediz are significantly high

- Annually 317.18 tonnes of PAHs are discharged into the inner Bay, which may create 0.78 mg/L PAHs concentration.

- The major Ni sources are Melez, Old Gediz and Manda rivers, which carries high loads of Ni especially in winter and spring seasons. The annual Ni entrance into the inner Bay is 2.3 tons that may create 0.006 mg/L (6 μg/L)of Ni concentration.

- Al discharge is generated by Manda and Old Gediz, dominantly and the total Al discharge is 29.5 tons annually. That amount may create Al concentration of 0.07 mg/L (70 μg/L) in inner Bay waters.

- Melez, Manda and Old Gediz carry the major part of the total Cr into the Bay (0.56 ton/year). Expected Cr concentration in the inner Bay is 0.0014 mg/L (1.4 μg/L).

- Copper load is mainly sourced Manda and Old Gediz. Annual discharge from the investigated rivers is 2.1 ton/year that may create 0.005 mg/L of Cu concentration (5 μg/L) in the inner Bay waters.

- Old Gediz, Manda and Melez are the rivers that carry Pb dominantly. The total annual Pb discharge into the Bay is 0.59 ton, which may create 0.0012 mg/L (1.2 μg/L) of water concentration.

- Zn load originated from Old Gediz is significantly high, and the total Zn amount carried into the Bay from the studied rivers is 20.7 tons/year. That amount may cause 0,05 mg/L Zn concentration (50 μg/L) in the inner Bay waters.

- The total settlable solid fraction discharged into the Bay in a year is 3.931.813 tones. If sediment density is accepted as 1.75 tons/m^3, and the area of inner Bay is 57 km^2, this amount of settlable solids result with 4 cm of average annual sediment accumulation in the bottom of the inner Bay. The height of accumulation will be higher in the regions close to the shore, where the water circulation is poor and the water depth is short. This is an important issue for Izmir, since inner Bay is an international and commercially active harbour, which is previously dregged to remove the sediment that accumulated in the docking line of the ships.

- It is seen that the rivers flowing through the inner city collect high loads of TPHs and/or PAHs from unit area, which are sourced from the burning of coal and fuel. Additionally, Manda and Melez rivers are washing considerable amount of heavy metals from their unit catchment area.

- Higher Cr and Ni loads collected from unit area of Harmandalı basin may be sourced from the landfill area which is located at the springhead of this river.

- Old Gediz passes through an industrial zone and because of that Cu, Pb and Zn loads are higher.

- Settlable solids load from unit basin area are also high in Manda and Melez rivers.

- According to the amount of contaminant load collected from unit basin area, the investigated rivers can be ranked in descending order as follows:

Melez > Manda > Old Gediz > Bostanlı > Sepetçi > Bornova > Harmandalı

Since there is considerable amount of organic and inorganic pollutants in the rivers discharging Izmir Bay, the water circulation in Izmir Bay should be investigated in details in the future studies for better understanding and definition of contaminant transport in the Bay.

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Appendix

Table1-A Raw data obtained for each of the 16 PAHs for the river waters (mg L^{-1})

Season	River	PAHs							
		Acenaphthene	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**
Spring	**Melez**	0,18084	0,43992	0,41772	0,63132	0,14766	0,01866	0,02328	0,17286
	Manda	**0,24618**	**0,93174**	**0,52554**	**0,84372**	**0,15984**	**0,02442**	**0,04554**	**0,23976**
	Harmandalı	0,19	0,78	0,49	0,74	0,09	0,02	0,03	0,21
	Old Gediz	0,19	0,79	0,51	0,77	0,09	0,03	0,03	0,21
	Ilıca	0,19	0,52	0,57	0,87	0,16	0,03	0,04	0,23
	Bornova	0,12	0,36	0,45	0,66	0,07	0,02	0,02	0,17
Summer	**Bostanlı**	0,12	0,31	0,34	0,52	0,07	0,02	0,02	0,14
	Old Gediz	0,07	0,24	0,19	0,31	0,04	0,02	0,01	0,08
	Bornova	0,07	0,30	0,20	0,31	0,05	0,01	0,01	0,09
	Bostanlı	0,07	0,24	0,22	0,35	0,04	0,01	0,01	0,09
	Harmandalı	0,08	0,23	0,21	0,31	0,03	0,01	0,01	0,09
	Melez	0,09	0,23	0,28	0,39	0,12	0,01	0,02	0,13
	Manda	0,10	0,23	0,33	0,52	0,10	0,02	0,02	0,13
Autumn	**Harmandalı**	0,17	0,73	0,55	0,93	0,10	0,02	0,03	0,23
	Old Gediz	0,17	0,47	0,68	0,63	0,02	0,02	0,02	0,18
	Bostanlı	0,21	0,54	0,67	1,04	0,02	0,02	0,05	0,29
	Sepetçi	0,16	0,72	0,42	0,81	0,04	0,02	0,02	0,18
	Bornova	0,12	0,52	0,34	0,58	0,02	0,02	0,02	0,14
	Manda	0,27	1,15	0,70	1,06	0,02	2,82	0,04	0,32
	Melez	0,20	0,66	0,44	0,75	0,16	0,04	0,03	0,18
Winter	**Harmandalı**	0,14	0,40	0,42	0,70	0,01	0,02	0,03	0,17
	Old Gediz	0,21	0,62	0,59	0,96	0,04	0,03	0,04	0,24
	Sepetçi	0,21	0,77	0,50	1,06	0,06	0,02	0,04	0,22
	Bornova	0,17	0,42	0,44	0,14	0,02	0,02	0,03	0,16
	Manda	0,20	0,51	0,44	0,10	0,66	0,02	0,02	0,17
	Melez	0,03	0,59	0,65	0,98	0,03	0,02	0,04	0,25
	Bostanlı	0,19	0,52	0,52	0,79	0,02	0,02	0,04	0,21

Table1-A Continued

Season	River	PAHs							
		Benz (a) anthrancene	**Chrysene**	**Benzo (b) fluoranthene**	**Benzo (k) fluoranthene**	**Benzo (a) pyrene**	**Indeno (1,2,3cd) pyrene**	**Dibenz (a,h)anthrancene**	**Benzo (g,h,i) perylene**
Spring	**Melez**	0,11778	0,35316	0,00324	0,00738	0,00678	0,0021	0,00528	0,00186
	Manda	**0,11544**	**0,11262**	**0,00858**	**0,00426**	**0,0144**	**0,00366**	**0,0111**	0,00426
	Harmandalı	0,11	0,06	0,00	0,00	0,00	0,00	0,01	0,00204
	Old Gediz	0,19	0,09	0,01	0,00	0,01	0,03	0,12	0,01074
	Ilıca	0,12	0,04	0,02	0,02	0,02	0,02	0,01	0,02346
	Bornova	0,14	0,09	0,01	0,02	0,02	0,02	0,03	0,02022
Summer	**Bostanlı**	0,11	0,08	0,00	0,00	0,01	0,00	0,01	0,00144
	Old Gediz	0,06	0,04	0,00	0,00	0,01	0,00	0,02	0,00567
	Bornova	0,06	0,10	0,00	0,00	0,00	0,00	0,00	0,00159
	Bostanlı	0,06	0,05	0,00	0,00	0,00	0,00	0,01	0,00069
	Harmandalı	0,05	0,02	0,00	0,00	0,00	0,00	0,00	0,00099
	Melez	0,06	0,16	0,00	0,00	0,01	0,00	0,02	0,00327
	Manda	0,07	0,06	0,00	0,00	0,00	0,00	0,02	0,00099
Autumn	**Harmandalı**	0,20	0,09	0,01	0,02	0,02	0,01	0,05	0,0048
	Old Gediz	0,12	0,26	0,01	0,01	0,01	0,01	0,02	0,01236
	Bostanlı	0,15	0,10	0,01	0,01	0,05	0,03	0,04	0,04428
	Sepetçi	2,60	0,91	0,01	0,01	0,08	0,03	0,04	0,01752
	Bornova	0,78	4,32	0,04	0,02	0,11	0,02	0,05	0,02094
	Manda	1,83	0,04	0,02	0,03	0,01	0,01	0,15	0,0159
	Melez	0,27	0,69	0,07	0,11	0,05	0,05	0,07	0,02436
Winter	**Harmandalı**	0,66	0,31	0,02	0,02	0,04	0,01	0,07	0,11034
	Old Gediz	1,16	0,34	0,01	0,01	0,01	0,02	0,02	0,01026
	Sepetçi	1,16	0,77	0,04	0,03	0,01	0,19	2,16	0,01248
	Bornova	0,79	0,42	0,03	0,01	0,03	0,01	0,07	0,01566
	Manda	0,72	0,19	0,05	0,02	0,03	0,03	0,11	0,01356
	Melez	1,25	0,61	0,03	0,04	0,07	0,03	0,07	0,02388
	Bostanlı	1,43	4,00	0,05	0,02	0,06	0,02	0,05	0,02952

Tablo1-B Raw data obtained for each of the 16 PAHs for the river sediments.(mg kg^{-1})

Season	River	PAHs							
		Acenaphthene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Carbazole	Fluoranthene	Pyrene
Spring	Bornova	2,79	5,72	5,36	7,83	1,37	0,46	0,65	2,78
	Old Gediz	1,69	3,96	4,36	5,83	0,33	0,21	0,28	1,91
	Harmandalı	0,66	1,95	2,48	3,20	0,14	0,08	0,28	1,00
	Manda	3,20	7,24	5,98	8,36	1,01	0,72	0,62	2,82
Autumn	Harmandalı	0,63	2,15	2,20	2,85	0,23	0,07	0,41	1,20
	Old Gediz	1,25	3,38	4,01	6,22	1,16	0,20	0,34	1,97
	Sepetçi	1,46	4,32	3,98	5,20	0,18	0,13	0,38	1,60
	Bornova	2,42	4,44	5,87	15,82	2,00	0,58	15,72	15,70
	Manda	1,81	3,90	4,15	5,62	0,85	0,19	0,65	1,79
Winter	Bornova	1,96	5,16	4,83	7,25	0,29	0,26	2,04	3,35
	Old Gedi z	1,16	2,98	3,39	4,69	2,89	0,18	0,40	1,42
	Sepetçi	1,59	3,54	4,18	6,18	0,53	0,19	1,21	2,38
	Harmandalı	2,37	5,31	4,83	7,03	0,41	0,23	0,86	2,37
	Manda	4,93	6,06	5,66	9,42	1,34	0,19	0,98	2,77
Summer	Old Gediz	1,67	5,06	4,00	5,55	0,59	0,19	0,24	1,59
	Harmandalı	2,86	5,50	6,09	9,09	1,09	0,39	0,46	2,63
	Bornova	2,05	7,96	5,36	7,40	0,56	0,22	0,54	2,53
	Sepetçi	3,90	9,61	11,68	17,62	1,20	0,57	1,77	7,42
	Manda	2,52	7,74	5,30	7,68	0,59	0,20	0,31	2,41

Tablo1-B Continued

Season	River	PAHs								
		Benz (a) anthrancene	Chrysene	Benzo (b) fluoranthene	Benzo (k) fluoranthene	Benzo (a) pyrene	Indeno (1,2,3-cd)pyrene	Dibenz (a,h)anthrancene	Benzo (g,h,i) perylene	Total
Spring	Bornova	25,91	41,24	0,66	0,37	0,52	0,31	0,91	0,56	97,45
	Old Gediz	1,31	52,59	0,06	0,09	0,06	0,05	0,61	0,03	73,37
	Harmandalı	1,21	22,75	0,09	0,08	0,20	0,56	0,39	0,57	35,61
	Manda	1,97	9,49	0,09	0,26	0,23	0,22	0,49	8,82	51,52
Autumn	Harmandalı	1,42	38,61	0,11	0,12	0,12	0,20	0,21	0,21	50,76
	Old Gediz	1,96	73,84	0,06	0,12	0,17	0,13	0,14	0,15	95,05
	Sepetçi	1,37	62,16	0,09	0,15	0,11	0,07	0,03	0,11	81,33
	Bornova	4,22	17,67	1,55	1,71	1,33	1,00	0,49	1,18	91,70
	Manda	1,95	13,38	0,09	0,08	0,11	0,03	0,06	0,10	34,77
Winter	Bornova	1,72	2,96	0,22	0,24	0,21	0,11	0,10	0,23	30,94
	Old Gedi z	1,23	9,24	0,06	0,12	0,03	0,03	0,05	0,09	27,94
	Sepetçi	1,64	6,31	0,27	0,28	0,23	0,13	0,19	0,26	29,13
	Harmandalı	1,29	3,44	0,10	0,11	0,08	0,04	0,21	0,12	28,79
	Manda	1,63	3,13	0,13	0,19	0,10	0,03	0,07	0,05	36,68
Summer	Old Gediz	1,44	1,44	0,05	0,11	0,09	0,03	0,09	0,04	22,15
	Harmandalı	1,50	30,94	0,08	0,10	0,22	0,06	0,22	0,02	61,28
	Bornova	1,77	8,28	0,10	0,16	0,09	0,06	0,16	0,04	37,28
	Sepetçi	1,51	6,59	0,30	0,63	0,45	0,12	0,24	0,16	63,76
	Manda	1,85	0,81	0,09	0,05	0,05	0,02	0,08	0,04	29,75