

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**ORGANIC POLLUTANT DYNAMICS OF PASSIVE SAMPLERS, SEDIMENTS
AND MUSSELS IN COASTAL MARINE ENVIRONMENT**

Ph.D. THESIS

Burak KARACIK

Ocean Engineering Department

Ocean Engineering Programme

JUNE 2014

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Thesis Advisor: Prof. Dr. Oya OKAY

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**KIYISAL DENİZ ORTAMINDA PASİF ÖRNEKLEYİCİLER, SEDİMENTLER
VE MİDYELER İLE ORGANİK KİRLETİCİ DİNAMİKLERİ**

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To my family,

FOREWORD

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ABBREVIATIONS

(END)-I	: Endosulfan-I
(END)-II	: Endosulfan-II
1234678-HpCDD	: 1,2,3,4,6,7,8-heptachlorodibenzodioxin
1234678-HpCDF	: 1,2,3,4,6,7,8-heptachlorodibenzofuran
1234789-HpCDF	: 1,2,3,4,7,8,9-Heptachlorodibenzofuran
123478-HxCDD	: 1,2,3,4,7,8-hexachlorodibenzodioxin
123478-HxCDF	: 1,2,3,4,7,8-hexachlorodibenzofuran
123678-HxCDD	: 1,2,3,6,7,8-hexachlorodibenzodioxin
123678-HxCDF	: 1,2,3,6,7,8-Hexachlorodibenzofuran
123789-HxCDD	: 1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin
123789-HxCDF	: 1,2,3,7,8,9-hexachlorodibenzofuran
12378-PeCDD	: 1,2,3,7,8-pentachlorodibenzo-p-dioxin
12378-PeCDF	: 1,2,3,7,8-pentachlorodibenzofuran
2,4'-DDD	: 2,4'-Dichlorodiphenyldichloroethane
2,4'-DDE	: 2,4'-Dichlorodiphenyldichloroethene
2,4'-DDT	: 2,4'-Dichlorodiphenyltrichloroethane
234678-HxCDF	: 2,3,4,6,7,8-Hexachlorodibenzofuran
23478-PeCDF	: 2,3,4,7,8-pentachlorodibenzofuran
2378-TCDF	: 2,3,7,8-tetrachlorodibenzofuran
4,4'-DDD	: 4,4'-Dichlorodiphenyldichloroethane
4,4'-DDE	: 4,4'-Dichlorodiphenyldichloroethene
4,4'-DDT	: 4,4'-Dichlorodiphenyltrichloroethane
AC	: Acenaphthene
ACL	: Acenaphthylene
AN	: Anthracene
ASTM	: American Society for Testing and Materials
BaA	: Benzo(a)anthracene
BAF	: Bioaccumulation factor
BaP	: Benzo(a)pyrene
BbFA	: Benzo(b)fluoranthene
BCF	: Bioconcentration factor
BghiP	: Benzo(ghi)perylene
BjFA	: Benzo(j)fluoranthene
BkFA	: Benzo(k)fluoranthene
BR	: Butyl Rubber
C_B	: Chemical concentration in the organism
c-CHL	: cis-Chlordane
c-HE	: cis-Heptachloroepoxide
CHR	: Chrysene
CPAH	: Carcinogenic PAH
CSQG	: Canadian Sediment Quality Guidelines
C_w	: Water concentrations

C_{wd}	: Freely dissolved chemical concentration in the water
C_{w-sed}	: Sediment-based aqueous concentrations
C_{w-spm}	: SPMD-based aqueous concentrations
d	: day
DBahA	: Dibenzo(a,h)anthracene
dl-PCB	: Dioxin like PCB
DMSO	: Dimethyl Sulfoxide
EPA	: Environmental Protection Agency
ERL	: Effects Range-low
ERM	: Effects Range-median
FA	: Fluoranthene
FL	: Fluorene
GPS	: Global Positioning System
HCA	: Hierarchical Cluster Analysis
HCB	: Hexachlorobenzene
HEPES	: 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid
HMW	: High molecular weight
HPLC	: High-performance Liquid Chromatography
IP	: Indeno(1.2.3-cd)pyrene
K_{oc}	: Sediment organic carbon–water partition coefficient
K_{ow}	: Octanol-Water Partition Coefficient
K_{sw}	: Sampler-water partition coefficient
LDPE	: Low-density Polyethylene
LMW	: Low molecular weight methoxychlor
MOC	: Methoxychlor
MW	: Molecular Weight g mol ⁻¹
NAP	: Naphthalene
nd	: not detected
NLS	: Non-linear least squares
NOAA	: National Oceanic and Atmospheric Administration
NRR	: Neutral Red Retention
OCDD	: 1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin
OCDF	: Octachlorodibenzofuran
OCP	: Organochlorine Pesticides
OCS	: Octachlorostyrene
OXC	: oxy-Chlordane
PAH	: Polycyclic Aromatic Hydrocarbons
PCA	: Pentachloroanisole
PCB	: Polychlorinated Biphenyls
PCB #101	: 2,2',4,5,5'-Pentachlorobiphenyl
PCB #105	: 2,3,3',4,4'-Pentachlorobiphenyl
PCB #114	: 2,3,4,4',5-Pentachlorobiphenyl
PCB #118	: 2,3',4,4',5-Pentachlorobiphenyl
PCB #123	: 2',3,4,4',5-Pentachlorobiphenyl
PCB #126	: 3,3',4,4',5-Pentachlorobiphenyl
PCB #138	: 2,2',3,4,4',5'-Hexachlorobiphenyl
PCB #153	: 2,2',4,4',5,5'-Hexachlorobiphenyl
PCB #156	: 2,3,3',4,4',5-Hexachlorobiphenyl
PCB #157	: 2,3,3',4,4',5'-Hexachlorobiphenyl
PCB #167	: 2,3',4,4',5,5'-Hexachlorobiphenyl

PCB #169	: 3,3',4,4',5,5'-Hexachlorobiphenyl
PCB #180	: 2,2',3,4,4',5,5'-Heptachlorobiphenyl
PCB #189	: 2,3,3',4,4',5,5'-Heptachlorobiphenyl
PCB #28	: 2,4,4'-Trichlorobiphenyl
PCB #52	: 2,2',5,5'-Tetrachlorobiphenyl
PCB #77	: 3,3',4,4'-Tetrachlorobiphenyl
PCB #81	: 3,4,4',5-Tetrachlorobiphenyl
PCDD	: Polychlorinated Dibenzo-p-dioxins
PCDF	: Polychlorinated Dibenzofurans
PeCB	: Pentachlorobenzene
PHE	: Phenanthrene
POP	: Persistent Organic Pollutants
PRC	: Performance Reference Compounds
PY	: Pyrene
QA/QC	: Quality Assurance/Quality Control
QSAR	: Quantitative Structure Activity Relationships
R_s	: Sampling Rate
SCUBA	: Self Contained Underwater Breathing Apparatus
SPE	: Solid-phase Extraction
SPMD	: Semipermeable Membrane Devices
SQG	: Sediment Quality Guidelines
St	: Station
t-CHL	: trans-Chlordane
TEF	: Toxicity Equivalency Factor
TEQ	: Total Toxic Equivalent
TEQ_{BaP}	: Total toxic benzo[a]pyrene equivalent
t-HE	: trans-Heptachloroepoxide
T-OCP	: Total Concentration of OCP
T-PAH	: Total Concentration of PAH
T-PCB	: Total Concentration of PCB
UNEP	: United Nations Environment Programme
US EPA	: United States Environmental Protection Agency
WHO	: World Health Organization
α-HCH	: alpha-Hexachlorocyclohexane
β-HCH	: beta-Hexachlorocyclohexane
γ-HCH	: gamma-Hexachlorocyclohexane
δ-HCH	: delta-Hexachlorocyclohexane
ε-HCH	: epsilon-Hexachlorocyclohexane

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ORGANIC POLLUTANT DYNAMICS OF PASSIVE SAMPLERS, SEDIMENTS AND MUSSELS IN COASTAL MARINE ENVIRONMENT

SUMMARY

The research was conducted in two phases. In the first phase: sampling 2007, the detailed distribution and source of polychlorinated biphenyl (PCB), polychlorinated dibenzo-p-dioxin/furan (PCDD/F) and organochlorine pesticides (OCP) in the Istanbul Strait were determined by sampling sediments and mussels (*Mytilus galloprovincialis*) along the Strait area. Sediment and mussel samples were analyzed for six indicator PCB, 12 dioxin-like PCB (dl-PCB) and 17 polychlorinated dibenzo-p-dioxin/furan (PCDD/F) congeners. Samples contained different concentrations of PCB and among these, congeners 153, 75, 105 and 118 in sediments and congeners 153, 138 and 118 in mussels were most abundant. The concentration levels of total PCB and PCDD/Fs in sediments ranged from 17.9 to 539,746 pg g^{-1} dw and 2.04 to 60.5 pg g^{-1} dw, respectively. The total WHO-TEQ values ranged between 0.01 and 17.8 pg g^{-1} dw in sediments and 0.98-1.01 pg g^{-1} ww in mussels. None of the sediment and mussel samples analyzed exceeded the limits suggested in the sediment quality guideline and safe values set by the European Community for seafood intended for human consumption respectively. The total concentrations of OCP were found in the range of 40-13852 pg g^{-1} dw for sediments and 5195-12322 pg g^{-1} ww for mussels. The levels of OCP in both sediments and mussels were dominated by DDTs and HCHs; β -HCH, 4,4'-DDD, and 4,4'-DDE were the major pollutants. The degree of sediment pesticide contamination was more severe in the inner part of the strait. OCP concentrations in sediments and mussels were compared with the sediment guideline values and legal limits for human health respectively. The results showed that OC pesticide contamination in the strait might not pose a serious threat to the health of the marine inhabitants at most of the stations.

In the second phase: sampling 2009, passive sampling systems were used together with transplant and local mussel samples. The results were compared to find out transplant mussel, semipermeable membrane devices (SPMD) and Butyl rubber (BR) sorbent performance. Water concentrations of polycyclic aromatic hydrocarbons (PAH), PCB and OCP were estimated from SPMD and from sediment pollutant concentrations. SPMD were deployed in the Istanbul Strait and Marmara Sea and retrieved after 7 and 21 days. Performance reference compounds (PRC) were used to determine the site-specific sampling rates of the compounds. Water concentrations (C_w) of the analyzed compounds estimated by using two different calculation methods for SPMD were found similar. C_w of total PAH estimated from SPMD (C_{w-spmd}) were found between 13-79 ng L^{-1} and between 7.0-68 ng L^{-1} for 7 and 21 days of deployments respectively. Water concentrations of PCB using sediment data was found as between 0.001 and 11.0 ng L^{-1} . The highest value of C_{w-spmd} for two deployments were 2.8 ng L^{-1} for OCP. C_w estimated from sediment concentrations were generally higher than those estimated from SPMD. Sampling results from BR sorbent are similar with SPMD. In general, BR sorbent has much better sampling

capacity for PCB, OCP and HMW PAH. Transplanted mussel data show similar trend with the passive samplers. Depurations of the pollutants are visible in clean sites. On the other hand, mussels are more sensitive to temperature, salinity and seasonal changes.

Obtain data from this study provided relevant information for future risk assessment and passive sampling studies.

KIYISAL DENİZ ORTAMINDA PASİF ÖRNEKLEYİCİLER, SEDİMENTLER VE MİDYELER İLE ORGANİK KİRLETİCİ DİNAMİKLERİ

ÖZET

İnsanoğlunun gelişmesi ile birlikte çevresi ile olan ilişkisinde artmış ve değişmiştir. Yerleşik yaşama geçen insanlık, çevresi ile daha iç içe bir konuma gelmiştir. Sanayi devrimi ve gelişen teknolojiler çevremizi daha çok etkilememize ve daha büyük miktarlarda kirletmemize sebep olmuştur. Kalıcı organik kirleticiler (KOK) ve poli aromatik hidrokarbonlar (PAH) bir çok kaynaktan sisteme girmektedir. Doğada parçalanmayan dayanıklı yapıları ve canlıların bünyesinde birikip istenmeyen etkiler göstermeleri (kanserojenik, mutojenik vb.) bu kimyasalları izlemek ve haklarında bilgi edinmek gerekliliğini doğurmuştur.

Kıyı ekosistemleri nüfusun ve sanayinin yoğun olduğu ve buna paralel olarak da gemi taşımacılığının önemli rol oynadığı ortamlar haline gelmektedir. Bu noktalarda kirleticilerin etkilerinin ve değişik medyalarda (sediman, biyota, pasif örnekleyici, su vb) dağılımlarının incelenmesi, bu kirleticilerin kontrolü bakımından önem taşımaktadır. Bu amaçla canlıları taklit eden yapısıyla pasif örneklem sistemleri ve midyeler gibi suyu filtre ederek beslenen organizmalar sıklıkla kullanılmaktadır. Bu çalışma kapsamında İstanbul Boğazındaki kalıcı organik kirleticiler ve poliaromatik hidrokarbonlar kirliliğinin çeşitli ortamlardaki (midye, sediman, pasif örnekleyici ve su) miktarı, kaynakları ve birbirleri ile olan ilişkisi incelenmiştir.

Yapılan çalışma iki aşamada gerçekleşmiştir. Birinci aşamada: 2007 örnekleme; İstanbul Boğazı'ndan toplanan midye (*Mytilus galloprovincialis*) ve sedimanlarda Poliklorlu Bifeniller (PKB), Dioksin/Furan (PCDD/F) ve Organoklorlu Pestisitlerin (OKP) analizleri yapılmıştır ve olası kaynakları araştırılmıştır. İkinci aşamada : 2009 örnekleme; pasif örneklem sistemleri ve transplante midyeler seçilen örnekleme noktalarına yerleştirilmiştir. Sediman ile birlikte toplanan pasif örnekleyicilerde, PAH, PKB ve OKP analizleri yapılmıştır. Yarı geçirgen membran örnekleyici ve sediman verileri kullanılarak kirleticilerin su konsantrasyonları hesap edilmiştir. Toplam olarak 16 tane PAH, 18 tane PKB, 6 tane PCDD, 10 tane PCDF ve 28 tane OCP İstanbul Boğazı ve Marmara Denizi'nden toplanan sediman, midye, SPMD ve BR sorbente analiz edilmiştir.

Kalıcı organik kirleticiler lipofilik yapıları dolayısıyla canlılarda birikim yapmaktadır. Bu kirleticiler, insanın da içinde bulunduğu besin zincirinin daha üst seviyelerinde birikmektedirler. Deniz canlılarının tüketilmesi bu kirleticilere maruz kalınmasına sebep olmaktadır. Bu kirleticiler, düşük su çözünürlükleri dolayısıyla suda çok düşük konsantrasyonlarda bulunmaktadır. Bu durum analizlerinin yapılmasını zorlaştırmaktadır. Yakın zamanda birçok pasif örnekleyici sudaki çözünmüş serbest organik kirleticileri miktarlarını belirlemek için geliştirilmiştir. SPMD'ler bu amaçla en çok kullanılan örnekleyicilerden biridir. SPMD düşük yoğunlukta polietilen filmler içerisine doldurulmuş trioleinden oluşmaktadır. Kirleticileri metabolize etmemeleri ve zaman aralıklarında konsantrasyon

miktarlarını göstermeleri SPMD'leri avantajlı kılmıştır. Hazırlanması sırasında yapısına performans referans bileşiklerinin (PRB) eklenir. PRB'lerin kullanımı su konsantrasyonlarının geri hesap edilmesini olanaklı hale getirir. Bunun için Huckin'in geliştirdiği 80/20 ve Booi ve Smedes'in NLS methodu çalışma kapsamında kullanılmıştır. 80/20 metodu PKB'lerin %20 ve %80 azalmasına dayanmaktadır. NLS metodu ise bütün PKB'lerin dispersiyonunu kullanmaktadır. Çalışma kapsamında iki metod da kullanılmış ve bütün PKB'lerin kullanılması ve daha iyi sonuçlar vermesi dolayısıyla NLS metodu seçilmiştir. İstanbul Teknik Üniversitesi'nde sentezlenen ve esas üretim amacı petrol dökülmelerine müdahale olan Butil kauçuk (BR) sorbent ilk defa bu çalışma kapsamında kullanılan diğer pasif örnekleyicidir.

İstanbul Boğazı konumu ve çift tabakalı akıntı sistemi ile dünya üzerinde özel bir yere sahiptir. Çanakkale Boğazı ile birlikte Karadeniz'i Marmara Denizi ve Akdeniz'e bağlar. Yılda ortalama 50000 geminin geçtiği önemli ticaret yollarından biri üzerinde bulunmaktadır. Yapılan çalışmalar İstanbul Boğazı'nın ağır metaller ve PAH'lar açısından yoğun bir şekilde kirletildiğini göstermektedir. Çalışma kapsamında birinci örneklemede 24 istasyondan midye ve sediman örnekleri toplanmış ve analizleri yapılmıştır. İkinci örneklemede seçilen 5 istasyona SPMD, BR sorbent ve transplante midyeler yerleştirilmiş ve 7. ile 21. günlerde örnekler analiz için toplanmıştır. Aynı noktalardan yerel midyeler toplanmış ve sediman örnekleri alınmıştır. Alınan sedimanlar ile pore suyu deneyleri laboratuvar ortamında gerçekleştirilmiştir. Ayrıca midyeler ile biyogösterge deneyleri yapılmıştır. Toplanan örnekler homojenize edilmiş ve kimyasal analizler yapılana kadar -20°C sıcaklıkta saklanmıştır. Sedimanlar elek analizi yapılarak partikül boyları belirlenmiştir. Sediman organik karbon miktarları ölçümü ayrıca yapılmıştır. Kimyasal analizler internal standartlar kullanılarak Yüksek Performans Gaz Kromatografisi ve Yüksek Performans Kütle Spektrometresi (YPGC/YPKS) ile Almanya'da Helmholtz Zentrum München Molecular EXposomics laboratuvarında yapıldı. Midye, BR sorbent ve sediman örnekleri hızlandırılmış solvent ekstraktörü, SPMDler siklohexan yardımıyla ekstrakte edilip iki temizleme aşamasından geçirilip YPGC/YPKS'ne verilerek analizleri yapılmıştır.

Sonuçlar iki aşamada değerlendirilmiştir. Birinci aşamada, sedimanlarda PCB 153 (12 ve 23. örnekleme istasyonları hariç), 1,2,3,4,6,7,8-HpCDF (18 ve 20. örnekleme istasyonları hariç) baskın olarak bulunmuştur. Sedimandaki toplam PKB konsantrasyonu 17,9 ile 539746 pg g⁻¹ kuru ağırlık (ka) arasında değişmektedir. En yüksek ve en düşük konsantrasyonlar 1 ve 6 nolu örnekleme istasyonlarında bulunmuştur. 6 nolu örnekleme istasyonunun da bulunan yüksek PKB miktarının çalışması 1991 yılında biten tersanenin etkisi olduğu düşünülmektedir. Bunun dışında 4,6,7 ve 18 nolu istasyonlardaki yüksek PKB konsantrasyonları bu bölgelerdeki evsel ve endüstriyel atıksu girdilerinden kaynaklandığı gözükmektedir. Sedimandaki toplam PCDD/F konsantrasyonu 2,04 ile 60,5 arasında pg g⁻¹ ka arasında değişmektedir. Sedimanda PCDD konsantrasyonunun daha fazla olduğu bulunmuştur. Midyelerdeki toplam PKB konsantrasyonu 1026 ile 35983 pg g⁻¹ ıslak ağırlık (ıs) arasında değişmektedir. En yüksek konsantrasyon 23 nolu istasyonda ölçülmüştür. İstanbul Boğazı'nın Karadeniz girişinde bulunan 3 nolu istasyonda en düşük konsantrasyon değeri bulunmuştur. Midye örneklerinde rastlanan en baskın grup PKB indikatör PKB bileşikleridir (%64-81). Midyelerden hesaplanan toksik etki (TOE) değerleri Avrupa Birliği'nin insan sağlığı için belirlediği değerlerden düşüktür.

Sedimanda DDT ve HCH bileşiklerinin baskın olduğu gözlemlenmiştir. β -HCH, 4,4'-DDD, 2,4'-DDD ve 4,4'-DDE'nin sedimandaki toplam OKPlerin ortalama %69'unu oluşturmaktadır. Heptachlor, t-HE, aldrin bütün örneklerde ve OCS, OXC, endrin, (END)-I, mirex bir çok sediman örneğinde ölçülememiştir. Bölgedeki DDT kirlenmesinin geçmişte kullanım nedeniyle olduğu görülmektedir. Sedimandan elde edilen sonuçlara benzer olarak midyelerde de DDT ve HCH bileşikleri baskındır. En yüksek OKP konsantrasyonu 2 nolu istasyonda ölçülmüştür.

Çalışmanın ikinci aşamasında, SPMD'lerde ki toplam birikmiş PAH konsantrasyonları 7 ve 21 gün için 66 - 280 ng g⁻¹ SPMD ile 120-810 ng g⁻¹ SPMD arasında değişmektedir. En yüksek toplam PAH konsantrasyonu tersaneler bölgesi 24 nolu istasyonda ölçülmüştür. Bir çok istasyonda naftalin ve piren gibi düşük molekül ağırlığındaki PAH'lar sedimanda baskın bulunmaktadır. PKB'lerin SPMD'lerde üretimden kaynaklı olarak yüksek seviyede olmaları SPMD'lerde PKB ölçümlerinin yapılamamasına sebep olmuştur. SPMD'lerde toplam OKP miktarı 2.1 ng g⁻¹ - 5.4 ng g⁻¹ SPMD 7 gün ve 4.6 ng g⁻¹ - 41 ng g⁻¹ SPMD 21 gün arasındadır. En yüksek konsantrasyon 24 nolu istasyon ve en düşük konsantrasyon 12 nolu istasyonda ölçülmüştür. (DDE + DDD)/DDT > 0.5 oranına bakıldığında 0.5 ile 14.5 arasında olduğu görülmüş ve DDT kirlenmesinin geçmişte olduğu belirlenmiştir. PRB'leri kullanılarak SPMD'lerden geri hesaplanan toplam PAH su konsantrasyonu 13 - 79 ng L⁻¹ 7 gün ile 7.0 - 68 ng L⁻¹ 21 gün arasında değişmektedir. OKP konsantrasyonları bütün istasyonlar için benzer olup en düşük 23. istasyon (0.38 ng L⁻¹) ve en yüksek 6a istasyonudur (2.8 ng L⁻¹).

Toplam PAH konsantrasyonu BR sorbent de 7 ve 21 gün için 82 - 769 ng g⁻¹ BR sorbent ile 71 - 1306 ng g⁻¹ BR sorbent aralığında ölçülmüştür. En düşük ve en yüksek değerler 12 ve 24 nolu istasyonlarda ölçülmüştür. Toplam PKB değerleri 7 ve 21 gün için 122-1435 pg g⁻¹ BR sorbent ve 177-3940 pg g⁻¹ BR sorbent aralığında değişmektedir. İstanbul Boğazı girişi (no12) en düşük değerlere sahipken tersaneler bölgesi (no24) en yüksek PKB değerine sahiptir. Toplam OKB 6,4 - 16,4 ng g⁻¹ BR sorbent ile 7,3 - 124 ng g⁻¹ BR sorbent aralığında ölçülmüştür. Tersane bölgesi en yüksek OKP konsantrasyonuna sahiptir ve bunun büyük bir kısmını (%72) (END)-I ve (END)-II oluşturmaktadır. Aynı istasyonda DDT bileşikleri toplam OKP'nın %24'nü oluşturmaktadır. Bunun kaynağı gemi inşaatı ve onarımında kullanılan anti fouling boyalar olabileceği gibi pestisitler ile muamele görmüş ahşaplarda olabilir. Ayrıca tersanelerde ilaçlama amaçlı bol miktarda pestisit kullanıldığı bilinmektedir.

Örnekleme sırasında SPMD ve BR sorbentler aynı kafeslere yerleştirilmiştir. Örnekleme performanları karşılaştırıldığında BR sorbent 1,09 ile 2,97 kat daha fazla toplam PAH örnekleme yapmıştır. Aynı şekilde 2 ile 3,4 kat daha fazla OKP örnekleme yaptığı gözlemlenmiştir. BR sorbentin daha iyi bir örnekleme kapasitesine sahip olduğu görülmektedir. Fakat SPMD ile BR sorbentin örnekleme mekanizmalarının farklı olduğu göz ardı edilmemelidir. SPMD'ler serbest halde suda çözünmüş kirlenmeleri örneklerken BR sorbent daha hidrofobik olup sudaki askıda katı maddeleri de yapısında toplamaktadır.

İkinci örneklemede (2009) sedimandaki en yüksek kirlenici miktarı 24 nolu istasyonda bulunmuştur. Bu istasyondaki toplam PAH konsantrasyonu 25000 ng g⁻¹ olarak ölçülmüştür. Aynı şekilde en düşük kirlenici miktarı 12 nolu istasyonda bulunmuştur. Kirlenicilerin kaynakları incelendiğinde genelde yanma kökenli olduğu gözlemlenmiştir. Sedimandan yapılan geri su hesaplamaları SPMD verilerinden yapılan geri su hesaplamalarına göre daha yüksek değerler vermektedir. Yapılan çalışmalar SPMD'lerden yapılan geri su hesaplamalarının daha güvenilir olduğunu göstermiştir.

Genel olarak yerel midye, transplante midye ve pasif örnekleyiciler arasında konsantrasyon farklarının az olduđu gözükmemektedir. Transplante midyelerin pasif örnekleyiciler ile aynı şekilde örnekleme verileri verdiđi fakat temiz istasyonlarda yapılarından kirleticileri atarak temizlendikleri gözlemlenmiştir. Özellikle 12 nolu istasyonda kontrol için alınan midyelerden daha temiz oldukları belirgin bir şekilde gözükmemektedir.

Çalışma sonucunda İstanbul Boğazı ekosistemi ile ilgili önemli bir veri tabanı oluşması sağlanmıştır. İki kez yapılan örnekleme çalışması aynı noktalardan alınan örneklerin benzer sonuçlarını ortaya koymuştur. Özellikle deniz ekosistemi gibi narin ekosistemler için önem taşıyan ve uluslararası kurallar ile kısıtlanmış olan kirleticilerin düzenli olarak izlenmesi gerekmektedir. Biyolojik izleme dışında pasif örnekleme yöntemleri bu konuda önemli bir katkı sağlayacaktır.

1. INTRODUCTION

The bound between humans and environment has been changed along with the development of humans. The industrial revolution and emerging technologies affect our environment more than the historical times. Polycyclic aromatic hydrocarbons (PAH) and persistent organic pollutants (POP) enter the ecosystem in large quantities during the last centuries and most of the sources are anthropogenic. Because of their persistent properties, they accumulate in the living organisms and show adverse effects. This reveals the necessity to monitor their distributions, sources and fates in the environment.

Coastal zones are the most industrialized and populated places. Maritime transport has also increased in parallel. Monitoring the pollutants in different medias (such as biota, sediment and water) is important to understand their distributions and effects on coastal environments. In this study, polycyclic aromatic hydrocarbons and persistent organic pollutants concentrations at Istanbul Strait were analyzed in passive samplers, sediment and mussels. Their source and relationships were investigated.

1.1 Purpose of Thesis

The research was conducted in two phases:

In the first phase (sampling 2007), the detailed distribution and sources of polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/F) and organochlorine pesticides (OCP) in the Istanbul Strait were determined by sediment and mussel sampling along the Istanbul Strait.

In the second phase (sampling 2009), passive sampling systems were used together with the transplanted and local mussel samples. The samples were analyzed for PAH, PCB and OCP. The water concentrations were calculated from SPMD and sediment data.

All results were compared considering the sampling media, sampling period/time, localities, sources and pollutant levels.

1.2 Literature Review

Lipophilic environmental contaminants such as polycyclic aromatic hydrocarbons and persistent organic pollutants have been frequently identified in several compartments of the global ecosystems (Zhou et al., 2008). Polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, dibenzofurans and organochlorine pesticides are four families of such global persistent organic pollutants (Mörner et al., 2002) and they are widespread in the abiotic and biotic environmental compartments as complex mixtures of their congeners. They are derived from human activities, ubiquitous, very persistent in the aquatic environment (Villeneuve et al. 1999) and have long-term adverse effects on ecosystems and human health (Doong et al. 2002).

The contamination by PAH and persistent organic pollutants and their toxic effects have been an emerging environmental issue and received considerable attention during the last decades. POP, due to their physicochemical properties have been detected even in the remote areas, such as the Polar Regions (Ballschmiter et al., 1997; Stegeman et al., 2001). Since many of these compounds have an affinity for particulate matter, they can accumulate in sediments and once disturbed, the sediments can be resuspended and the contaminants can reenter the marine aquatic environment and circulate in ecosystems, resulting in a second contamination (Zeng and Venkatesan 1999). Due to their lipophilic nature, they also tend to accumulate in organisms (Voorspoels et al. 2004). They biomagnify in the food chain and reach very high levels in consumers, including humans. The consumption of marine organisms is considered to be the main route of human exposure to these compounds (Pompa et al., 2003; Domingo, 2004). As a result, the concentrations of these compounds in sediments and mussels as rather ubiquitous and sedentary organisms have been successfully used in the pollution monitoring studies in several different coastal areas of the World (e.g. the Mussel Watch programs) to indicate the ecosystem quality and to evaluate their potential health risk to humans (de Mora et al. 2004; Serrano et al. 1995; Sole et al. 2000; Lauenstein and Daskalakis, 1998; Chase et al., 2001).

On the other hand, because of their low water solubility, they exist at very low levels in the water phase. Therefore, the analysis of those pollutants in water samples is still very difficult. Several passive samplers have been developed in the past decades to estimate the freely dissolved organic pollutants in water (Hofelt and Shea, 1997; Booij et al., 1998; Meadows et al., 1998; Huckins et al., 1999). However, lipid-containing semipermeable membrane devices (SPMD) have been most commonly utilized for sampling organic contaminants in water (Figure 1.1) (Ellis et al., 1995; Herve et al., 1995; Prest et al., 1995; Huckins et al., 2006). SPMD have also an advantage over grab sampling and organisms in that they provide time weighted-average concentrations and they do not metabolize chemicals (Rantalainen et al., 2000).

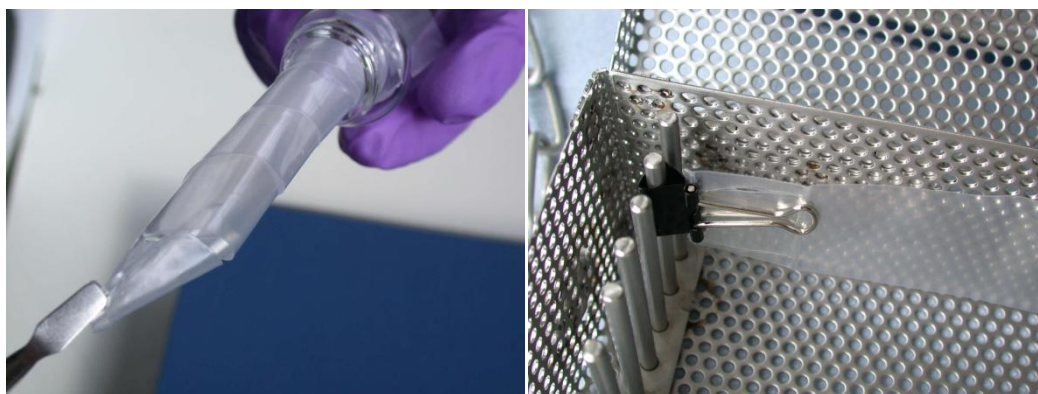


Figure 1.1 : Semipermeable membrane devices (SPMD) in the vials prior to sampling and in the sampling cages.

Furthermore, SPMD may be installed to highly polluted sites where biomonitoring programs cannot be applicable. Accumulation of organic pollutants in SPMD is driven by passive diffusion and thermodynamic partitioning between surrounding water and LDPE membrane + triolein in the samplers. The sampling rate of SPMD is affected by the environmental parameters such as the temperature, water flow or fouling on the samplers (Williamson et al., 2002). To overcome those problems relating the fluctuations of the environmental factors in the sampling sites, a method involving use of SPMD containing performance reference compounds (PRC) was introduced (Huckins et al., 2002; Huckins et al., 2006). The dissipation kinetics of performance reference compounds (PRC) spiked into the passive samplers during their preparation were used to estimate the site-specific sampling rate of the chemicals for each SPMD. Theoretically, the rate of PRC losses is proportional to the rate of analyte uptake. Recently, Booij and Smedes (2010) suggested an

improved method (nonlinear least-square method) to use all PRC retention data for estimation of sampling rates.

Butyl rubber (BR) sorbent (Figure 1.2) is another material used as passive sampler in this study. The BR sorbent was synthesized at İstanbul Technical University, Department of Chemistry - Polymeric Gels Research Laboratory (Ceylan and Okay, 2007). The sorbent was produced from butyl rubber with uses of sulfur monochloride S_2Cl_2 as a cross-linking agent. The original aim for the production of the sorbent was to be used during the oil spills. The sorbent was used first time as a passive sampler in this study.

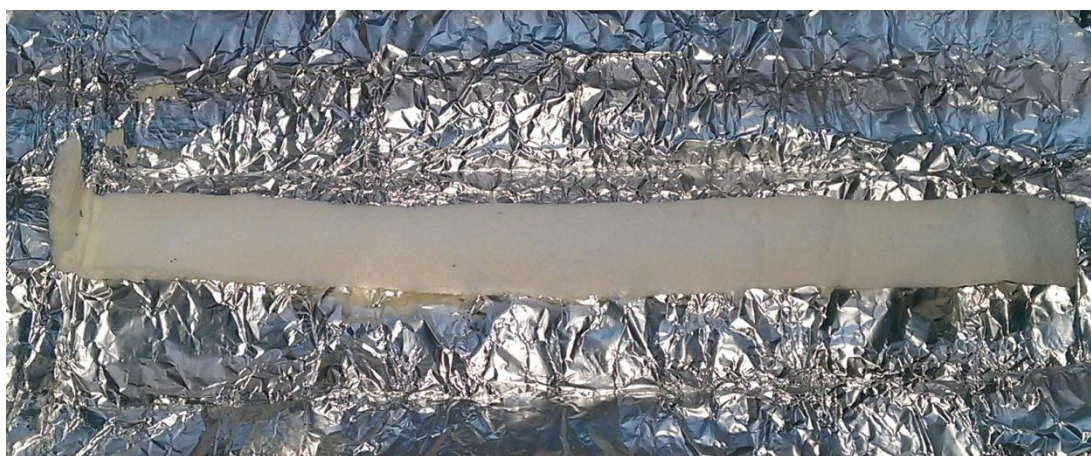


Figure 1.2 : Butyl rubber (BR) sorbent..

1.2.1 Polycyclic aromatic hydrocarbons (PAH)

Polycyclic Aromatic Hydrocarbons are a group of organic compounds that consist two or more fused aromatic rings. Naphthalene is the simplest PAH (Figure 1.3).

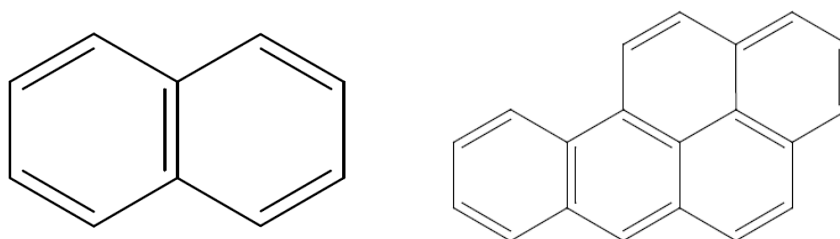


Figure 1.3 : The Simplest PAH naphthalene and carcinogenic PAH benzo(a)anthracene (Mackay et al.2006).

PAH may be produced either by organisms (biogenic) or derived from incineration processes (pyrolytic), from fossil fuels (petrogenic) or derived from transformation processes in soils and sediments (diagenic) (Hylland, 2006). Majority of the sources

are anthropogenic and originated from heavily urbanized and industrialized regions. Those anthropogenic sources of PAH could be oil spills, coal and wood burning, petroleum and diesel combustion and manufacturing processes. Shipyards are a good example for PAH because of the constant production and repairing practices. PAH are generally produced as a mixture, and the relative molecular concentration ratios are considered characteristic of the source. The ratios used to identify the pollution sources such as; petrogenic or pyrolytic (Tobiszewski and Namieśnik, 2012). The sources or the 16 United States Environmental Protection Agency (EPA) priority PAH were also investigated in this study (Table 1.1).

Table 1.1 : Analyzed PAH(Mackay et al.2006).

Chemicals	Abbreviations	log K_{ow}	MW (gr mol ⁻¹)
Naphthalene	NAP	3.37	128
Acenaphthylene	ACL	4	154
Acenaphthene	AC	3.92	152
Fluorene	FL	4.18	166
Phenanthrene	PHE	4.57	178
Anthracene	AN	4.54	178
Fluoranthene	FA	5.22	202
Pyrene	PY	5.18	202
Benzo(a)anthracene	BaA	5.91	228
Chrysene	CHR	5.86	228
Benzo(b)fluoranthene	BbFA	5.78	252
Benzo(j)fluoranthene	BjFA	6.2	252
Benzo(k)fluoranthene	BkFA	6.35	252
Benzo(a)pyrene	BaP	6.51	276
Indeno(1.2.3-cd)pyrene	IP	6.9	276
Benzo(ghi)perylene	BghiP	6.5	278
Dibenzo(a,h)anthracene	DBahA	3.37	128

1.2.2 Persistent organic pollutants (POP)

POP include many chemical families (e.g PCB, OCP, dioxin and furans). They are persistent in the environment and having very long half-life in different medias (Jones and Voogt, 1999). POP can enter the aquatic environments in a variety of ways such as run-off from non-point sources, atmospheric deposition, river inputs, discharge of industrial and sewerage wastewater and wet/dry deposition.

Considering to their harmful effects on human and ecosystem, during the last 30 years, many international agreements are coming into the effect to reduce the environmental burden of POP. Since the mid 1970s, most of the POP have been removed from active use in most countries, however because of their properties, they are still ubiquitous in the environmental components. They are regulated under the Stockholm Convention signed by 125 nations including Turkey.

PCB were classified into three groups (Figure 1.4). The first group of PCB is called as indicator PCB and consists of six congeners, the second group of PCB is non-ortho, and the third group is mono-ortho PCB. Twelve non-ortho and mono-ortho PCB are classified as dioxin like PCB (dl-PCB). Seven dioxins, ten furans, and dl-PCB containing four to eight chlorine atoms are the most toxic, bioaccumulative and pose a major health risk (DeVito et al., 1995) due to certain molecular characteristics.

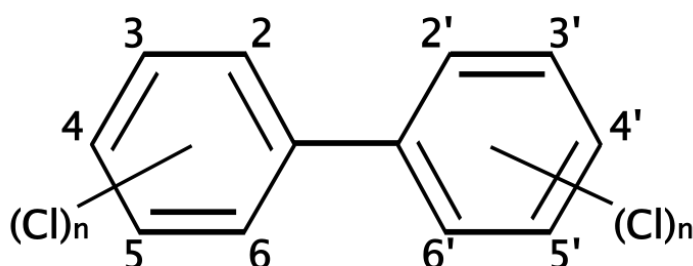


Figure 1.4 : Chemical structure of PCB (Ur1-1).

The use of the total toxic equivalent (TEQ) approach for risk assessment and management purposes has been formally adopted by many countries (eg. Kutz et al., 1990). TEQ is operationally defined by the sum of the concentration of each congeners in a mixture multiplied by its toxic equivalency factors (TEF) (Van den Berg et al., 2006). Analyzed PCB, PCDD and PCDF were shown in Table 1.2 and Table 1.3

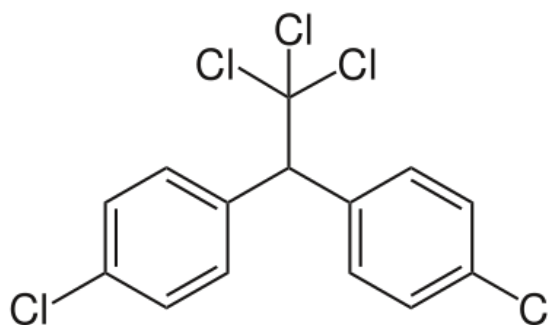
Table 1.2 : Analyzed PCB (Mackay et al.2006).

Chemicals	Abbreviations	log K_{ow}	MW (gr mol ⁻¹)
2,4,4'-Trichlorobiphenyl	PCB #28	5.66	258
2,2',5,5'-Tetrachlorobiphenyl	PCB #52	5.91	292
2,2',4,5,5'-Pentachlorobiphenyl	PCB #101	6.33	327
2,2',3,4,4',5'-Hexachlorobiphenyl	PCB #138	7.22	361
2,2',4,4',5,5'-Hexachlorobiphenyl	PCB #153	6.87	361
2,2',3,4,4',5,5'-Heptachlorobiphenyl	PCB #180	7.16	396
3,3',4,4'-Tetrachlorobiphenyl	PCB #77	6.48	292
3,4,4',5-Tetrachlorobiphenyl	PCB #81	6.24	292
3,3',4,4',5-Pentachlorobiphenyl	PCB #126	6.67	327
3,3',4,4',5,5'-Hexachlorobiphenyl	PCB #169	7.41	361
2,3,3',4,4'-Pentachlorobiphenyl	PCB #105	6.61	327
2,3,4,4',5-Pentachlorobiphenyl	PCB #114	6.47	327
2,3',4,4',5-Pentachlorobiphenyl	PCB #118	6.49	327
2',3,4,4',5-Pentachlorobiphenyl	PCB #123	6.5	327
2,3,3',4,4',5-Hexachlorobiphenyl	PCB #156	7.11	361
2,3,3',4,4',5'-Hexachlorobiphenyl	PCB #157	6.97	361
2,3',4,4',5,5'-Hexachlorobiphenyl	PCB #167	6.82	361
2,3,3',4,4',5,5'-Heptachlorobiphenyl	PCB #189	6.15	395

Table 1.3 : Analyzed PCDD and PCDF (Mackay et al.2006).

Chemicals	Abbreviations	log K _{ow}	MW (gr mol ⁻¹)
1,2,3,7,8-pentachlorodibenzodioxin	12378-PeCDD	6.84	356.416
1,2,3,4,7,8-hexachlorodibenzodioxin	123478-HxCDD	7.8	390.861
1,2,3,6,7,8-hexachlorodibenzodioxin	123678-HxCDD	7.58	390.861
1,2,3,7,8,9-Hexachlorodibenzodioxin	123789-HxCDD	7.58	390.861
1,2,3,4,6,7,8-heptachlorodibenzodioxin	1234678-HpCDD	7.66	425.308
octachlorodibenzodioxin	OCDD	8.48	459.751
2,3,7,8-tetrachlorodibenzofuran	2378-TCDF	6.46	305.978
1,2,3,7,8-pentachlorodibenzofuran	12378-PeCDF	6.99	340.418
2,3,4,7,8-pentachlorodibenzofuran	23478-PeCDF	7.11	340.418
1,2,3,4,7,8-hexachlorodibenzofuran	123478-HxCDF	7.53	374.863
1,2,3,6,7,8-Hexachlorodibenzofuran	123678-HxCDF	7.57	374.863
1,2,3,7,8,9-hexachlorodibenzofuran	123789-HxCDF	7.76	374.863
2,3,4,6,7,8-Hexachlorodibenzofuran	234678-HxCDF	7.65	374.863
1,2,3,4,6,7,8-heptachlorodibenzofuran	1234678-HpCDF	8.00	409.308
1,2,3,4,7,8,9-Heptachlorodibenzofuran	1234789-HpCDF	8.23	409.308
Octachlorodibenzofuran	OCDF	8.03	443.753

Organochlorine pesticide (OCP) contamination of the environment is an important problem. They are known to disrupt the hormone endocrine system and induce cancer in a range of organisms. In that way, they present a significant risk to ecosystems and human health (Patlak, 1996). In Turkey, the use of pesticides started with the use of DDT (Figure 1.5) against all kinds of pests in the 1960s. The usage of OCP, including aldrin, endrin, DDT, dieldrin, HCHs, heptachlor, chlordane, and toxaphene, was prohibited in Turkey between 1971 and 1989.

**Figure 1.5 :** Chemical structure of DDT (Url-2).

However, they are still being used illegally in some parts of Turkey, imported illegally and are sold in markets (Kolonkaya, 2006). Total annual pesticide usage in Turkey was approximately 33000 tons between 1998 and 2004 (State Planning Organization, 2008) and the estimations show increased pesticide usage for the years 2009-2012 (Özbek and Fidan, 2009). Despite the restrictions, the previous studies have shown that some OC pesticides for example DDT was present in Turkish rivers, streams and domestic and industrial discharges indicating their illegal use (Tuncer et

al. 1998; Bakan and Ariman, 2004). There is, however, still a lack of information on OCP concentrations in the coastal areas in Turkey. Analyzed OCP in this study were given on Table 1.4.

Table 1.4 : Analyzed OCP (Mackay et al.2006).

Chemicals	Abbreviations	log K _{ow}	MW (gr mol ⁻¹)
alpha-Hexachlorocyclohexane	α-HCH	3.94	291
beta-Hexachlorocyclohexane	β-HCH	3.84	291
gamma-Hexachlorocyclohexane	γ-HCH	3.7	291
delta-Hexachlorocyclohexane	δ-HCH	4.14	291
epsilon-Hexachlorocyclohexane	ε-HCH	4.26	291
Pentachlorobenzene	PeCB	5.19	250
Hexachlorobenzene	HCB	5.64	285
Pentachloroanisole	PCA	5.48	280
Octachlorostyrene	OCS	6.2	380
4,4'-Dichlorodiphenyltrichloroethane	4,4'-DDT	5.47	355
2,4'-Dichlorodiphenyltrichloroethane	2,4'-DDT	5.59	355
4,4'-Dichlorodiphenyldichloroethane	4,4'-DDD	5.75	320
2,4'-Dichlorodiphenyldichloroethane	2,4'-DDD	6.08	320
4,4'-Dichlorodiphenyldichloroethene	4,4'-DDE	6.14	318
2,4'-Dichlorodiphenyldichloroethene	2,4'-DDE	5.56	318
trans-Chlordane	t-CHL	5.38	410
cis-Chlordane	c-CHL	5.38	410
oxy-Chlordane	OXC	5.48	424
Heptachlor		5.94	373
cis-Heptachloroepoxide	c-HE	4.51	389
trans-Heptachloroepoxide	t-HE	4.51	389
Aldrin		6.24	365
Dieldrin		4.76	381
Endrin		4.71	381
Endosulfan-I	(END)-I	4.94	407
Endosulfan-II	(END)-II	4.78	407
Methoxychlor		7.13	346
Mirex		5.38	546

2. MATERIALS AND METHODS

2.1 Properties of the Study Area

The study site, Istanbul Strait which is one of the major waterways in the world connecting the Black Sea and the Mediterranean, has been strongly affected by urbanization, harbor activities, ship traffic, commercial fishing and also by the pollutants entering from the Black Sea basin. The strait is one of the most important shipping route handling annually 50,000 ships.

The Strait has a two-layer water system. The salinity of the top layer is 18-25 ppt and bottom layer is 33-38 ppt originating from the Black Sea and Mediterranean Sea, respectively. The length of the Strait is approximately 31 km and its width varies from 0.7 km to 3.5 km. Water depths vary around a mean of 33 m with a maximum depth of 110 m. Although several studies have been carried out on the oceanographic characteristics and pollution status of Istanbul Strait, this is the first systematic data on pollutants especially for POP and for the pollutants in water by using SPMD. The previous studies in the Strait showed that some parts of the ecosystem were heavily contaminated by heavy metals (Okay et al. 2008) and polycyclic aromatic hydrocarbons (Karacık et al. 2009).

In this study, we measured PAH (16 compounds), PCB (18 compounds), PCDD (6 compounds), PCDF (10 compounds) and OCP (28 compounds) in semi permeable membrane devices (SPMD), in sediments and in mussels from several stations in the Istanbul Strait and Marmara Sea (Table 2.1).

The analyzed compounds are given in Table 1.1-1.4. In this study Octanol-Water Partition Coefficient ($\log K_{ow}$) values used during the calculations were obtained from Mackay et al., (2006) and Huckins et al., (2006).

Mussels are preferred food for many people in the region; therefore, data on distribution of pollutants in mussels is important not only for ecological aspects, but also for human health perspectives.

In this study, the water pollutant concentrations were estimated by using the sediment and SPMD data and compared. During the calculations of water concentrations from SPMD data, two methods presented by Huckins et al., (2006) and Booij and Smedes, (2010) were used.

Table 2.1 : Sampling time, locations, matrix, analyzed chemicals.

Station No	Station Name/Location	Time Period	Analyzed Media	Analysis
1	Rumeli Feneri	2007	Sediment	PAH, PCB, OCP
2	Garipçe	2007	Sediment, Mussel	PAH, PCB, OCP, PCDD, PCDF
3	Rumeli Kavağı	2007	Sediment, Mussel	PAH, PCB, OCP
4	Büyükdere	2007	Sediment, Mussel	PAH, PCB, OCP
5	Tarabya	2007	Sediment, Mussel	PAH, PCB, OCP
6	İstinye	2007-09	Sediment, Mussel, SPMD, BR	PAH, PCB, OCP, PCDD, PCDF
6a	İstinye Dere içi	2009	Sediment, Musse, SPMD, BR	PAH, PCB, OCP
7	Balta Limanı	2007	Sediment, Mussel	PAH, PCB, OCP
8	Bebek	2007	Sediment, Mussel	PAH, PCB, OCP, PCDD, PCDF
9	Ortaköy	2007	Sediment, Mussel	PAH, PCB, OCP
10	Beşiktaş	2007	Sediment, Mussel	PAH, PCB, OCP, PCDD, PCDF
11	Ahırkapı	2007	Samples couldn't collected	-
12	Anadolu Feneri	2007-09	Sediment, Mussel, SPMD, BR	PAH, PCB, OCP
13	Poyraz	2007	Sediment, Mussel	PAH, PCB, OCP, PCDD, PCDF
14	Anadolu Kavağı	2007	Mussel	PAH, PCB, OCP
14a	Midyeciler	2007-09	Mussel	PAH, PCB, OCP, PCDD, PCDF
15	Yalıköy-Beykoz	2007	Mussel	PAH, PCB, OCP
16	Çubuklu	2007	Mussel	PAH, PCB, OCP
17	Kavacık	2007	Mussel	PAH, PCB, OCP
18	Kandilli	2007	Sediment, Mussel	PAH, PCB, OCP, PCDD, PCDF
19	Kuzguncuk	2007	Sediment, Mussel	PAH, PCB, OCP
20	Üsküdar	2007	Sediment, Mussel	PAH, PCB, OCP, PCDD, PCDF
21	Moda	2007	Sediment, Mussel	PAH, PCB, OCP
22	Büyük ada1	2007	Mussel	PAH, PCB, OCP
23	Büyük ada 2	2007-09	Sediment, Mussel, SPMD, BR	PAH, PCB, OCP, PCDD, PCDF
24	Tuzla	2009	Sediment, Mussel, SPMD, BR	PAH, PCB, OCP

Figure 2.1 shows the location of the Strait and sampling stations. Four main freshwater tributaries are connected to the strait from the stations of 4, 6, 7 and 18.

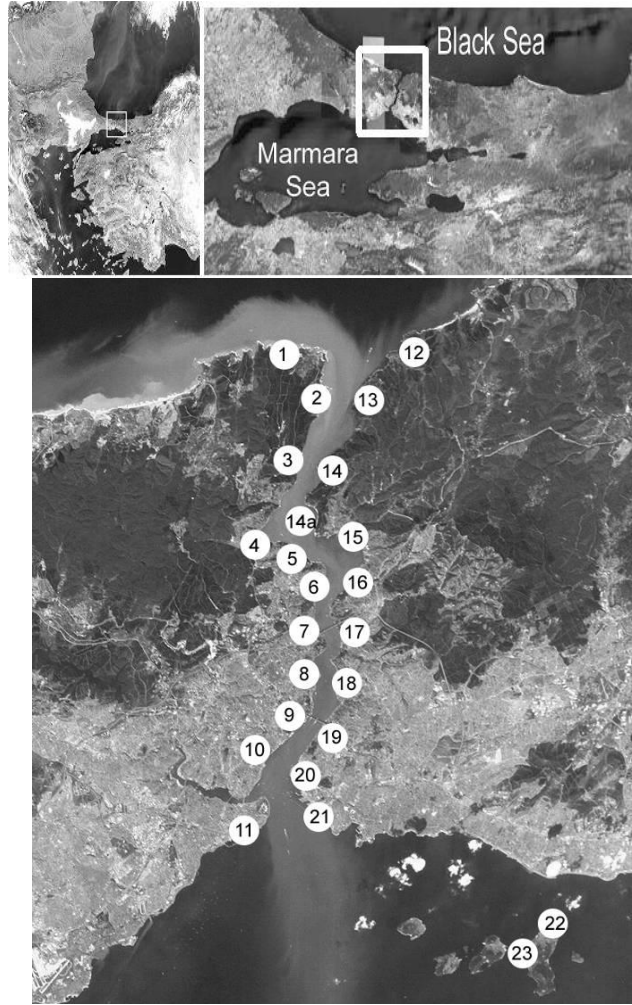


Figure 2.1 : Map of the Istanbul strait and sampling stations (2007).

Stations of 22 and 23 are located in the Büyükada Island (Marmara Sea). Commercial mussel catchers collect mussels from the natural mussel beds at Station 14a. Mussels from that site are consumed extensively in Istanbul markets and restaurants.

2.1.1 Sampling campaign 2007

Surface sediments (0-10 cm depth from sediment surface) from 1 to 6 meters water column depth and mussels (*Mytilus galloprovincialis*; 4-5 cm) were collected from the coastal stations (Figure 2.1) of the Istanbul strait and an island coasts in the Marmara Sea during the period of January-February 2007. Sediment and mussel samples were collected by SCUBA and/or free diving methods from 17 and 21 stations respectively. The sampling water depth range was recorded as one to five meters. Sediment samples were collected according to UNEP sampling procedures (UNEP/MAP, 2006).

The sediment samples could not be collected between stations of 13 and 18 due to the rocky characteristics of the sea bottom.

All samples were analyzed for PCB and OCP. However, the concentrations of PCDD/F congeners were analyzed only from two stations (14a and island stations). These stations were selected for the following reasons: a) the mussel beds at station 14a have been used commercially for long years and the mussels harvested from that station have been distributed to the markets, restaurants in the vicinity of Istanbul b) PCB concentration in mussels was highest at the island station (23) and exhibited a different pattern than sediments.

2.1.2 Sampling campaign 2009

Depending on the results obtained from the first sampling, three station (6, 12 and 23) were selected for the second sampling and two additional stations were included (6a, 24) (Figure 2.2). 6a is situated at the creek (İstinye) mouth and 24 is the main shipyards area of Turkey (Tuzla).



Figure 2.2 : Sampling stations (2009).

Surface sediments and local mussels were collected from the stations by SCUBA and/or free diving methods during the period of March-April 2009. Station 12 and 24 contain no appropriate sized (4-5cm) local mussel populations.

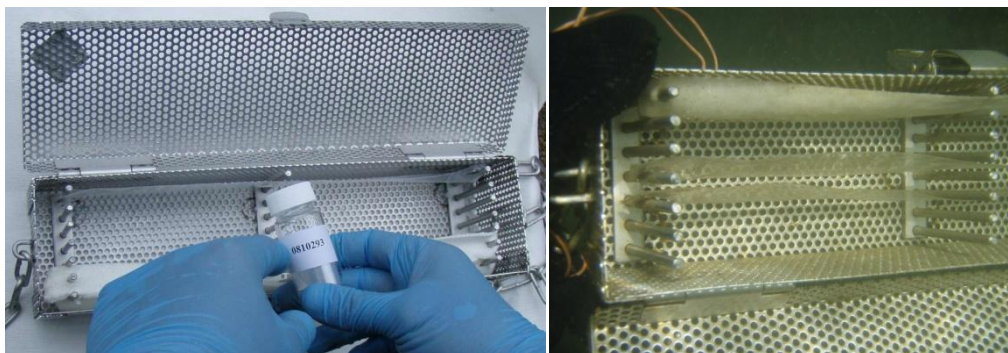


Figure 2.3 : Preparation of SPMD cages and after 7 days of exposure underwater.

SPMD and BR sorbents were deployed to the stations in specially designed stainless steel cages in March 2009 (Figure 2.3). The samplers were retrieved from the sites after 7 and 21 days of deployment. After cleaning the surfaces of the SPMD's with ambient sea water, they were transferred to the laboratory and stored at -20°C until analysis. Production (control samples; analyzed after production- not carried to the site) and transportation blank SPMD were used to correct for possible contamination. Transportation blank samples were carried to the sampling sites during deployment without exposing them to the air and kept in dark at the sampling site. The blank samplers were extracted and analyzed in the same manner as the deployed SPMD. PAH, PCB and OCP were analyzed in the samples.

To prepare the pore water exposed SPMD and BR sorbents in laboratory, sediment samples of the same volume (1.8 L) collected from second sampling sites were placed into glass aquariums (280 mm x 110 mm x 70 mm) in the static systems and allowed to consolidate overnight. Then, SPMD were buried into one cm depth from the sediment surface. Aquariums were covered with aluminum foil and sealed with parafilm. After 7 and 21 days of exposure time SPMD were removed, and transferred into glass vials and frozen at -20 °C until analysis. The exposures were performed in a thermostated room adjusted to the *in situ* temperature of 8 °C.



Figure 2.4 : Local and transplanted mussels.

Mussels (*Mytilus galloprovincialis*; 4-5 cm) obtained from the mussel farmers (Anadolu kavağı) were transplanted at the same locations together with the passive samplers and retrieved (Figure 2.4).

2.1.3 Properties of the sampling sites

Sampling sites were carefully selected considering the possible pollution sources. River mounts, small marinas and industrial sites are some of those sampling stations. Table 2.2 shows the descriptions of each sampling locations.

2.1.4 Transfer and storage of the samples

Samples were immediately transferred to the laboratory in foam boxes filled with ice. Sediment samples were homogenized from approximately 1 kg of sediment. Mussels were dissected in the laboratory and were homogenized by ultra-turrax(IKA). All samples were stored in glass vials with a Teflon cap at -20°C until analysis. All glassware used in sampling and storage were cleaned by HPLC grade solvents and were burned in the oven. Also SPMD and BR sorbents were transferred into glass vials and frozen at -20°C until analysis.

2.1.5 Total organic carbon in sediments

The presence of total organic material was estimated by weight loss after heating at 450°C for 5 h. The basic principle for the quantification of total organic carbon relies on the destruction of organic matter present in the sediment. All carbon forms in the sample are converted to CO_2 which is then measured directly or indirectly and converted to total organic carbon or total carbon content, based on the presence of inorganic carbonates (Schumacher, 2002).

Table 2.2 : Table shows the station numbers/names, short description of the sampling sites and GPS coordinates of the stations.

Station No	Station Name/Location	Description	Coordinates
1	Rumeli Feneri/EP ¹	a low contaminated area, fishing boats	41° 14.455 N - 029° 05.855 E
2	Garipçe / EP	a low contaminated area, fishing boats	41° 12.818 N - 029° 06.594 E
3	Rumeli Kavağı/EP	a low contaminated area, fishing boats	41° 11.022 N - 029° 04.574 E
4	Büyükdere/EP	River mouth	41° 09.207 N - 029° 02.324 E
5	Tarabya/ EP	Small yacht marina	41° 08.232 N - 029° 03.444 E
6	İstinye/ EP	River mouth, hospital , fishing boats , historical shipyard area	41° 06.633 N - 029° 03.515 E
6a	İstinye Dere içi/EP	River mouth	41° 113762 N - 029° 054395 E
7	Balta Limanı/EP	River mouth, hospital	41° 05.963 N - 029° 03.256 E
8	Bebek /EP	Small yacht marina	41° 04.803 N - 029° 03.084 E
9	Ortaköy/EP	Local ships, harbour activities, restaurants etc	41° 02.829 N - 029° 01.639 E
10	Beşiktaş/EP	Local ships, harbour activities	41° 02.429 N - 029° 00.343 E
11	Ahırkapı /EP	International harbour activities	41° 00.256 N - 028° 58.981 E
12	Anadolu Feneri/AP ²	a low contaminated area, fishing boats	41° 12.907 N - 029° 09.109 E
13	Poyraz /AP	a low contaminated area, fishing boats	41° 12.334 N - 029° 07.596 E
14	Anadolu Kavağı/AP	a low contaminated area, fishing boats	41° 10.191 N - 029° 05.190 E
14a	Midyeciler(Mussel Catchers)	Commercially used mussel beds	-
15	Yalıköy-Beykoz/AP	Local ships, harbour activities	41° 08.149 N - 029° 05.288 E
16	Çubuklu/AP	Local ships, harbour activities	41° 06.808 N - 029° 05.189 E
17	Kavacık/AP	Local ships, harbour activities	41° 05.221 N - 029° 03.974 E
18	Kandilli/AP	River mouth	41° 04.451 N - 029° 03.541 E
19	Kuzguncuk/AP	Local ships, harbour activities	41° 02.380 N - 029° 02.144 E
20	Üsküdar/AP	Local ships, harbour activities	41° 01.285 N - 029° 00.411 E
21	Moda/AP	Local ships, harbour activities	40° 58.786 N - 029° 01.488 E
22	Büyük ada1/MS ³	Local ship harbour activities, close to mooring area	40° 52.481 N - 029° 08.144 E
23	Büyük ada 2/MS	Swimming area, close to mooring area	40° 51.550 N - 029° 06.769 E
24	Tuzla/AP	Shipyard	40° 834009 N - 029° 278218 E

¹EP: European part

²AP: Asian part

³MS: Marmara Sea

2.1.6 Particle size determination of the sediments

Particle size distribution and classifications were performed according to the ASTM D-2487 standard method (2006). The analytical sieve shaker Retsch AS200 was used for the analysis. Sediment median grain sizes were obtained from phi scale. Sediment (150gr) was dried at 105°C overnight. Sieves were placed on the shaker. After 20 min wet sieving each sieve was dried at 105°C overnight. The dried sieves were weighted and results were recorded.

2.1.7 Preparation of SPMD

SPMD were prepared from 29 cm x 2.5 cm low-density polyethylene lay-flat (LDPE) tubing (VWR Ismaning, Germany) with a membrane thickness of approximately 65 μm . The triolein-containing part of the sampler excluding the mounting loops has a surface area of 115 cm^2 . 700 μL of triolein (Sigma, Munich, Germany, 99 %) was spiked with the following performance reference compounds (PRCs): Naphthalene- $^{13}\text{C}_6$, Acenaphthylene- $^{13}\text{C}_6$, Acenaphthene- $^{13}\text{C}_6$, Fluorene- $^{13}\text{C}_6$, Phenanthrene- $^{13}\text{C}_6$, Anthracene- $^{13}\text{C}_6$, Fluoranthene- $^{13}\text{C}_6$, Pyrene- $^{13}\text{C}_3$, Benz(a)anthracene- $^{13}\text{C}_6$, Chrysene- $^{13}\text{C}_6$, Benzo(b)fluoranthene- $^{13}\text{C}_6$, Benzo(k)fluoranthene- $^{13}\text{C}_6$, Benzo(a)pyrene- $^{13}\text{C}_4$, Indeno(1,2,3-cd)pyrene- $^{13}\text{C}_6$, Benzo(ghi)perylene- $^{13}\text{C}_{12}$, Dibenz(a,h)anthracene- $^{13}\text{C}_6$. PRCs (5 $\text{ng } \mu\text{L}^{-1}$) in toluene (0.32 μL per gr of triolein) were added as close as possible to the sealed bottom by using a capillary pipette. Air was removed first by squeezing the triolein towards the sealed end using a triangle stainless steel loaf, and then pushing the triolein front towards the open end. A second heat-seal was applied just above the triolein front at a distance of 23 cm from the first seal. Mounting loops were made by applying a third and fourth heat-seal at the empty end parts of the tubing. All these procedures were conducted in a purified glovebox under nitrogen atmosphere to avoid contaminations. The prepared SPMD were placed in closely aluminum sealed heat cleaned 10 mL glass vials, further stored at -20°C and kept cooled during transportation until deployment.

2.1.8 Preparation of butyl rubber sorbents

Butyl rubber sorbent was synthesized at the İstanbul Technical University, Department of Chemistry - Polymeric Gels Research Laboratory. The sorbent was prepared from Butyl 365, Exxon Chemical Co. with 2.3 mol % isoprene and 33 Mooney viscosity. Sulfur monochloride S_2Cl_2 was used as a cross-linking agent.

Benzene, toluene, hexane and methanol (all HPLC grade) were used for swelling and deswelling during the preparation and purification process. (Ceylan and Okay, 2007)

Butyl rubber (BR) sorbent sheets in a form of 24 cm to 40 cm were prepared by solution cross-linking technique at 5 w/v % rubber and 6 v/w % cross-linker concentrations. The preparation scheme: BR (100g) was dissolved in 2 L of benzene overnight at 20 °C. Then, sulfur monochloride (6.0 mL) was added under stirring. The solution was transfer into the aluminum containers sealed with glass plates. The reaction was conducted for 24 h at -18 °C and then the Sorbent was squeezed to remove benzene. They were washed several times with toluene and then with methanol. Finally, hexane was used for purification and the sorbents were dried under vacuum at room temperature. The dry sorbent sheets were cut into pieces (23 cm x 2 cm) and were placed in aluminum sealed, heat cleaned 20 mL glass vials, further stored at -20°C until deployment.

2.2 Chemical Analysis

2.2.1 General information, instrumentation and QA/QC

Chemical analysis were performed with a high resolution mass spectrometer Finnigan MAT 95S (Thermo Electron GmbH, Bremen, Germany) coupled with an Agilent GC 6890 (Agilent Technologies, Palo Alto, CA, USA). All solvents used were of picograde quality and purchased from LGC Standards (Wesel, Germany). The laboratory operates a quality management system according to DIN EN ISO/IEC 17025 and is accredited for the type of analyses applied. The ¹³C-isotope dilution method was used for the quantification. Procedures were validated using internal reference materials and approved by means of international interlaboratory comparison studies. The quantification criteria included confirmation of retention times and isotope ratios of the labeled standards and respective analytes. Internal standards in nonane for PAH were Naphthalene-D8, Acenaphthylene-D8, Acenaphthene-D10, Fluorene-D10, Phenanthrene-D10, Anthracene-D10, Fluoranthene-D10, Pyrene-D10, Benzo(a)anthracene-D12, Chrysene-D12, Benzo(b)fluoranthene-D12, Benzo(k)fluoranthene-D12, Benzo(a)pyrene-D12, Indeno(1,2,3-cd)pyrene-D12, Benzo(ghi)-perylene-D12, Dibenzo(a,h)anthracene-D14 and for PCB: IUPAC Nos.28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157,167, 169, 180, 189 and for OCP: Pentachlorobenzene-¹³C₆, alpha-

HCH- $^{13}\text{C}_6$, gamma-HCH- $^{13}\text{C}_6$, beta-HCH- $^{13}\text{C}_6$, delta-HCH- $^{13}\text{C}_6$, Pentachloroanisole- $^{13}\text{C}_6$, Hexachlorobenzene- $^{13}\text{C}_6$, Heptachlor- $^{13}\text{C}_{10}$, Aldrin- $^{13}\text{C}_{12}$, Octachlorostyrene- $^{13}\text{C}_6$, oxy-Chlordane- $^{13}\text{C}_{10}$, Heptachlorepoxy- $^{13}\text{C}_{10}$, 2,4'-DDE- $^{13}\text{C}_{12}$, 4,4'-DDE- $^{13}\text{C}_{12}$, *trans*-Chlordane- $^{13}\text{C}_{12}$, Endosulfan-I- $^{13}\text{C}_9$, Endosulfan-II- $^{13}\text{C}_9$, 4,4'-DDD-D8, Dieldrin- $^{13}\text{C}_{12}$, 2,4'-DDT- $^{13}\text{C}_{12}$, 4,4'-DDT- $^{13}\text{C}_{12}$, Methoxychlor- $^{13}\text{C}_{12}$, Mirex- $^{13}\text{C}_{10}$). Routinely, the mass fragment with the highest intensity of the molecular or fragment ion cluster was used for quantification. Concentrations were calculated by comparison of the signal heights of the analyte with its respective labeled analogue. QC samples (laboratory blanks and control samples) were included in the analytical batch every 5-10 samples. the results of these blanks were subtracted from the environmental samples. Meanwhile, amounts smaller than the blanks by a factor of about 2 were abandoned. The recovery standard ($^{13}\text{C}_{12}$ -1,2,3,4-TCDD for PCB, Pentachlorotoluene and $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD for OCP and PAH) was used for the calculation of the recoveries of the labeled internal standards. The mean recoveries for OCP, PCB and PAH were in the range of 30%–130%, 30%–90% and 30%–110%, respectively. The three-time signal/noise ratio was set as the limit of detection.

2.2.2 Analysis procedures; extraction and clean up

The mussel and sediment samples were homogenized prior to analysis. A wet 10-20 g portion of the samples were thoroughly mixed with diatomaceous earth (Separtis, Germany), placed into the extraction cells and then the mixture was spiked with internal standards of ^{13}C -labeled OCP, PCB (LGC Standards, Germany) and deuterated PAH (Dr. Ehrenstorfer, Germany). The samples were extracted with accelerate solvent extraction system (DIONEX ASE 200) using a hexane/acetone (75:25 v/v) mixture as extraction solvent at a temperature of 120 °C and a pressure of 12 MPa. Two static cycles of 10 min were applied for a complete extraction. All solvents used were of picograde quality purchased from LGC Standards (Wesel, Germany). The volume of the extracts was reduced to appr. 1 mL in a rotary evaporator and, to remove interferences, the concentrated crude extracts were cleaned-up by several sequential chromatography steps and eluted with acetonitrile. The eluate was then transferred into 2 mL GC vials and reduced to 20 μL with a gentle stream of nitrogen.

BR sorbents were cut into pieces and were mixed with diatomaceous earth. The mixture were placed into extraction cells and was spiked with internal standards. The following extraction and clean up procedure was same as sediment and mussels samples.

To analyze SPMD, first they were cut into small pieces and extracted overnight with 100 mL cyclohexane containing internal standards in a 250 mL Erlenmeyer flask at 200 rpm in a constant temperature shaker. The organic phase of the extracts was dried by passing anhydrous sodium sulfate and cyclohexane was removed in a vacuum rotary evaporator to isolate triolein residues. The triolein was dissolved again in appr. 1-2 mL of *n*-hexane:dichloromethane (1:1) mixture and the solutions were purified using a mixed column (silica gel from Wesel Germany, grade 60; 3 cm diameter column containing, from the bottom upward, 10 g silica, 5 g alumina with 3 % H₂O, 5 g anhydrous sodium sulfate). The extracts were eluted with 100 mL mixture of *n*-hexane and dichloromethane (1:1) and reduced to 1 mL. The residues were further purified through a C18 SPE cartridge for which acetonitrile was used as eluting solvent. After adding a recovery standard, the extracts were concentrated to 20 µL using a gentle flow of nitrogen.

2.2.3 Effect studies neutral red retention (NRR) assay

Neutral red retention (NRR) assay or also called– Lysosomal membrane stability was performed using the transplanted and local mussels. The details of the method was explained by Lowe et al. (1995). To perform the assay, stock solution was prepared by dissolving 20mg of neutral red dye in 1mL of DMSO. Then, working solution was prepared by using 10 µL of the stock solution diluted with 5 mL of physiological saline (HEPES, sodium chloride, magnesium sulfate, potassium chloride and calcium chloride). The blood taken from mussels mixed with 1mL physiological saline and 50 µL of the cell suspension was dispensed onto a microscope slide and placed in a dark humidity chamber for 15 min at room temperature to allow the cells to settle. A cover slip was applied after the addition of 40 µL of neutral red working solution. After 15 min, the microscope slides were inspected under a microscope (Ivymen series, Model 2000-A, Spain). After a further 15 min incubation, the slides were checked again and examined systematically afterward at 30 min intervals to determine the time course of uptake into and dye loss. The test for each replicate was

terminated when the dye loss was evident in 50% of the small granular hemocytes and the time was recorded. The test ends after 180 min. The mean retention time was then determined for 10 individual mussels.

2.2.4 Statistical analysis

Statistical analysis for hierarchical cluster analysis (HCA) to emphasize natural grouping in the data performed by using KyPlot program (Version 2.0 beta 15, 1997-2001, Koichi Yoshioka).

3. RESULTS AND DISCUSSION

3.1 Sampling Campaign 2007

3.1.1 PCB and PCDD/F

The results in Table 3.1 present the concentration levels of the individual PCB congeners in sediment samples from the first sampling in a pg g^{-1} in dry weight (dw) basis. Analysis results of PCB in mussels are given in Table 3.2 and PCDD/F values for both sediment and mussel samples are compiled in Table 3.3.

The dominant congeners for each group of chemicals in sediment samples were: PCB-153 (except stations of 12 and 23) for indicator PCB, PCB-77 for non-ortho-PCB, PCB-118 for mono-ortho-PCB, OCDD for PCDDs and 1,2,3,4,6,7,8-HpCDF (except stations 18 and 20) for PCDFs. The source of high PCB-153 is not clearly known, but it may be due to sewage inputs via the small tributaries into the strait or from atmospheric inputs. The predominance of PCB-153 was also reported from industrial and urban impacted site sediments from Venice lagoon (Frignani et al., 2001). PCB 118 and PCB 105 were the dominant dl-PCB. These two congeners represent 60-80 % (except station 6) of the total dl-PCB. The predominance of PCB 118 has been reported in various matrices in the environment (Gatehouse, 2004; Kim and Masunaga, 2004). The total concentrations of dl-PCB were higher than those of PCDD/F, only at station 13, the total PCDD/F concentration was higher compared to total dl-PCB concentration.

The concentration levels of total PCB in sediments ranged from 17.9 to 539,746 pg g^{-1} dw (Table 3.1). The highest PCB concentrations in sediments were measured at stations of 6, 7, 8 and 19; the total PCB concentrations for those stations were 539,746 pg g^{-1} , 1425 pg g^{-1} , 897 pg g^{-1} , and 825 pg g^{-1} dw respectively.

Table 3.1 : Concentrations of PCB and WHO-TEQ_{PCB} values in coastal sediments of the Istanbul Strait and island station (pg g⁻¹dw) (Sampling2007).

Chemicals	Stations																
	1	2	3	4	5	6	7	8	9	10	12	13	18	19	20	21	23
PCB-28	1.54	2.30	1.69	39.3	3.57	893	331	158	67.0	31.1	0.54	1.38	35.2	27.0	6.72	26.1	3.21
PCB-52	2.39	2.38	2.62	17.6	4.39	8273	160	95.6	123	44.7	1.79	2.03	42.1	32.7	4.88	59.7	9.62
PCB-101	2.93	2.92	3.16	26.7	11.4	76530	173	104	106	56.1	2.96	2.75	68.4	91.9	5.52	117	20.4
PCB-138	2.08	1.38	2.23	26.8	14.4	91755	132	90.4	71.3	43.2	1.79	2.61	69.6	136	4.24	73.6	14.1
PCB-153	3.08	3.46	3.31	51.7	26.6	191349	198	169	132	76.2	3.90	6.30	137	236	8.16	111	16.6
PCB-180	1.16	2.30	1.23	23.2	14.3	114146	96.6	82.2	59.9	34.3	4.13	11.0	78.6	134	3.52	38.1	5.00
Σindicator PCB	13.2	14.7	14.3	185	74.6	482946	1090	699	559	286	15.1	26.1	431	657	33.1	425	69.0
PCB-77	0.29	0.62	0.32	3.65	1.66	1246	30.5	14.4	7.06	5.06	0.48	0.26	5.08	6.55	1.04	9.95	1.04
PCB-81	nd	nd	nd	nd	0.33	509	1.40	1.12	nd	nd	nd	nd	nd	0.58	nd	nd	nd
PCB-126	nd	nd	nd	0.23	0.52	126	1.11	1.72	0.48	0.43	0.12	nd	0.34	0.84	0.19	0.55	0.53
PCB-169	nd	nd	nd	nd	nd	15.8	nd	1.20	nd	nd	nd	nd	nd	nd	nd	nd	0.54
Σ non-ortho PCB	0.29	0.62	0.32	3.88	2.51	1897	33.0	18.5	7.54	5.49	0.59	0.26	5.43	7.97	1.23	10.5	2.11
PCB-105	1.31	1.61	1.39	12.1	4.48	5374	85.6	41.5	35.4	21.1	1.01	1.23	22.2	39.5	2.40	32.5	12.4
PCB-114	0.16	nd	0.17	0.77	0.57	859	4.43	3.36	2.40	1.37	0.22	0.17	1.63	2.70	0.32	1.84	0.97
PCB-118	2.39	1.92	2.62	25.9	9.62	21207	164	101	71.2	45.9	2.26	2.46	46.3	77.7	4.96	55.3	23.6
PCB-123	0.14	nd	0.10	0.69	0.42	2844	3.32	2.32	1.94	1.04	0.38	nd	0.91	1.80	0.21	2.43	0.47
PCB-156	0.20	0.63	0.22	4.14	2.98	13727	25.5	15.8	10.7	6.99	0.34	0.44	8.41	21.2	0.75	8.77	3.28
PCB-157	0.10	nd	0.11	1.47	0.56	1334	5.90	3.66	1.94	1.37	0.16	nd	1.33	4.30	0.24	2.95	0.97
PCB-167	0.14	0.25	0.15	2.25	1.33	6701	10.8	8.52	5.27	3.21	0.16	0.29	4.42	10.3	0.34	5.38	1.64
PCB-189	nd	nd	nd	0.60	0.61	2859	3.02	3.81	1.40	1.37	nd	0.12	1.51	3.15	0.65	0.81	2.09
Σmono-ortho PCB	4.44	4.42	4.74	47.9	20.6	54903	302	180	130	82.3	4.55	4.71	86.7	161	9.87	110	45.4
ΣPCB	17.9	19.8	19.3	237	97.7	539746	1425	897	697	373	20.3	31.1	523	825	44.2	545	117
ΣWHO-TEQ_{PCB}	0.00	0.00	0.00	0.03	0.05	15.0	0.12	0.22	0.05	0.05	0.01	0.00	0.04	0.09	0.02	0.06	0.07

The high PCB results at station 6 may be due to the presence of a historical shipyard, which had operated for over 70 years. Although the shipyard stopped its activities in 1991, it is well known that a shipyard is a workplace contaminated with spilled petroleum, paints, solvents, etc. in relation to shipbuilding and repair activities (Chiu et al., 2006; Lee et al., 2003). Operation of the shipyard probably caused several pollutants to accumulate in sediments. On the other hand, there are four main freshwater tributaries, which are collecting small industrial discharges as well as domestic wastewaters connected to the strait from the stations of 4, 6, 7 and 18 probably resulting in an increase in the concentration of PCB at those stations. Although all PCB congeners were observed in most of the sediment samples, PCB congeners no. 81, 126, 169 (non-ortho PCB) were not detected in the samples from stations at the strait entrance (1, 2, 3, 12 and 13). Those sites are far from major sewage outfalls, urban centers and industrial areas. The most abundant PCB congeners were the indicator PCB constituting 73.6-89.5 % of the total amount of PCB in all sites except site 23 (island station in Marmara Sea) which is represented 59.2 % of the total amount of the PCB (Figure 3.1). Aune et al. (1999) stated that these six congeners are environmentally very persistent and account for ca. 50 % of the commercial mixtures of PCB. The contribution of mono-ortho PCB to the total amount of PCB concentration was calculated as between 10.2 % (station 6) and 24.8 % (station 1), however the contribution of island station was found higher (39 %). The contribution of non-ortho PCB to the total PCB amount was found lowest (0.35-3.13 %) for all stations. Gardinali et al. (1996) also found lower non-ortho PCB congeners compared to other PCB congeners in coastal sediment samples.

Table 3.2 : Concentrations of PCB and WHO-TEQ_{PCB} values in mussels of the Istanbul Strait and island stations (pg g⁻¹ ww).(Sampling 2007).

Chemicals	Stations																				
	2	3	4	5	6	7	8	9	10	13	14	14a	15	16	17	18	19	20	21	22	23
PCB-28	199	44.2	93.4	123	65.2	141	108	169	229	93.4	66.3	147	111	61.5	155	239	144	409	183	220	257
PCB-52	161	43.2	114	122	152	153	107	152	271	72.4	105	125	98.2	56.5	108	201	140	248	216	214	3157
PCB-101	253	85.5	260	263	784	276	181	315	558	127	356	203	189	120	185	301	321	356	390	345	8566
PCB-138	284	198	304	394	1041	298	219	334	531	144	376	208	195	170	187	269	384	347	346	305	4849
PCB-153	570	418	652	871	2144	622	448	678	1113	303	672	485	414	381	389	547	796	751	736	632	5940
PCB-180	170	27.7	48.7	138	147	57.4	51.3	86.7	146	31.8	51.2	37.2	55.3	41.4	59.8	105	108	124	74.8	40.1	222
Σindicator PCB	1637	815	1472	1911	4333	1547	1114	1735	2848	772	1627	1205	1063	830	1084	1662	1893	2235	1946	1756	22991
PCB-77	20.6	7.30	21.1	19.7	17.1	25.3	18.7	19.7	33.9	16.1	13.7	23.2	17.5	10.4	17.8	27.8	25.7	36.8	28.7	29.7	50.2
PCB-81	2.40	1.40	2.80	2.60	3.10	3.90	2.40	2.6	2.4	2.90	2.20	3.40	1.80	2.30	2.20	3.50	4.00	2.70	1.60	2.10	6.40
PCB-126	2.50	1.20	2.20	4.1	2.80	2.60	1.80	2.1	3.00	3.00	3.70	4.30	1.90	1.70	2.50	2.70	3.10	2.80	2.40	2.80	4.50
PCB-169	nd	nd	nd	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.30	nd	nd	nd	nd	nd	nd	nd
Σ non-ortho PCB	25.5	9.90	26.1	27.7	23.0	31.8	22.9	24.4	39.3	22.0	19.6	30.9	21.2	15.7	22.5	34.0	32.8	42.3	32.7	34.6	61.1
PCB-105	74.6	44.9	76.1	110	174	96.5	69.4	97.2	197	65.4	157	97.1	61.1	47.6	80.3	98	118	141	122	130	3245
PCB-114	7.40	4.00	6.00	9.4	21.4	7.3	5.20	8.00	16.0	5.10	12.3	7.40	5.4	3.90	6.30	7.40	10.2	10.2	9.00	10.4	205
PCB-118	205	119	216	296	601	274	184	279	489	139	408	221	166	130	169	264	288	343	345	350	8020
PCB-123	3.70	3.2	4.20	5.9	12.9	7.00	3.60	6.40	9.30	3.40	7.30	3.70	3.4	3.50	4.20	5.30	5.80	6.90	7.00	7.30	137
PCB-156	36.7	13.2	23.2	47.1	108	31.7	23.9	36.6	65.3	15.5	49.8	24.2	19.6	16.4	22.6	28.8	44.2	39.8	34.1	31.5	746
PCB-157	7.30	5.00	6.70	12.8	26.2	8.20	6.60	9.4	15.0	4.40	13.4	6.60	6.6	4.80	6.20	8.30	10.3	10.1	7.50	9.20	196
PCB-167	15.3	11.1	17.8	36.4	89.2	22.2	16.3	26.1	40.7	10.7	30.3	16.7	13.2	12.7	14.8	17.9	29.1	29.6	25.1	23.7	366
PCB-189	4.00	1.30	2.8	5.2	10.9	3.30	2.70	3.10	6.20	1.8	1.90	4.00	2.20	2.70	3.10	3.40	5.70	5.00	2.80	2.20	15.4
Σmono-ortho PCB	354	202	353	523	1044	450	312	466	839	245	680	381	278	222	307	433	511	586	553	564	12930
ΣPCB	2017	1026	1851	2462	5400	2029	1449	2225	3726	1039	2326	1617	1361	1068	1413	2129	2437	2863	2531	2355	35983
ΣWHO-TEQ_{PCB}	0.26	0.13	0.23	0.47	0.31	0.28	0.19	0.23	0.33	0.31	0.39	0.45	0.20	0.22	0.26	0.29	0.33	0.30	0.26	0.30	0.85

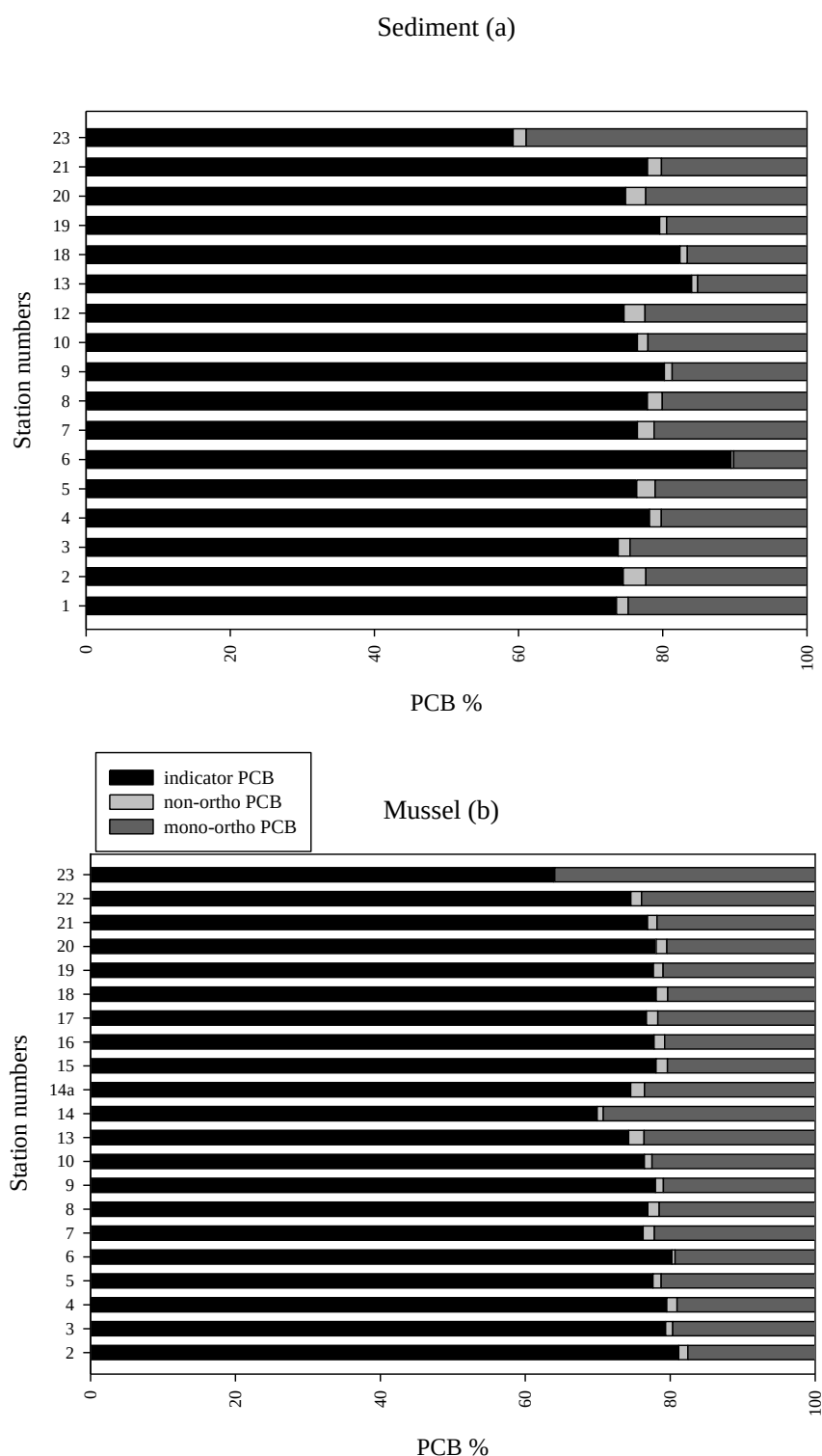


Figure 3.1 : Indicator, non-ortho and mono-ortho PCB in the sediments (a) and in the mussels (b) sampled from the Istanbul Strait and island stations.

The concentration levels of total PCDD/Fs in sediments ranged from 2.04 to 60.5 pg g^{-1} dw (Table 3.3). The highest values were measured at stations of 6, 18 and 8. The PCDD:PCDF ratio show that PCDD is dominant in all sediment samples; it was found between 75.5 and 97.6 % of the total amount of PCDD/Fs (Table 3.3). The

PCDD/F distribution in sediment was characterized mainly by 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF. These four compounds together account from 81.3 to 100 % of the 17 toxic compounds. It is known that the OCDD isomer is present in high proportions in sewage sludge (Baker and Hites, 2000) and is produced in combustion by-products of fuel oil mixtures (Hellou and Payne, 1993). The other congeners were not significantly present in the sediment samples. 2,3,7,8-TCDD, the most toxic compound of the dioxin group, is a very minor component with a contribution of less than 0.75 % to the total PCDD/F.

Table 3.3 : Concentrations of PCDD, PCDF and WHO-TEQ_{PCDD/F} values in coastal sediments (pg g⁻¹ dw) and mussels (pg g⁻¹ ww) of the Istanbul Strait and island station (Sampling 2007).

Chemicals	Sediments								Mussels	
	St 2	St 6	St 8	St 10	St 13	St 18	St 20	St 23	St 14a	St 23
2378-TCDD	nd	0.35	0.37	0.04	0.04	0.37	nd	nd	0.38	nd
12378-PeCDD	nd	0.94	0.65	0.09	0.09	0.91	nd	0.07	nd	nd
123478-HxCDD	nd	0.59	0.37	0.12	0.07	0.36	0.15	0.16	nd	nd
123678-HxCDD	nd	1.18	0.65	0.09	0.11	0.53	nd	0.07	nd	nd
123789-HxCDD	nd	1.57	1.20	0.06	0.21	1.57	0.06	0.08	nd	nd
1234678-HpCDD	0.66	8.79	5.83	0.63	0.87	7.14	0.31	0.60	0.46	0.38
OCDD	2.61	41.7	37.0	3.37	7.61	49.7	1.52	7.16	3.40	0.60
Σ PCDD	3.27	55.1	46.1	4.40	9.00	60.5	2.04	8.14	4.24	0.98
2378-TCDF	nd	2.04	0.20	0.10	nd	0.22	nd	nd	0.74	0.69
12378-PeCDF	nd	0.69	0.16	0.07	nd	0.11	nd	nd	0.18	nd
23478-PeCDF	nd	1.88	0.30	0.16	0.02	0.18	nd	nd	0.35	0.20
123478-HxCDF	nd	1.73	0.19	0.13	0.04	0.09	nd	0.02	nd	nd
123678-HxCDF	nd	0.75	0.22	0.13	0.04	0.14	nd	0.02	nd	nd
123789-HxCDF	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
234678-HxCDF	nd	0.59	0.25	0.08	0.02	0.10	nd	nd	nd	nd
1234678-HpCDF	0.08	2.59	0.82	0.45	0.14	0.67	0.07	0.07	0.20	0.12
1234789-HpCDF	nd	0.49	nd	nd	nd	0.10	nd	nd	nd	nd
OCDF	nd	2.75	0.82	0.31	0.10	0.79	0.10	0.06	nd	nd
Σ PCDF	0.08	13.5	2.96	1.43	0.36	2.40	0.17	0.17	1.47	1.01
Σ PCDD/F	3.35	68.6	49.0	5.83	9.36	62.9	2.21	8.31	5.71	1.99
Σ WHO-TEQ_{PCDD/F}	0.01	2.85	1.50	0.26	0.20	1.73	0.03	0.11	0.57	1.50

WHO-TEQ values calculated for eight sediment samples using TEF proposed by WHO for dl-PCB and PCDD/Fs ranged from 0.00 to 15 pg TEQ g⁻¹ dw and from 0.01 to 2.85 pg TEQ g⁻¹ dw respectively (Table 3.3). The total WHO-TEQ (TEQ_{PCB} + TEQ_{PCDD/F}) values ranged between 0.01 and 17.9 pg TEQ g⁻¹ dw. Therefore, a safe sediment value of 20 pg TEQ g⁻¹ dw (Evers et al.,1996) was not exceeded for any of sediment samples analyzed. 1,2,3,7,8-PeCDD in terms of total WHO-TEQ was the highest. Although the concentrations of PCB 105 and PCB 118 were high, WHO-TEQ values (TEQ_{PCB105} + TEQ_{PCB118}) were low; the contribution was highest at station 6 (4.5 % of the total WHO-TEQ value). In contrast, the WHO-TEQ of PCB

126 contributed higher, due to its high toxic equivalency factor (Van den Berg et al., 1998). The contribution of PCB 126 to the total WHO-TEQ value was found 29 %, 43 and 71 % at stations of 23, 20 and 6 respectively. Generally, TEQ_{PCDF} values were higher than those of TEQ_{PCDD} in sediment samples.

The results of the individual PCB congeners in mussel samples are given in Table 2 in a pg g^{-1} wet weight (ww). PCB levels in mussels were high, not only in stations close to urban centers such as stations of 6 and 10, but also at stations situated on the coastline of less urbanized areas such as stations 2 and 13 suggesting that it may be due to non-sewage related inputs. Among the stations, surprisingly, the highest total PCB concentration in mussels was detected in the mussels collected from the island station (23). This site is a sandy beach away from the industrial and urbanized areas. The higher levels of PCB may be due to the wastewater outfalls of the Istanbul city and/or due to the high number of ships, which use the area for mooring. The general circulation pattern as well as stratification and upwelling may probably be effective in the area for the transportation of those pollutants from several sources. PCB concentrations in mussels ranged from 1026 to 35983 pg g^{-1} ww. Higher values were observed at stations of 6 and 10 and the lowest were at the entrance part of the strait (station 3). The most abundant PCB congeners in mussels were the indicator PCB constituting 63.9-81.2 % of the total amount of PCB in all sites. The lowest percentile for the indicator PCB was found for the island mussels as was in sediments (Figure 3.1b). The PCB pattern found in mussels showed a predominance of PCB-153 followed by PCB-138 and PCB-101 for indicator PCB. PCB-77 was dominant for non-ortho PCB, whereas PCB-118 and PCB-105 exhibited higher values for mono-ortho PCB. In general, both sediment and mussels exhibited a predominance of the same PCB congeners suggesting a homogeneous situation throughout the strait. The predominance of hexachlorinated PCB in mussels, especially PCB-153 and PCB-138, has been reported by several authors for different coastal areas in the western Mediterranean (Porte and Albaige's, 1993) and in the Adriatic Sea (Bayarri et al., 2001; Piersanti et al., 2006). PCB 153 was also predominant congener in fish species from the Mediterranean (Ferreira et al., 2004; Storelli et al., 2007) and in fish from other seas (Coelhan et al., 2006; Yang et al., 2006). PCB 153 has chlorines at 2-4 or 5 positions in one or both ring. This property seems to be responsible of the persistency and bioaccumulative properties (Bright et

al.,1995). It was also reported that the uptake by particulate matter in sea water is the most important for PCB 153 with up to 90 % of the total concentration being on particles and, calculated mass budgets for several organochlorine chemicals showed that PCB 153 is controlled predominantly by the local sources (Llyina, 2006).

The concentration of PCB were found much higher in mussels compared to that of the sediments due to the fact that the mussels are filter feeders and have the ability to bioconcentrate pollutants in their tissues at very high levels. In Figure 3.2, PCB concentrations measured in the sediments are plotted against those measured in the mussels. It is seen that a strong positive correlation exists between the levels of PCB in the sediments and in the mussels. The larger the PCB concentration in mussels, the larger its concentration in sediments. Except two stations (6 and 23), all the data collected from various sites can be represented by a single regression line. The deviations of the PCB data taken from those stations were expected since those sites the most polluted sites with the highest sediment (station 6) and mussel (station 23) PCB concentrations among the stations.

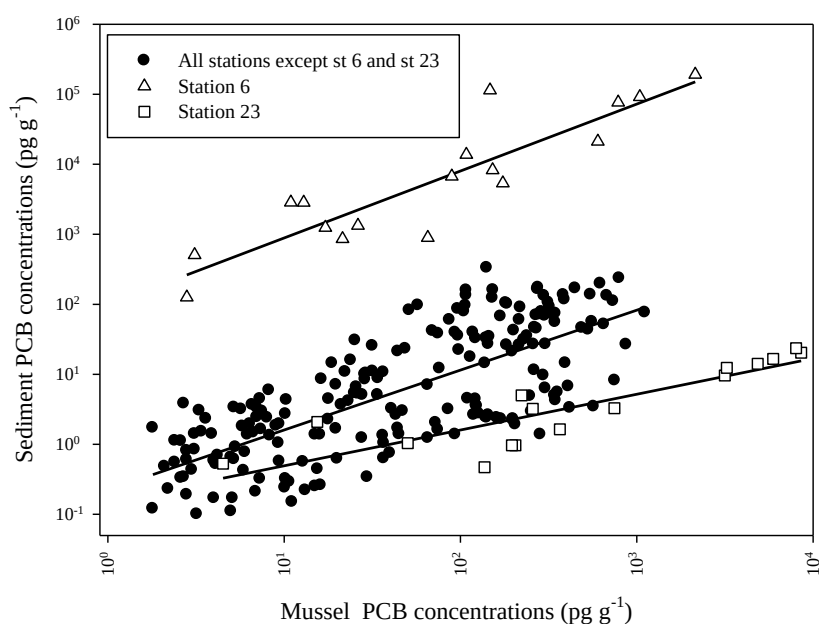
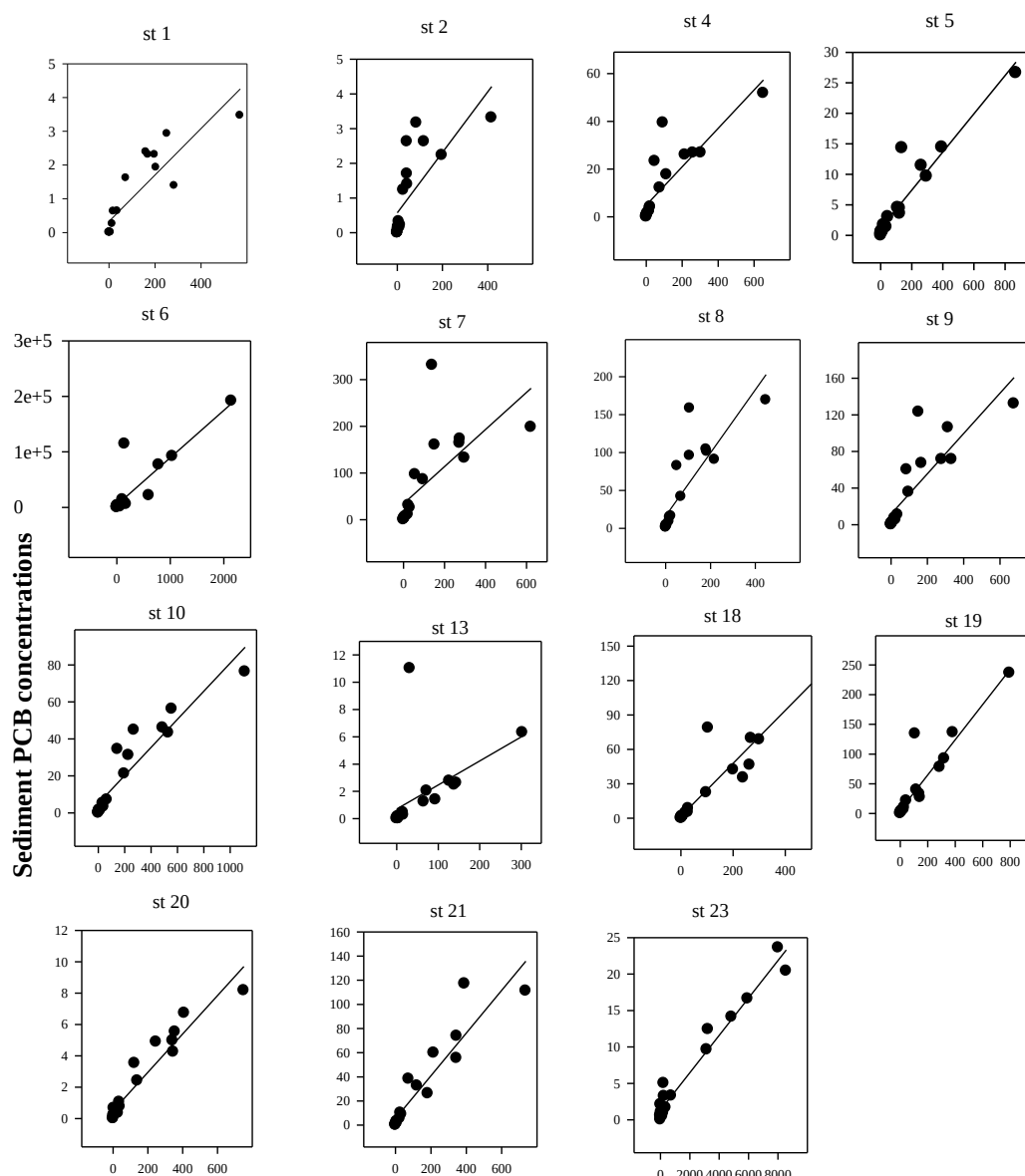


Figure 3.2 : Correlation between the sediment and mussel PCB concentrations.



Mussel PCB concentrations

Figure 3.3 : The correlation between the mussel and sediment PCB concentrations for each station.

One of the most important pollution sources of Istanbul Strait is the surface currents from the Black Sea. As is well known, the north-western part of the Black Sea receives a number of land-based sources of pollution (i.e. the Danube, Dniepr and Dniestr rivers) and the Danube River is an important source of organochlorine substances, as it flows through several regions with intensive agriculture and industrial activities (Veningerova et al., 1996). Previous studies showed that the Danube River estuary contains $4.3\text{--}57.4 \text{ pg L}^{-1}$ of PCB in the particulate matter and $77.7\text{--}102 \text{ pg L}^{-1}$ of PCB in dissolved phase showing the relevance of the river to the

transport of PCB into the Black Sea waters (Maldonado and Bayona, 2002). Those values reported for the Black Sea are higher compared to the reported data from the other regions, for example PCB values for the particulate and dissolved phase were found in the Mediterranean Sea to be 28-63 pg L^{-1} and 1.7-16.6 pg L^{-1} respectively (Dachs et al., 1997).

The highest PCDD/F congeners in mussels sampled from two stations were OCDD for PCDDs and 1,2,3,4,6,7,8-HpCDF for PCDFs. The most toxic 2,3,7,8-TCDD was consistently low (0.38 pg g^{-1} for station 14a) and 1,2,3,7,8-PeCDD was not detected at both stations.

In general, the PCB levels found in sediments and mussels are higher than the levels of PCDD/Fs. This is probably due to the fact that besides thermal formation, significant amounts of PCB were and still are released via diffuse emissions from industrial products (CHEMICALS, 2002).

The TEQ values measured in mussel tissues (0.98-1.01 pg g^{-1}) were below the maximum limits of 4 $\text{pg WHO-PCDD/F- TEQ g}^{-1}$ ww and 8 $\text{pg WHO-PCDD/F- PCB-TEQ g}^{-1}$ ww (Figure 3.4) set by the European Community for seafood intended for human consumption (EU, 2006).

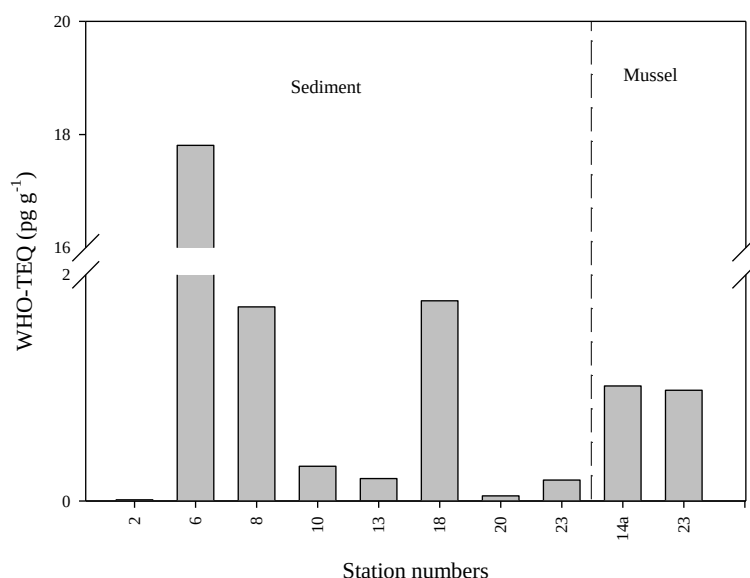


Figure 3.4 : Total WHO-TEQ values for sediment (pg g^{-1} dw) and mussel samples (pg g^{-1} ww).

PCB and PCDD/F concentrations in various environmental matrices have been reported for different aquatic systems although the comparison of data is not always easy due to the different modes of expression. For example, the data in the literature may be given as individual component concentrations or sum of different congeners. In case of mussels, several expressions are used such as fresh weight basis, fat basis or dry mass basis etc. A recent monitoring study showed that the PCB levels in the sediments of Istanbul Strait (except station 6) is comparable with those found in the Mediterranean (Gomez-Gutierrez et al., 2007). In the same study, PCB ranges in sediments were given as 1-16,916 ng g⁻¹ dw for harbours; 0.9-5600 ng g⁻¹ for coastal lagoons; 0.4-15,815 ng g⁻¹ for urban influenced regions; 0.5-1500 ng g⁻¹ for river influenced regions; 0.05-1200 ng g⁻¹ for the continental shelf and 0.3-48 for open sea (depth > 1000 m). Perugini et al (2004) detected total PCB levels (sum of congeners 28, 52, 101, 118, 138, 153, 180) in Mediterranean mussel as between 3430 and 9810 pg g⁻¹ ww. PCDD/F concentrations in surface sediments and mussels were 0.150-1.6 ng⁻¹ dw and 13-21 pg g⁻¹ dw respectively in a Mediterranean coastal lagoon (Maldonado and Bayona, 2002). Our PCB results are lower than those reported in the earlier studies in the Marmara Sea. Telli-Karakoç et al (2002) analyzed mussels from the Izmit Bay (Marmara Sea) which is one of the most industrialized and populated region of Turkey and the samples were found to contain PCB between 4688 and 28,068 ng kg⁻¹.

Soil sample from the island station were also analyzed for PCB to find out the source of high PCB concentration on mussel in the first sampling campaign. High PCB concentrations on the soil sample indicate that the source is land based and carried by runoff. Personal observation by the author reveals that scrap collectors in the area could be the PCB source in the soil samples.

3.1.2 OCP

Concentrations of various organochlorines in sediments (Sampling 1) are summarized in Table 3.4. HCH and DDT related compounds together contribute for 46-78 % at the stations situated closer to the Black Sea entrance in both parts of the strait (1,2,3 and 12,13) and for 80-96 % at the other stations including the island stations (Figure 3.5a). β -HCH, 4,4'-DDD, 2,4'-DDD and 4,4'-DDE were the four major pollutants detected; together they accounted for 69.4 % (average) of the total

pesticide concentration in the sediments. Heptachlor, t-HE, aldrin in all and OCS, OXC, endrin, (END)-I, mirex in most sediment samples were undetectable.

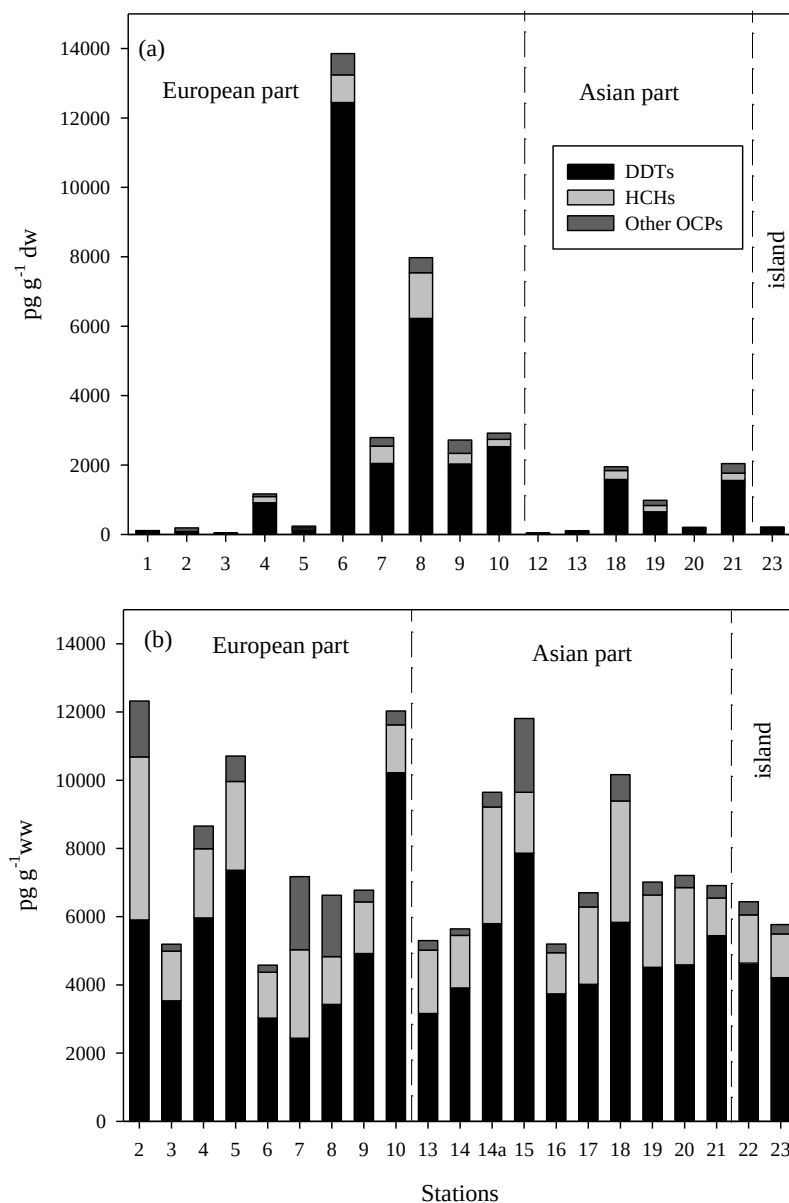


Figure 3.5 : The total concentration profiles of OCP at different sampling locations in the Istanbul strait a) sediments b) mussels.

HCH concentrations (the sum of α , β , γ , δ and ϵ isomers) in sediments were found to be in the range of 6–1317 pg g^{-1} dw (Table 3.4). These values were lower than those in samples collected from Black Sea coast (Samsun) of Turkey (Bakan and Ariman 2004) and from Asian countries (Fung et al. 2005; Doong et al. 2002; Hong et al. 1995; Hong et al. 2006).

Table 3.4 : Concentration (pg g^{-1}) of OCP in sediments from the Istanbul strait and from island station in the Marmara Sea (Sampling 2007).

Chemicals	Stations																
	1	2	3	4	5	6	7	8	9	10	12	13	18	19	20	21	23
α-HCH	2.16	2.53	nd	32.2	1.74	70.6	147	358	78.3	23.0	0.55	1.30	33.6	9.32	1.68	25.8	3.80
β-HCH	38.3	30.9	4.70	138	56.0	316	298	817	182	174	11.5	20.3	208	165	30.3	166	20.0
γ-HCH	1.93	1.92	1.31	7.94	3.32	395	22.8	87.4	31.3	9.56	0.78	2.97	7.38	6.30	3.68	12.5	2.01
δ-HCH	0.38	0.56	nd	2.88	0.52	13.3	23.9	38.8	12.0	5.46	0.23	0.29	6.71	1.73	0.79	5.90	0.75
ϵ-HCH	nd	nd	nd	0.64	nd	4.94	7.67	14.9	3.26	1.69	nd	nd	2.18	nd	nd	1.47	0.63
PeCB	1.39	76.3	1.16	11.7	2.57	80.9	36.5	30.0	73.4	10.6	0.38	4.35	13.1	22.9	1.68	6.93	0.49
HCB	19.0	21.7	6.47	42.0	31.2	286	64.7	66.1	81.4	39.0	8.89	33.8	36.2	46.7	23.1	24.8	21.1
PCA	nd	nd	nd	0.62	nd	12.6	6.93	nd	3.33	1.37	nd	nd	1.51	nd	0.37	14.4	nd
OCS	nd	nd	nd	0.46	nd	nd	nd	nd	nd	0.45	nd	nd	nd	nd	0.20	0.46	nd
4,4'-DDT	1.31	7.99	4.39	351	5.72	482	47.6	650	116	125	2.50	3.41	92.6	20.0	19.0	338	25.3
2,4'-DDT	0.45	2.23	0.92	18.4	1.91	162	15.6	30.6	23.3	28.0	0.67	0.94	24.3	3.41	4.32	108	4.10
4,4'-DDD	19.1	12.1	5.39	270	39.3	5725	1011	3211	926	1292	2.81	9.86	674	272	56.0	436	37.9
2,4'-DDD	7.70	3.99	2.77	73.1	13.7	4389	285	1122	268	336	0.94	3.04	205	72.0	15.6	167	10.3
4,4'-DDE	13.3	24.4	12.2	195	66.1	1567	657	1157	658	698	8.81	21.2	569	274	36.3	483	68.9
2,4'-DDE	0.38	0.73	0.28	7.02	1.82	119	29.2	53.1	39.2	47.5	0.23	0.45	18.5	9.89	1.60	24.6	1.57
t-CHL	1.00	0.92	1.23	6.25	1.82	23.1	21.3	14.0	21.3	10.9	1.09	0.87	4.42	3.66	0.68	10.1	0.82
c-CHL	nd	0.34	nd	1.83	0.91	9.50	15.0	10.5	7.21	4.58	0.25	nd	2.54	1.93	0.35	5.38	nd
OXC	nd	nd	nd	nd	nd	nd	nd	nd	0.75	0.29	nd	nd	nd	nd	nd	nd	nd
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
c-HE	0.45	0.31	nd	0.98	0.81	2.75	2.29	2.84	17.5	1.20	0.19	0.39	0.97	2.18	0.35	1.55	0.25
t-HE	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Aldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dieldrin	1.46	1.31	0.53	5.90	6.22	115	92.9	181	98.5	86.8	0.52	0.72	39.3	22.3	1.76	31.0	2.76
Endrin	nd	nd	nd	nd	nd	53.3	nd	15.6	3.80	nd	nd	nd	1.39	nd	nd	167	nd
(END)-I	nd	nd	nd	nd	nd	nd	nd	22.2	37.0	nd	nd	nd	2.90	25.3	nd	5.01	nd
(END)-II	nd	nd	nd	3.37	3.57	nd	nd	n.n	36.5	5.06	nd	0.80	2.72	21.9	0.80	3.46	0.82
MOC	0.58	nd	0.55	1.26	nd	25.6	4.50	91.9	4.81	18.3	nd	nd	4.60	2.06	5.60	2.36	14.0
Mirex	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.60	nd	0.12	nd	nd

However, the contamination levels of total HCHs were higher than those in the marine surface sediments from Mediterranean open waters (Burns and Villeneuve 1987) and comparable with those sediments from Alexandria Harbour, (Barakat et al, 2002), Baltic Sea (Dannenberd 1996; Pikkarainen, 2007), Istanbul strait entrance (Fillmann et al. 2002), Danube delta (Fillmann et al. 2002), Meriç delta (Turkey) (Kolonkaya 2006) and Caspian Sea (de Mora et al.,2004). Although the concentrations of lindan (γ -HCH) are generally low, a high percentage of the γ -HCH is recorded at sampling location 6 (49%), indicating the use of lindane as a pesticide in the region (Figure 3.5a). Lindane contains mainly the γ -congener (>99%), α -HCH and β -HCH are by-products of γ -HCH. On the other hand, technical HCH which is also used as a pesticide contain high proportions of the α -congener (c.70%), followed by γ congener (c. 14%), β -congener (c. 9%) and δ -congener (c.6%) (Iwata et al., 1995). In Figure 3.5a, it is clearly seen that, at all stations (except station 6), β -HCH appears as the dominant isomer. The results are similar to those found in the previous investigations by Jiang et al. (2000) and Fillmann et al. (2002). One possible reason for its dominance may be the β -isomer has the lowest water solubility and the highest bioconcentration factors among the HCH isomers, and high resistance to biodegradation resulting in higher levels of this isomer in some sediment samples (Ramesh et al. 1991). A large amount of α -HCH isomer may be converted to β -HCH in the environment (Wu et al. 1997). α -HCH/ γ -HCH ratios of 4.0 – 7.0 and zero suggest the presence of industrial HCHs and lindane, respectively (Iwata et al. 1995). The ratio between the α - and γ -isomers was lower for most of the sediments along the strait coastline (i.e., between 0.0- 4.0). These low values confirm the agricultural use of lindane in the region. On the other hand, relatively high values (4.1 - 6.4) found at stations of 4, 7, 8 and 18 suggest that HCH contamination at some locations arises through use of both formulations. On the other hand, the ratio of α -HCH / β -HCH is much lower than that of technical HCH, which reflects that the technical HCH contamination was mainly due to historical usage.

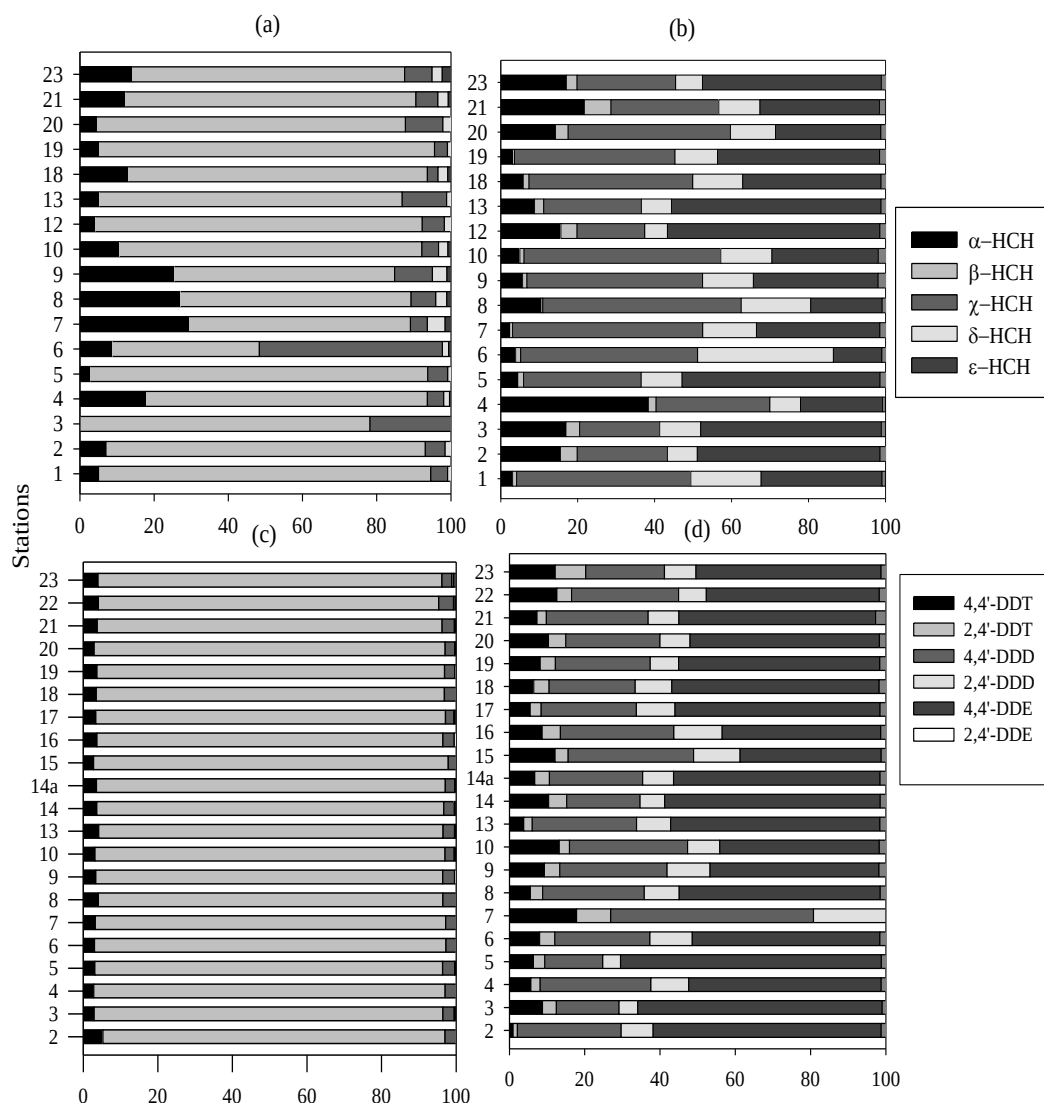


Figure 3.6 : Congener ratio of HCH and DDT components from the Istanbul strait: a)HCH congeners in sediments b) DDT congeners in sediments c) HCH congeners in mussels d) DDT congeners in mussels (Sampling 2007).

T-DDT concentrations in sediments were found to be in the range of 16-12443 pg g^{-1} dry wt (Table 3.4). The highest concentrations of T-DDT in sediments were found in the samples taken from the stations of 6 and 8 (Figure 3.6b). The sediments from stations of 4, 7, 9, 10, 18 and 21 were also found to contain relatively high concentrations. Some of those locations (4, 6, 7 and 18) are influenced by discharges from the small freshwater tributaries. Comparatively low concentrations of T-DDT were found in proximity to the Black Sea (1,2, 3, 12,13).

Concentrations of DDT and related compounds in sediments from the Istanbul Strait are shown to be higher than those reported for the Mediterranean (Burns and

Villeneuve 1987; Tolosa et al., 1995), Baltic Sea (Pikkarainen, 2007) and Caspian Sea (Russian Federation) (de Mora et al. 2004). They are generally lower than those measured in most Asian sites (Fung et al. 2005; Hong et al. 1995; Hong et al. 2006), Danube coastline in the Black Sea (Fillmann et al. 2002), Saronikos Gulf (Galanopoulou et al., 2005) while comparable, than those reported for the Black Sea – Istanbul strait entrance (Fillmann et al. 2002). On the other hand, Fowler (1990) reported that DDT concentrations in near-shore surface sediments worldwide ranged between <0.1 and $44 \text{ ng g}^{-1}\text{dw}$. This means that the contamination of DDTs in sediments from İstanbul Strait is low as compared to the other areas. DDT can be biodegraded to DDE and DDD which are not present in technical DDT, thus, the relative concentration of the parent DDT compound and its metabolites, DDD and DDE, can be used for assessing possible pollution sources. $(\text{DDE} + \text{DDD})/\text{DDT} > 0.5$ is indicative of DDT being subjected to a long-term weathering (Hites and Day, 1992). Figure 3b shows the relative composition of the DDT and related compounds in the sediments. In this study, DDT compositional ratios $(\text{DDE} + \text{DDD})/\text{DDT}$ throughout the Strait show large variations between stations (1.5-31). The values are generally higher (13-27) in the inner part of the strait and lower (4-8) along the coastline adjacent to the Black Sea and Marmara Sea (except station 1). The ratio was found also lower (4) in the island station. Of the DDT related compounds, 4,4'-DDD and 4,4'-DDE, which are more stable and persistent than their parent compound, together accounted for a majority (51–84%) of the total DDTs recorded in all sediment samples. The percentages were found relatively lower for stations 4 (51%) and 6 (59%) in the strait and at the island station 21 (59%). Overall, those results suggest that the DDTs in the studied surface sediments are generally weathered DDTs used in the past and redistributed between water and sediment in the upstream sites of the strait, which were previously dominated by agriculture. Concentrations of DDD were comparatively higher than those of DDE in most sediment samples collected in this study. This finding agree with most of the previous studies (for example Barakat et al., 2002; Hong et al., 2006), and does not agree with the results reported by Zhang et al. (2003) and Fung et al. (2005). The reason for the dominance of DDDs or DDEs is strongly related to the sediment conditions. The higher amount of DDDs compared to the amount of DDEs in sediments indicates reductive dechlorination of DDTs to DDDs under anaerobic conditions (ATSDR, 2002). The results obtained for the Strait is in agreement with

this fact that the levels of DDDs were higher in the inner part of the Strait, especially in the semi-closed bays through the strait with restricted water exchange compared to the sediment DDD levels at the entrance of the Strait.

Several other organochlorinated pesticides were measured in the sediment samples from the Istanbul strait, and the distribution ranges are presented in Table 3.4. The concentrations of other pesticides were not high as found for the DDTs and HCHs, and were generally not of concern (Figure 3.6). Concentrations of HCB were 7-286 $\mu\text{g g}^{-1}$ dry weight, and these two extreme values were recorded at stations of 3 and 6, respectively. Those values are lower than the concentrations reported for different coastal sediments of the world varying between <0.2 and 39 ng g^{-1} dry weight (Tolosa et al.1995; Loganathan et al. 2001; Fillmann et al. 2002; de Mora et al. 2004). HCB is not only used as fungicide but also released into the environment as a byproduct of industrial processes and is formed by combustion (Van-Birgelen 1998). Relatively elevated concentrations of HCB were also observed at stations 7, 8 and 9. CHL, HE and dieldrin were notably higher in concentration at stations 6,7,8, 9 and 21 than other stations. CHL values in this study are lower than reported for Meriç estuary (Turkey) (Kolonkaya 2006), Asian countries (Fung et al. 2005; Hong et al. 1995; Hong et al. 2006), and Caspian Sea (de Mora et al. 2004). PeCB concentrations were higher among the all measured OCP at stations of 2 and 6. The production and use of pentachlorobenzene has ceased over the last decades, but it cannot be excluded that PeCB is produced and used elsewhere or a product of reductive dehalogenation of HCB under anaerobic conditions. Pentachlorobenzene is very toxic to aquatic organisms and unintentional release of pentachlorobenzene as a by-product of incomplete combustion appears to be the most important source in the environment (Draft Risk Profile, 2007). Concentrations of endrin ($\text{nd-}167 \text{ pg g}^{-1}$) varied considerably among locations. The maximum concentration was measured at station 21. Concentrations of END (sum of I and II isomers) ranged from $\text{nd-}73.5 \text{ pg g}^{-1}$ and the highest concentrations were recorded in the samples from stations 9,19 and 8. Those values recorded in this study for endrin and END are much higher compared to the reported value for the Caspian Sea (de Mora et al. 2004) but much lower than the concentration measured in Meriç estuary sediments (Kolonkaya, 2006) and in the sediments sampled from Pearl River delta (Fung et al. 2005).

Maximum concentrations of DDTs and HCHs were recorded in sediments from stations 6 and 8 respectively. In addition, levels of OC pesticide contamination (sum of concentrations of all pesticide contaminants except HCHs and DDTs) at station 6 (609 pg g^{-1}) and 8 (434 pg g^{-1}) were the most severe compared to all the other stations. These results indicate that OCP contamination at those stations was the most serious amongst all the sampling locations. Apart from stations of 6 and 8, four other stations in the strait (7, 9, 10 and 18) locating all along the European part and island station 21 also have severe contamination by OCP. These sampling locations, therefore, may be ranked as the second most contaminated areas by OCP. Additional to that, the sediments of the European part of the strait was found more polluted by OCP than that of the sediments sampled from Asian part. Although the correlation between total organic carbon and total pesticide concentration in the studied sediments was low ($R^2 = 0.15$), the average total organic carbon contents of the European part was found slightly higher than the Asian part. The highest values were measured for stations of 4 and 8.

Sediment Quality Guidelines (SQGs) were used to identify the potential hazards on aquatic organisms. SQGs were developed from variety of empirical methods and biological effect data (Long and Morgan 1990, MacDonald 1993, Long et al., 1995). In this study, OCP and PAH results of sediment data were compared to the ERL/ERM (Effects Range Low/Effects Range Medium) values developed by the National Oceanic and Atmospheric Administration (NOAA) (Long and Morgan, 1990). ERL were calculated as lower than 10 % and ERM were 50 % of effect concentrations. When the contamination levels are higher than ERM, the sediments are predicted to be toxic.

OCP concentrations in sediments were compared with the effects range-low (ERL) and effects range-median (ERM) sediment guideline values (when available) from the US National Oceanic and Atmospheric Administration (NOAA, 1999) to assess the potential environmental risks and the results are summarized in Table 3.5. None of the OCP concentrations exceed the ERM values, while 4,4'-DDD and total DDT levels are higher than ERL limit values at stations 6,8,10 and 6,8 respectively. Thus, the results suggest that the OCP under investigation in sediments may not pose serious hazards at most of the strait stations while they may cause few risks for stations of 6, 8 and 10 in the strait ecosystem.

Table 3.5 : Comparison of the OCP sediment concentrations with the Canadian Sediment Quality Guidelines (CSQG) (Sampling 2007).

Chemicals	Concentration (pg g ⁻¹ dw)	Effects range-low (ERL) values (pg g ⁻¹ dw)	Effects range-median (ERM) values (pg g ⁻¹ dw)
4,4'-DDT	1.31-650	1190	4770
4,4'-DDD	2.81- 5725	1220	7810
4,4'-DDE	12.2-1567	2070	374000
Total-DDTs (DDT+DDD+DDE)	16.0-12443	3890	51700
CHLs (trans+cis+oxy)	0.82-36.3	2260	4790
Dieldrin	0.52-181	710	4300
Endrin	nd ¹ -167	2670	62400
HEs(trans+cis)	nd - 17.5	600	2740

The data set was analyzed with hierarchical cluster analysis (HCA) to emphasize natural grouping in the data by using KyPlot (Version 2.0 beta 15, 1997-2001, Koichi Yoshioka). A hierarchical cluster analysis of OCP distributions in sediments was carried out on the sampling stations (Figure 3.7).

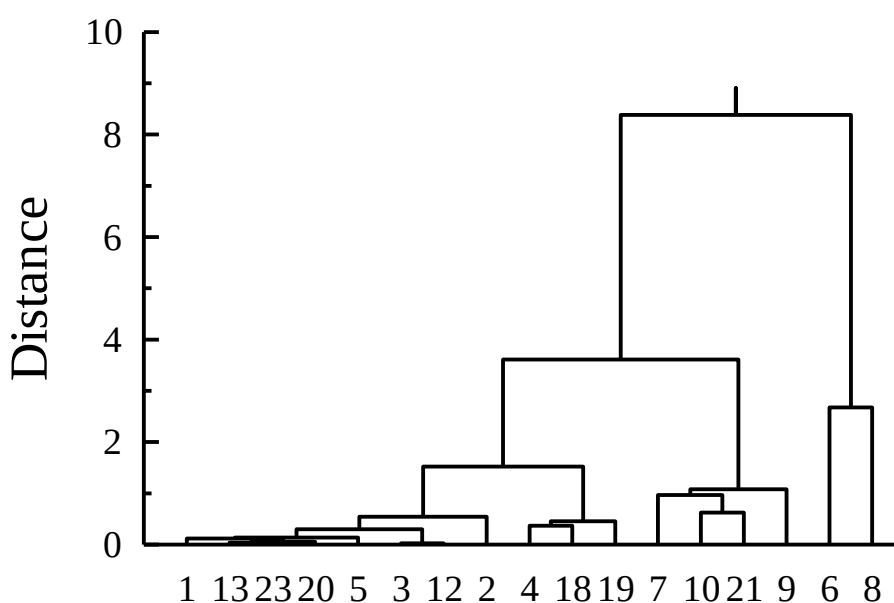


Figure 3.7 : Dendrogram of hierarchical cluster analysis for sediments on the sampling stations.

The results show the presence of various clusters. The first cluster consists of two sampling stations (stations 6 and 8). This confirms the analysis results as at those stations, we found a greater total OCP concentrations than at the other stations. Those sites are located in the inner bay and heavily polluted by the river inflow from station 6. The second cluster consists of stations 7,9,10,21 and the third of stations 4, 18, 19. This differentiation is confirmed partly by the geographical position of the sampling sites and also by OCP concentrations. Station 19 may be under the

influence of the river inflow from station 18 which are very similar both in their geographic location and their profiles, which explain their close link in the diagram. According to the other clusters distinguished, OCP assemblages at stations 1,13 and 2,12,3 are significantly linked, showing probably the hypothesis of the influence of Black Sea inflow.

Table 3.6 : Concentration (pg g⁻¹ww) of OCP in mussel from the Istanbul strait and from island station in the Marmara Sea (Sampling 2007).

	Stations																				
Chemicals	2	3	4	5	6	7	8	9	10	13	14	14a	15	16	17	18	19	20	21	22	23
α -HCH	252	42.3	56.9	81.3	40.5	83.2	56.8	50.8	44.2	77.0	56.1	120	49.3	44.4	76.3	123	77.8	66.6	41.2	57.3	51.0
β -HCH	4387	1362	1914	2427	1269	2438	1292	1409	1319	1718	1436	3200	1702	1119	2127	3324	1975	2133	1024	1290	1186
γ -HCH	142	43.5	59.5	83.8	36.8	72.5	49.4	47.7	35.0	57.0	42.5	85.9	37.7	36.4	50.6	113	59.0	57.6	36.6	56.3	33.4
δ -HCH	nd	4.07	nd	5.95	nd	nd	nd	6.31	4.02	4.79	4.15	4.77	nd	6.11	5.89	nd	4.52	4.47	2.65	6.15	6.30
ϵ -HCH	nd	3.38	nd	3.85	nd	nd	nd	nd	2.63	3.08	4.58	7.70	nd	nd	7.58	nd	2.16	4.28	2.19	3.26	8.98
PeCB	274	16.1	13.3	23.8	10.2	21.5	18.4	15.3	16.2	13.4	12.8	24.4	18.6	11.9	19.8	36.7	21.1	19.7	17.1	16.0	11.1
HCB	116	33.7	8.33	77.5	35.5	64.7	40.3	49.7	57.1	40.1	24.9	50.3	42.7	50.2	50.1	69.6	68.6	86.2	67.7	44.2	31.6
PCA	71.6	9.68	20.3	14.7	11.1	17.2	nd	9.64	10.8	7.59	nd	7.98	12.9	5.93	13.4	22.0	10.1	9.25	11.3	21.6	5.45
OCS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.70	nd	nd	nd	nd	nd	nd
4,4'-DDT	56.7	311	338	470	242	434	191	456	1355	121	408	389	955	325	221	378	369	476	399	585	512
2,4'-DDT	68.8	131	150	220	122	222	112	202	274	71.4	187	225	272	181	118	236	183	210	135	180	342
4,4'-DDD	1629	587	1754	1134	765	1313	925	1401	3207	876	763	1438	2619	1127	1016	1335	1138	1148	1472	1320	880
2,4'-DDD	501	176	597	348	341	468	319	562	874	285	255	475	972	479	412	566	339	366	443	343	354
4,4'-DDE	3577	2294	3049	5100	1507	nd	1831	2207	4332	1759	2240	3178	2945	1575	2188	3214	2413	2309	2843	2131	2069
2,4'-DDE	72.3	34.4	72.9	87.8	47.7	nd	51.4	88.8	178	49.1	57.3	89.3	96.7	50.3	60.8	103	73.7	76.8	149	79.6	53.4
t-CHL	33.7	10.9	26.0	29.1	11.6	nd	23.7	29.5	31.3	24.5	15.1	24.4	29.0	12.0	30.6	26.3	26.1	22.3	24.7	28.1	19.0
c-CHL	26.7	11.2	19.1	16.9	13.8	nd	29.5	35.5	19.5	21.2	19.2	82.3	32.0	13.1	51.4	37.4	24.5	25.6	25.8	22.3	16.4
OXC	28.0	nd	10.4	7.71	4.31	9.36	3.08	7.75	5.71	6.35	5.87	15.9	7.47	5.21	7.21	17.8	7.72	8.69	7.60	7.74	4.74
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.64
c-HE	76.4	17.7	30.7	41.6	18.7	40.7	25.3	23.7	21.9	32.6	22.2	51.6	27.8	16.2	29.5	62.6	37.8	34.4	18.7	28.7	18.1
t-HE	nd	nd	nd	271	nd	nd	165	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Aldrin	nd	nd	nd	17.3	nd	130	42.5	nd	6.55	19.2	nd	nd	8.92	nd	2.88	nd	nd	nd	nd	nd	nd
Dieldrin	217	69.7	98.4	172	66.8	126	90.0	92.6	161	95.3	73.4	147	386	55.4	119	254	127	114	101	107	83.1
Endrin	nd	nd	nd	nd	8.46	nd	nd	10.7	10.6	nd	4.18	7.69	50.3	46.4	11.0	nd	6.14	6.00	8.36	8.44	10.2
(END)-I	444	20.3	303	40.4	14.1	657	81.7	38.0	39.2	14.5	nd	12.1	32.4	18.6	52.9	84.0	29.7	17.7	53.0	75.1	50.0
(END)-II	179	13.9	87.1	23.6	nd	nd	42.3	25.6	21.1	nd	3.86	7.75	21.6	16.5	18.6	nd	16.3	6.28	21.6	24.5	18.1
MOC	167	nd	46.0	2.56	8.15	1081	570	3.80	1.36	2.38	1.51	nd	632	nd	4.91	162	1.09	0.81	1.12	nd	2.14
Mirex	4.66	2.99	nd	8.46	3.62	nd	669	4.36	3.35	2.16	4.63	3.70	862	3.24	3.61	nd	4.67	2.77	5.38	2.62	2.39
Total OCP	12324	5195	8654	10708	4577	7178	6628	6777	12031	5301	5641	9648	11812	5198	6701	10164	7015	7205	6911	6438	5770

Table 3.6 shows the OCP concentrations in the mussels collected from the Istanbul strait and from the island in the Marmara Sea (Stations 22 and 23). Bivalves have been widely accepted and used as organisms to monitor the concentration of pollutants in coastal marine environments (Chase, 2001; Khaled et al., 2004; Wang et al., 2007). Several kind of species such as oysters, mussels and clams have been used as bioindicator organisms in the national and international programs of “Mussel Watch” to monitor pollution resulting from POP and heavy metals. Mussels are suggested as the most suitable organisms used for bioaccumulation studies because mussels might have implications for human exposure and marketed immediately following collection and without depuration. Most OCP investigated were observed in mussels from the Istanbul Strait and island stations. Concentrations of OCP were in the range of 5195-12322 pg g^{-1} ww. The residual levels of OCP in mussels on wet weight basis were dominated by DDTs and HCHs similar to the results obtained for sediments (Table 3.6 and Figure 3.6c). The mean composition of DDTs, HCHs, and other OCP in mussels were 65%, 27% and 8%, respectively (Figure 3.6d). The maximum level of OCP was observed in mussels collected from station 1. The highest concentration of OCP in mussels from station 1 could attribute to surrounding agricultural fields.

Total HCHs in mussels were in the range of 1106-4781 pg g^{-1} , with a mean value of 2046 pg g^{-1} (Table 3.6). Isomers of α -, β -, γ -, δ - and ϵ -HCH were observed to contribute 3.60%, 93%, 2.88%, 0.16% and 0.13%, respectively (Figure 3.6c). The highest concentration for total HCHs was observed at station 1, followed by 18 and 14a. The β -HCH (the most toxicological active HCH isomer) was the predominant isomer in HCHs for all mussel samples similar to the results obtained by several researchers (for example Zhou et al. 2008). The γ -HCH concentrations measured in the mussels (0.03-0.09 ng g^{-1} ww) were below those recommended levels for human consumption by US EPA (2000) (3.78 ng g^{-1} ww).

Total DDTs concentrations in mussels ranged from 2436-10218 pg g^{-1} ww, with a mean value of 4975 pg g^{-1} ww (Figure 3.6c and Table 3.6). In all mussel samples analyzed, the levels of 4-4'-DDT were found to be lower than the DDT metabolite 4-4'-DDE and 4-4'-DDD (Table 3.6 and Figure 3.6d). The highest DDT concentrations were found for 4-4'-DDE followed by 4-4'-DDD and 4-4'-DDT similar to the results obtained by Perugini et al (2004) for the same species in the Central Adriatic

Sea and by Kolonkaya (2006) for fish species in the Eastern Egean Sea, Turkish coasts. As the commercial DDT mixture is principally composed of 4-4'-DDT, it can be assumed that these pesticides have not been used in agriculture after their ban. Nevertheless, 4-4'-DDT concentration in mussel tissues is not negligible at stations of 10 and 15. The concentrations of DDTs in mussels were lower than the limit of $14.4 \text{ ng g}^{-1} \text{ ww}$ for human consumption recommended by US EPA (2000).

Total other OCP concentrations in mussels ranged from $188\text{-}2163 \text{ pg g}^{-1} \text{ ww}$ and dieldrin was dominant among other OCP with the range of $55\text{-}254 \text{ pg g}^{-1} \text{ ww}$ (Table 3.6). Higher OCP values were measured in mussels compared to the sediments (Figures 3.6a and 3.6b). With regard to the spatial influence, differently from sediments, the mussel concentrations did not show big variations among the sampling locations (Figure 3.6b). The reason for that may be the difference in the accumulation and release processes of pollutants in the sediments and in the mussels as well as the environmental factors. Characteristics of sediments such as texture and organic carbon content may play an important role to control the deposition and leaching process in sediments. The OCP compounds accumulated in sediments may be released and removed by air and water movements and may result in lower concentrations in sediments, however, the uptake of a compound by the mussels depends on its partition in the dissolved and particulate phases. Thus, the tissue concentrations show the bioavailable fractions of those phases. For example Richardson et al., (2005) showed that HCH and dieldrin were bioaccumulated primarily from the dissolved phase and DDT from the particulate phase and the depuration rates of some OCP such as DDT from mussels are slow. On the other hand, tissue concentrations are governed by both passive and active processes. Active processes are affected by various environmental factors (such as pH, salinity) which may fluctuate considerably in coastal and enclosed monitoring sites.

The difference between the sediment and mussel OCP concentrations is the biggest at the Black Sea entrance. Aldrin and mirex were not detected in most of the sediment samples, in contrast, both were measured in mussel tissues. Maximum aldrin and mirex concentrations were $130 \text{ pg g}^{-1} \text{ ww}$ at station 7 and $862 \text{ pg g}^{-1} \text{ ww}$ at station 15 respectively. Those concentrations of mirex found in mussels is several orders of magnitude lower than the recommended limit of $0.1 \text{ } \mu\text{g g}^{-1} \text{ ww}$ for mirex in fish in the U.S.A. (U.S. Food and Drug Administration 1995). On the other hand,

similar to the results obtained from sediments, heptachlor was also not detected in mussel samples. Chlordane and metabolites were detected in mussel samples. Technical chlordane constituents cis and trans-nonachlor and cis-chlordane metabolites oxychlordane. Oxychlordane levels among the chlordanes were found lowest at most stations. Chlordane was directly applied to soil or foliage to control a variety of pests. Artificial pollution source of chlordane may enter the atmosphere through volatilization from plants, soil or water. Concentrations of chlordanes in mussels do not indicate a strong spatial variation in the Istanbul Strait coastal waters. The highest concentration of HCB measured in mussels was $0.12 \text{ ng g}^{-1} \text{ ww}$, which is below the US EPA Screening Criteria of $3.07 \text{ ng g}^{-1} \text{ ww}$ (US EPA 2000).

The comparison of the results obtained for mussels in different locations of the world is somewhat difficult because different bivalve species may be used in those studies and results from those are expressed in different ways such as dry weight, fat weight basis etc. However, in general, the residuals of total HCHs and DDTs as well as other OCP in this study are relatively lower than those measured in bivalve mollusks from many sites in other Asian countries (Sarkar et al. 2008; Zhou et al. 2008) except Korea (Khim et al. 2000) and Thailand (Siriwong et al. 1991). DDT results obtained in this study are also lower than those obtained for the *Mytilus* sp. collected from NW Mediterranean (Villeneuve et al. 1999), USA (Sericano et al. 1995; O'Connor and Beliaeff 1995) and France (Claisse 1989) coasts. On the other hand, the results of this study are comparable with those obtained in the *Mytilus galloprovincialis* collected from Turkish Black Sea coastal area (Kurt and Özkoç 2004). In another study, total DDT and HCH concentrations in the mussel samples collected from Turkish coastal areas (Trabzon and Sinop, Black Sea and Istanbul, Marmara Sea) varied between 17 and $52 \text{ ng g}^{-1} \text{ ww}$ and 0.5 and 24 ng g^{-1} respectively which are higher than those measured in this study (Telli 1991).

3.2 Sampling Campaign 2009

The results from second sampling were explained in detail in the following sections. In this second part of the monitoring study, SPMD, BR sorbent, sediment and mussel samples were analyzed for PAH, PCB and OCP.

3.2.1 SPMD

3.2.1.1 PAH concentrations in SPMD

Most of the PAH compounds were accumulated by SPMD after 7 days of the deployment. The variation between the deployed duplicate SPMD was small at all stations. The total amount of PAH accumulated in SPMD increased with exposure duration (Figure 3.8).

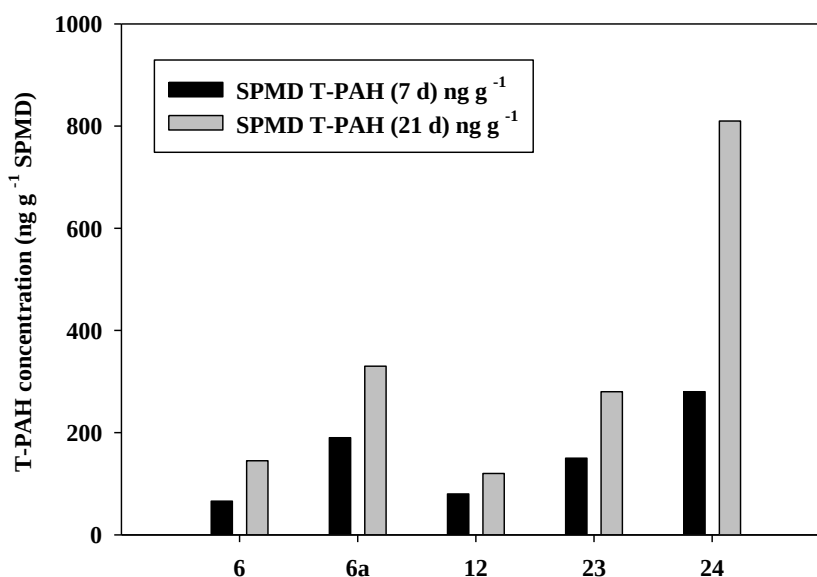


Figure 3.8 : Pollutant concentrations of T-PAH in SPMD (ng g⁻¹SPMD).

The concentrations of total PAH accumulated ranged from 66 to 280 ng g⁻¹ SPMD and from 120 to 810 ng g⁻¹ SPMD for 7 and 21 days exposures respectively (Table 3.8). Concentrations of PAH were highest in SPMD deployed to the shipyard area (site 24) compared to the concentrations measured in other stations. In most of the sites, the concentration of lower molecular weight PAH (naphthalene- pyrene) was dominant in SPMD, compared to the higher molecular weight (HMW) PAH. Only at site 24 with intense shipyard activity event, high concentrations of HMW-PAH (Benzo(a)anthracene-Benzo(ghi)perylene) were detected.

Several methods were used to identify the sources of PAH (Raoux, 1991; Budzinski et al., 1997). One of the methods to estimate the origin of PAH compounds, is to use the molecular indices (Table 3.7) based on thermodynamic stability of various isomeric compounds, e.g. phenanthrene (PHE) is more thermodynamically stable than anthracene (AN). Pyrolysis of organic matter at very high temperature generates PAH characterised by a low PHE/AN ratio (<10), while lower

temperatures cause much larger values (>25) (Soclo, 2000; Raoux, 1991). In this study PHE/AN, FA/PY, BaA/(BaA+CHR) and LMW/HMW molecular indices are used to find out the source of PAH pollution.

Table 3.7 : The molecular indices for the source identifications of PAH (Tobiszewski and Namieśnik, 2012).

PAH ratio	Value Range	Source
PHE/AN	<10	Pyrogenic
	>15	Petrogenic
FA/PY	<1	Pyrogenic
	>1	Petrogenic
BaA/(BaA+CHR)	0.2 - 0.35	Coal combustion
	>0.35	Vehicular emissions
	<0.2	Petrogenic
	>0.35	Combustion
LMW/HMW	<1	Pyrogenic
	>1	Petrogenic

The PAH source analysis by using the molecular indices from SPMD analyses data indicate a mainly petrogenic origin of PAH at site 6, 12 and 23. PHE/AN, FA/PY BaA/(BaA+CHR) and LMW/HMW molecular indices are 35, 6, 0.15, 80 for site 6, 25, 6, 0.09, 92 for site 12 and 47, 9, 0.11, 482 for site 23 which is a petrogenic indicator. The data indicate that Site 6a and 24 have pyrogenic source of PAH.

Table 3.8 : (PAH) The analysis results of pollutants in the SPMD (pg g⁻¹ SPMD) exposures of 7 and 21 days.

Chemicals ^a	Stations									
	6(7d)	6(21d)	6a(7d)	6a(21d)	12(7d)	12(21d)	23(7d)	23(21d)	24(7d)	24(21d)
NAP	1700	nd ^d	23000	34000	4500	nd	9700	7300	nd	nd
ACL	1400	1700	5000	5600	1800	1400	7100	8900	2800	3300
AC	950	1700	6000	11000	1200	1600	2400	3400	18000	30000
FL	14000	25000	25000	38000	18000	21000	24000	37000	16000	40000
PHE	27000	60000	67000	120000	33000	51000	68000	140000	44000	130000
AN	780	1900	9000	19000	390	2000	1600	3000	10000	42000
FA	14000	40000	23000	48000	16000	27000	33400	69000	90000	230000
PY	2600	6000	21000	46000	2000	4600	4700	7400	76000	230000
BaA	630	870	1000	2600	270	410	430	680	5900	20000
CHR	1900	5000	2000	4900	1900	4100	2500	5400	14000	50000
BbFA	560	1300	520	1140	590	900	310	390	2200	10000
BkFA	450	1100	330	750	460	780	280	510	1300	7300
BaP	80	160	250	630	80	100	nd	40	1200	6500
IP	160	330	280	490	210	260	nd	nd	530	2700
BghiP	90	90	340	620	nd	nd	nd	nd	370	2400
DBahA	nd	nd	70	80	90	nd	80	70	nd	610
T-PAH	66000	145000	190000	330000	80000	120000	150000	280000	280000	810000
CPAH	3780	8760	4450	10590	3600	6550	3600	7090	25130	97110
CPAH %	5.7	6.0	2.3	3.2	4.5	5.5	2.4	2.5	9.0	12.0
TEQ _{BaP}	279	570	490	1185	261	376	135	259	2333	11061

3.2.1.2 PCB concentrations in SPMD

Although, total PCB concentrations showed large variation in sediments, none of the PCB congeners were detected in SPMD (high production blank and blank values).

3.2.1.3 OCP concentrations in SPMD

SPMD total OCP concentrations ranged from 2.1 ng g⁻¹ to 5.4 ng g⁻¹ and from 4.6 ng g⁻¹ to 41 ng g⁻¹ for 7- day and 21 - day exposed SPMD (Table 3.9). The minimum and maximum values were detected at deployment sites of 12 and at the polluted site 24 as in sediments. ϵ -HCH, OCS, OXC, heptachlor, t-HE, aldrin and mirex in all SPMD samples were undetectable. (DDE + DDD)/DDT > 0.5 designates that DDT was subjected to a long-term weathering (Hitch and Day, 1992). In this study, (DDE + DDD) /DDT ratio in the SPMD samples were found between 0.5 and 14.5.

Table 3.9 : (OCP) The analysis results of pollutants in the SPMD (pg g⁻¹ SPMD); (7) and (21) indicate the results from the site exposures of 7 and 21 days.

Chemicals	Stations									
	6(7)	6(21)	6a(7)	6a(21)	12(7)	12(21)	23(7)	23(21)	24(7)	24(21)
α -HCH	120	320	120	290	160	370	140	310	130	400
β -HCH	380	880	440	950	560	1200	480	1200	530	1600
γ -HCH	74	150	170	190	nd	nd	nd	nd	nd	nd
δ -HCH	43	34	19	22	nd	nd	nd	nd	nd	24
ϵ -HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PeCB	130	300	97	180	110	210	75	170	130	370
HCB	400	610	nd	330	180	380	120	380	280	550
PCA	100	45	62	370	nd	nd	nd	87	nd	110
OCS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4,4'-DDT	290	280	130	620	450	330	350	510	670	2200
2,4'-DDT	93	130	76	210	140	nd	130	140	nd	480
4,4'-DDD	850	1800	1400	2700	570	1200	380	920	2300	8100
2,4'-DDD	240	530	720	1200	200	400	120	260	630	2100
4,4'-DDE	270	720	200	680	510	630	170	360	400	1300
2,4'-DDE	18	45	8,2	20	nd	23	12	18	23	86
t-CHL	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
c-CHL	nd	nd	9,5	15	nd	10	nd	nd	nd	nd
OXC	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
c-HE	nd	41	22	37	20	41	21	45	19	45
t-HE	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Aldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dieldrin	nd	nd	nd	nd	nd	79	46	140	100	270
Endrin	nd	83	27	nd	nd	nd	nd	nd	nd	140
(END)-I	nd	120	370	3700	nd	nd	49	68	140	20000
(END)-II	nd	nd	nd	620	nd	nd	nd	nd	nd	3000
MOC	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Mirex	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
T-OCP	3000	6100	3900	12000	2900	4900	2100	4600	5400	41000

3.2.1.4 Determination of water pollutant concentrations from SPMD data

PRC levels retained in the SPMD were used to calculate the sampling rates of the samplers for each station. Two different calculation methods were used; one of the method uses 20% to 80% retained PRCs for the R_s (Sampling rate) calculations (Huckins et al., 2006). This method is also known as 80/20 method (Booij and Smedes, 2010). In the other method (NLS), Booij and Smedes (2010) use all PRC retention data to calculate the R_s values, including the fractions that are close to 0% or 100%. Since the results obtained by using these two methods (Huckins et al., 2006; Booij and Smedes, 2010) for all of the sites were found in the same order of magnitude, only the details of nonlinear least squares (NLS) method to estimate sampling rates was given in the following:

The retained PRC fraction (f) is found by Equation 3.1.

$$f = \exp\left(-\frac{Bt}{K_{sw}M^{0.47}m}\right) \quad (3.1)$$

where B is adjustable parameter (proportionality factor that also contains factors to adjust the units), t is the exposure time (d), K_{sw} ($L\ kg^{-1}$) is the sampler-water partition coefficient. M is molecular weight ($g\ mol^{-1}$) and m is mass of the sampler (kg). B is a proportionality factor and can be calculated by fitting f as a function of $K_{sw}M^{0.47}$ using unweighted non-linear least square.

R_s can then be determined by Equation 3.2 (Rusina et al., 2010).

$$R_s = \frac{B}{M^{0.47}} \quad (3.2)$$

Since B is difficult to understand, the sampling rate R_s^{300} can be calculated by using B and molar mass (M) of $300\ g\ mol^{-1}$ (Booij and Smedes, 2010). Figure 3.9 shows an example (for site 6) of the retained PRC fractions calculated by NLS.

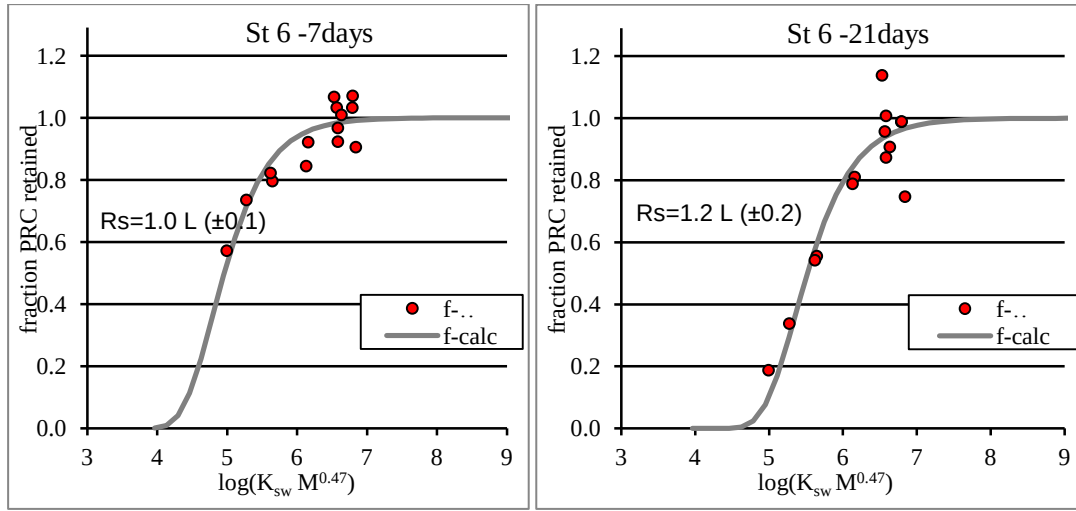


Figure 3.9 : Example of retained PRC fractions in Station 6 for 7 and 21 days. Black lines represent best fitted unweighted non-linear least square (NLS).

B obtained from PRC data by using the NLS were used to back-calculate the aqueous concentrations (C_w) of pollutants (Eq. 3.3).

$$C_w = \frac{N}{K_{sw}m(1 - e^{-\frac{Bt}{K_{sw}M^{0.47}m}})} \quad (3.3)$$

The calculated sampling rates (R_s^{300}) were found between 0.3 - 1.5 L d⁻¹ for both 7 and 21 days of exposures, nevertheless the R_s values for 21 days of deployments were generally higher compared to the results obtained for 7 days deployments for all sites. Those R_s values calculated in this study are generally much lower than the values found in most of the studies performed in a high flow-turbulence areas such as in the streams and in wastewater treatment plant outfalls (Augulyte and Bergqvist, 2007; McCarthy, 2008; Wang et al., 2009; Djedjibegovic et al., 2010) but comparable with the data obtained by some studies performed in relatively lower flow conditions (Verweij et al., 2004; Harman et al., 2009). Dissipation of PRCs was lowest at sampling site 6a situated at the mouth of a creek. Slow water flow and formation of a muddy layer from the domestic sources as well as from the sediment on the surface of the SPMD probably reduced dissipation of PRCs and accordingly uptake of the organic pollutants by the samplers at this exposure site. Furthermore, SPMD were deployed at that station near the water bed at relatively low flow velocities compared to the overlying water column. The highest values for dissipation of PRCs were determined in the Marmara Sea station situated at the coast of the main shipyard area (St 24). Many factors may affect sampling rates, those are

biofouling of the SPMD membrane, water temperature, flow-turbulence, photolysis of the chemicals etc. (Huckins et al., 2006). During the deployment period, temperature was consistently between 8 and 9 °C at all sites. Furthermore, the relationship between the temperature and the sampling rate was found to be weak in some studies (Huckins et al., 1999; Booij et al., 2003; McCarthy, 2008). On the other hand, it was reported that the hydrodynamics of the system is highly effective on the sampling rates (Booij et al., 1998). By the end of the study, heavy biofouling in site 6a and moderate biofouling in other sites were visually apparent after 21 days of deployment. Therefore, those differences in sampling rates between the sites were likely due primarily to fouling on the SPMD and hydrodynamic changes in the system.

Water concentrations (C_w) of the analyzed compounds are given in Table 3.10 for individual chemicals and in Figure 3.10 for total amounts of pollutants.

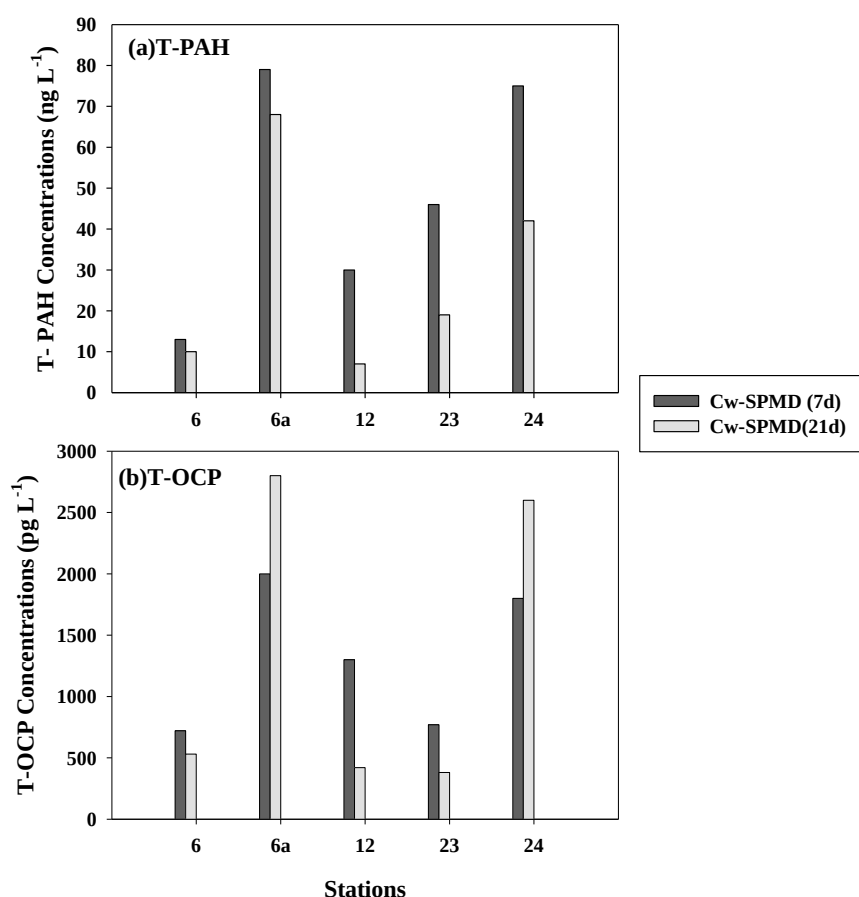


Figure 3.10 : Water concentrations of T-PAH (a), and T-OCP (b) estimated by using non-linear least square method.

C_w 's of total PAH range from 13 - 79 ng L⁻¹ for 7- days of exposure and found between 7.0 - 68 ng L⁻¹ after 21 days of deployment. The highest and lowest water total PAH concentrations were found for sites 6a and 12 respectively.

Table 3.10 : Estimated water concentrations (C_w - pg L⁻¹) from SPMD. (7) and (21) indicate the SPMD exposure durations in days.

Chemicals	Stations									
	6(7)	6(21)	6a(7)	6a(21)	12(7)	12(21)	23(7)	23(21)	24(7)	24(21)
NAP	800	nd ^a	13700	15100	2500	nd	4900	3100	nd	nd
ACL	300	170	2000	1100	700	140	2100	830	760	300
AC	210	200	2500	2300	500	180	730	370	4900	3300
FL	2700	2100	10000	7000	6500	1600	6700	2700	4300	2900
PHE	5200	3900	26600	21000	11800	2900	18900	7600	11500	7100
AN	150	130	3700	3300	140	120	440	170	2700	2300
FA	2800	2400	9400	8500	5800	1400	9600	3400	23900	10500
PY	510	350	8700	7900	740	230	1400	360	20200	10700
BaA	130	53	610	470	100	21	130	34	1600	940
CHR	370	310	910	900	740	210	740	260	3900	2300
BbFA	120	85	230	220	240	49	96	20	650	500
BkFA	94	69	150	140	190	42	88	26	390	350
BaP	16	10	110	120	32	5.0	nd	2.0	350	310
IP	36	22	130	98	86	14	nd	nd	160	130
BghiP	20	6.0	160	120	nd	nd	nd	nd	110	120
DBahA	nd	nd	35	17	34	nd	27	3.6	33	30
TPAH(ng L ⁻¹)	13	10	79	68	30	7	46	19	75	42
α-HCH	33	39	66	73	78	43	53	35	46	45
β-HCH	110	130	240	250	270	170	190	160	200	210
γ-HCH	12	28	99	56	nd	nd	nd	nd	nd	nd
δ-HCH	11	3.5	10	5.3	nd	nd	nd	nd	nd	2.1
ε-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PeCB	27	20	44	35	44	12	23	9.2	39	19
HCB	83	41	nd	68	78	22	40	21	86	28
PCA	22	3.0	30	74	nd	nd	nd	4.8	nd	5.8
OCS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4,4'-DDT	72	22	68	140	200	22	130	32	230	130
2,4'-DDT	23	10	40	47	58	nd	48	8.1	nd	28
4,4'-DDD	200	120	720	580	260	74	140	54	760	440
2,4'-DDD	56	37	360	240	87	24	42	15	210	110
4,4'-DDE	62	51	100	140	230	39	58	20	131	68
2,4'-DDE	4.2	3.2	4.2	4.3	nd	1.4	4.1	1.0	7.5	4.7
t-CHL	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
c-CHL	nd	nd	5.6	3.9	nd	0.6	nd	1.5	nd	nd
OXC	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
c-HE	nd	3.7	13	9.0	10	3.2	8.0	3.4	7.0	3.2
t-HE	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Aldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dieldrin	nd	nd	nd	nd	nd	5.6	18	10	39	18
Endrin	nd	7.0	15	nd	nd	nd	nd	nd	10	10
(END)-I	nd	10	210	890	5.3	nd	20	4.7	53	1300
(END)-II	nd	nd	nd	154	nd	nd	nd	nd	nd	203
MOC	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Mirex	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TOCP	720	530	2000	2800	1300	420	770	380	1800	2600

For all sites, the PAH water concentrations calculated from SPMD were lower for 21 days of exposure compared to 7 days, indicating that the equilibrium conditions between the seawater and SPMD were attained. Phenanthrene, Fluoranthene, Pyrene, Fluorene and Naphthalene were the dominant PAH compounds in seawater. The results of calculations showed that the water OCP concentrations were very similar in all sites with lowest values in site 23 (0.38 ng L^{-1}) and the highest in site 6a (2.8 ng L^{-1}).

3.2.2 BR sorbents

BR sorbents were deployed together with the SPMD in sites. The analyzed data were corrected by using the BR production blank analysis data and the laboratory blanks.

3.2.2.1 PAH concentrations in BR sorbents

BR sorbent data indicate that T-PAH concentrations accumulated in the samplers range from 82 to 769 ng g^{-1} BR sorbent and 71 to 1306 ng g^{-1} BR sorbent for 7 and 21 days exposures respectively (Table 3.11, Figure 3.11).

Table 3.11 : (PAH) The analysis results of pollutants in the BR sorbent (BR) ($\mu\text{g g}^{-1}$ BR) exposures of 7 and 21 days.

Chemicals	Stations									
	6(7d)	6(21d)	6a(7d)	6a(21d)	12(7d)	12(21d)	23(7d)	23(21d)	24(7d)	24(21d)
NAP	nd	nd	15440	16809	11293	6057	16777	nd	nd	nd
ACL	nd	nd	1991	949	nd	nd	4223	1724	506	nd
AC	2827	2611	4619	4888	10147	2807	231169	10390	32247	23021
FL	9038	15852	12370	8715	10869	8623	22755	15683	18545	13573
PHE	26216	44823	49645	54013	28269	22424	83696	72983	140326	167810
AN	986	2420	6696	10191	656	2135	2580	3578	15912	25950
FA	24001	50285	30391	51228	18960	16294	61518	70072	202914	311327
PY	5937	11129	30227	52777	2710	4102	11577	13848	166355	323010
BaA	859	1978	5070	10144	422	546	1398	18714	30275	62545
CHR	6576	12687	10640	17916	5638	4042	8555	13355	58520	125913
BbFA	2071	5109	5571	11033	990	1162	1204	1866	23721	62931
BkFA	1331	4006	3400	7161	651	912	1041	1883	14049	35198
BaP	396	1572	5845	10283	nd	357	nd	793	22454	62117
IP	1015	2857	5349	11146	236	1044	346	2211	15562	42390
BghiP	533	1847	8223	13050	nd	503	nd	1416	15026	40268
DBahA	147	394	936	1970	nd	110	nd	341	3726	10184
T-PAH	81933	157570	196413	282273	90841	71118	446839	228857	760138	1306237
CPAH	12395	28603	36811	69653	7937	8173	12544	39163	168307	401278
CPAH %	15.1	18.2	18.7	24.7	8.7	11.5	2.8	17.1	22.1	30.7
TEQ _{BaP}	1004	3133	7984	14608	286	775	484	3428	31773	84701

Fluorene, Phenanthrene, Fluoranthene, Pyrene and Chrysene are the dominant PAH in all sites. The highest concentration of T-PAH was measured in the shipyard area (site 24). The lowest total PAH concentration were measured in the Black Sea entrance of the Strait (site 12). The results indicate that high molecular weight (HMW) PAH are less accumulated than the low molecular weight (LMW) PAH in the BR sorbent. A similar trend was found also for the SPMD data. Only site 24 have a high concentration of HMW-PAH compared to the other sites.

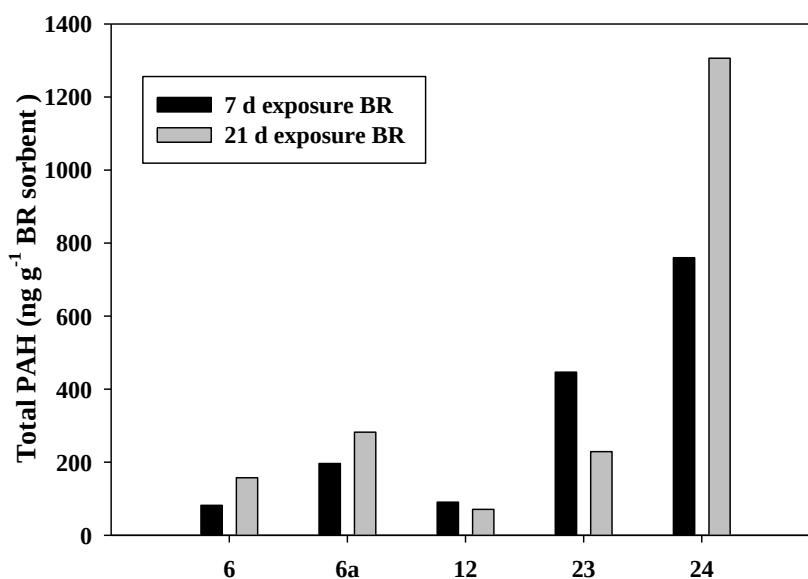


Figure 3.11 : Total concentrations of PAH in the BR sorbent at 7 and 21 days exposure.

At site 12 and 23, the T-PAH concentration were reduced during the 21 day exposure time. T-PAH concentrations were 91 to 71 ng g⁻¹ BR sorbent at site 12 and 447 to 229 ng g⁻¹ BR sorbent at site 23 for 7 and 21 days of exposure time respectively (Figure 3.11). This is a good indication of pollution input at sampling sites during the first 7 days of exposure. T-PAH concentration depurated after 7 days at site 12 and 23 as in case of transplanted mussels. Recent effects of shipbuilding and repair activities to the pollution levels can clearly be observed in the sampling station 24.

3.2.2.2 PCB Concentrations in BR sorbents

T-PCB concentrations accumulated in the BR samplers were in the range of 122 to 1435 pg g⁻¹ BR sorbent and 177 to 3940 pg g⁻¹ BR sorbent for 7 and 21 days exposures respectively (Table 3.12, Figure 3.12).

Table 3.12 : (PCB) The analysis results of pollutants in the BR sorbent (BR) (pg g⁻¹ BR); (7) and (21) indicate the results from the site exposures of 7 and 21 days.

Chemicals	Stations									
	6(7)	6(21)	6a(7)	6a(21)	12(7)	12(21)	23(7)	23(21)	24(7)	24(21)
Indicator PCB										
PCB #28	113	335	79	141	75.7	102	206	361	201	488
PCB #52	78.6	294	45.2	103	33.4	54.5	83	161	210	469
PCB #101	85.3	278	32	65.2	nd	3.4	39.2	35.5	221	562
PCB #138	79.3	260	26.3	42.1	nd	nd	nd	nd	152	502
PCB #153	101	346	45.5	60.9	nd	nd	nd	10.2	218	777
PCB #180	15.8	112	12.4	17.4	nd	nd	nd	nd	178	473
Non-ortho PCB										
PCB #77	8.3	22.3	7	17.8	nd	5.2	nd	19.1	27.8	54.5
PCB #81	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB #126	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB #169	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Mono-ortho PCB										
PCB #105	15	55	12.6	22.5	5.2	3.1	13.9	23.7	54.6	143
PCB #114	nd	5.6	1.3	nd	nd	nd	nd	nd	nd	10.7
PCB #118	40.5	147	26.3	46.7	nd	nd	nd	34.3	130	355
PCB #123	nd	nd	1.1	nd	nd	nd	nd	nd	nd	16
PCB #156	8.8	11.8	2.5	4.2	nd	nd	nd	nd	12.4	34.5
PCB #157	nd	6.9	1.9	4.4	nd	2.9	nd	nd	nd	9.8
PCB #167	15.6	26.8	4.4	10.3	7.5	6.1	nd	7.9	30.5	36.1
PCB #189	nd	nd	1.4	nd	nd	nd	nd	nd	nd	9.5
T-PCB	561	1900	299	536	122	177	342	653	1435	3940

The minimum and maximum T-PCB concentration were detected at sites 12 and at the polluted site 24. The most abundant PCB for all sites are PCB #28, PCB #52, PCB #101, PCB #77, PCB #105 and PCB #167. The levels of PCB are very low compared to the sediment data. Although most PCB congeners were observed in most of the BR samples PCB congeners no. 81, 126, 169 (non-ortho PCB) were not detected at any sites. The analysis results of site 24 shows the direct effect of shipyards. The results indicate that more exposure time is needed for PCB sampling in the clean sites.

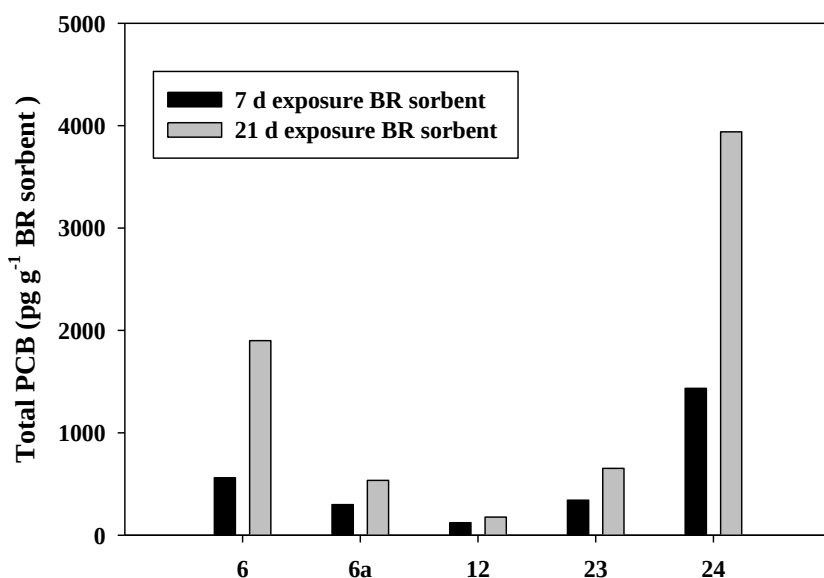


Figure 3.12 : Total concentrations of PCB in the BR sorbent at 7 and 21 days exposure.

3.2.2.3 OCP concentrations in BR sorbents

The total concentration of OCP (T-OCP) collected by BR sorbent is shown in Table 3.13 and Figure 3.13. Total OCP concentrations ranged between 6460 and 16492 pg g⁻¹ BR sorbent and between 7263 and 124418 pg g⁻¹ BR sorbent for 7 and 21 days exposures respectively. The minimum and maximum values were detected at deployment sites of 23 and at the polluted site 24 as in BR sorbent. ϵ -HCH, OCS, OXC, heptachlor, t-HE, aldrin and mirex in any BR samples were undetectable. α and β isomers of HCH and DDT related compounds were the dominant compounds in the samplers.

Shipyard area has the highest level of OCP concentrations. (END)-I and (END)-II contribute 72 % and DDT related compounds contribute 24 % of the total OCP concentration at site 24. The shipbuilding and repair industry use many pesticide products such as pesticide-treated wood and DDTs as the antifouling agent (Barakat et al. 2013). This could be one of the sources of high OCP concentration at the site 24.

(DDE + DDD) /DDT ratio in the BR sorbent showed large variations and found between 0.7 and 8.5. This indicates mainly the historical contamination of the site by DDT.

Table 3.13 : (OCP) The analysis results of pollutants in the BR sorbent (BR) (pg g⁻¹ BR); (7) and (21) indicate the results from the site exposures of 7 and 21 days.

Chemicals	Stations									
	6(7)	6(21)	6a(7)	6a(21)	12(7)	12(21)	23(7)	23(21)	24(7)	24(21)
α-HCH	499	878	354	433	736	545	610	456	814	613
β-HCH	1148	2312	1008	1869	1492	1153	1459	1308	1262	1412
γ-HCH	251	469	155	214	359	268	306	214	434	416
δ-HCH	20.1	24.9	15.6	30.6	24.4	17.6	40.9	16	nd	44.5
ε-HCH	nd	nd	14.7	nd	nd	nd	18	8.7	nd	24.1
PeCB	185	423	61.5	90.1	144	145	162	202	242	438
HCB	515	1170	155	288	363	363	503	600	500	894
PCA	62.9	122	64.6	232	104	38.7	115	89.4	141	228
OCS	6.6	11.8	4.7	nd	nd	11.4	nd	nd	nd	19.8
4,4'-DDT	309	592	6363	9149	1778	3107	732	484	2294	10866
2,4'-DDT	101	212	344	669	111	107	159	141	478	1433
4,4'-DDD	1439	3804	3055	4383	1391	1283	928	1319	5022	11266
2,4'-DDD	460	1119	1259	1937	347	378	316	452	1589	3209
4,4'-DDE	659	1827	737	1668	639	606	625	880	1736	2521
2,4'-DDE	36.3	101	26.1	44.1	40.3	31.2	31.8	41.5	79.7	185
t-CHL	25.5	33.3	7.6	35	nd	8.1	26	27.8	nd	57.7
c-CHL	12.3	39.9	7.3	nd	nd	9.4	25.6	33.8	nd	33.5
OXC	9	22.1	nd	nd	nd	nd	nd	nd	nd	nd
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
c-HE	135	318	29.7	43.9	116	115	120	162	90.2	230
t-HE	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Aldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dieldrin	332	917	149	208	305	308	317	459	378	1010
Endrin	20.7	38.9	22.8	45.9	68.3	95.9	30.9	41.4	nd	87.3
(END)-I	166	500	486	3325	91.6	86.7	189	276	1001	68691
(END)-II	61.7	117	225	1562	nd	30.3	68.9	42.7	431	20701
MOC	6	9.8	9.4	23	7.3	6	nd	8.3	nd	38.3
Mirex	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
T-OCP	6460	15062	14554	26250	8117	8713	6783	7263	16492	124418

The levels of OCP absorbed by BR sorbent were constant at station 12 and 23 after 7 and 21 days of exposure (Figure 3.13). The increasing trend of OCP levels in the other sampling sites indicate that OCP were still in uptake phase at those stations.

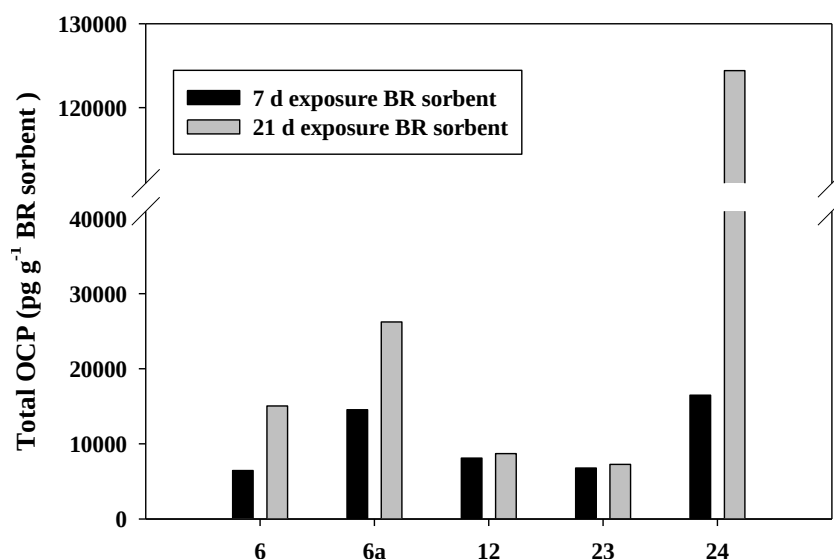


Figure 3.13 : Total concentrations of OCP in the BR sorbent at 7 and 21 days exposure.

3.2.2.4 Comparison of pollutant concentrations in BR sorbents and in SPMD

SPMD and BR sorbent were both similarly fixed on sampling cage and they have a similar surface area. The concentration of T-PAH in BR sorbent were between 1.09 - 2.97 and 0.59 - 1.61 times higher than the concentration in SPMD for 7 days and 21 exposure respectively (Figure 3.14).

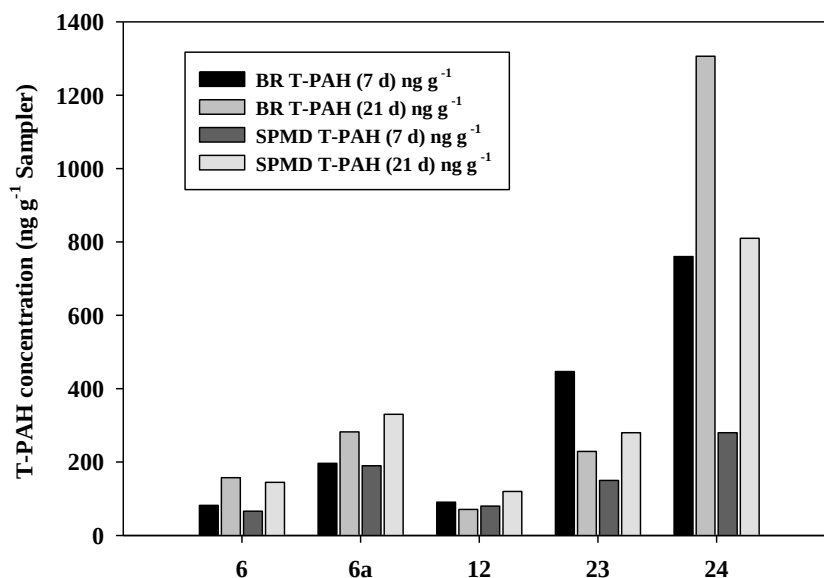


Figure 3.14 : Total concentrations of PAH in the BR sorbent and SPMD at 7 and 21 days exposure (ng g⁻¹ passive sampler).

In general, BR sorbents have a higher sampling capacity than that of the SPMD. The structure of the BR sorbent allows absorbing more PAH in short time (Ceylan et al 2009). SPMD have a LDPE membrane cover and it takes time to absorb the pollutant. This can explain the higher level of TPAH concentration in station 23 and 12 for 7 days exposure time. The PAH source analysis by using the molecular indices at site 23 and 12 for 7 days exposure indicate a petrogenic origin of PAH. PHE/AN, FA/PY BaA/(BaA+CHR) and LMW/HMW molecular indices are 32, 5.3, 0.14, 134 for site 23 and 43, 7, 0.07, 69 for site 12 which is a petrogenic indicator. Station 23 is a small touristic bay and leisure boats visit the bay regularly. Oil spills from those boats are always, then those spills can be easily absorbed by the BR sorbents. The coastal area of the station 12 is a small fishing village. Petrogenic PAH might be arising from those fishing boat activities.

The PCB congeners were not detected in SPMD due to high production blank values. Therefore, PCB concentrations in passive samplers could not be compared.

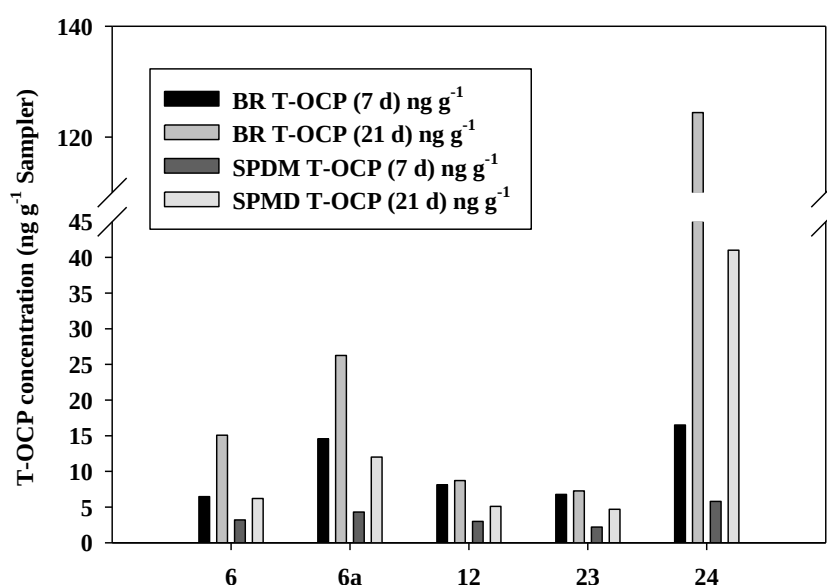


Figure 3.15 : Total concentrations of OCP in the BR sorbent and SPMD at 7 and 21 days exposure (ng g^{-1} passive sampler).

Total OCP concentrations in BR sorbent were 2 – 3.4 and 1.5 - 3 times higher than the concentration in SPMD for 7 and 21 days exposures respectively (Figure 3.15). This indicates that BR sorbent has a better sampling potential. Although, the sampling mechanisms are different between two samplers, both samplers accumulate pollutants in the same order of magnitude. SPMD only collect the dissolved phase of

chemicals. On the other hand, BR sorbents are more hydrophobic and absorb suspended particles in the surrounding water.

3.2.3 Sediment

Sediment analysis data show that the most polluted site is station 24, which is located in the main shipyard district of Turkey with more than thirty establishments. While, Station 12 is the least polluted site situated at the Asian entrance of the Black Sea, which was not extensively influenced by urbanization and by other anthropogenic activities. Table 3.14 shows the properties of the sediments.

Table 3.14 : Properties of the sediments.

Sampling Sites No	Sampling Sites Name	median grain size (mm)	Sediment Type	Total org. carbon con. (%)
6	Istinye	0.6	fine sand	2.0
6a	Istinye dere içi	0.04	silt with peat	17.3
12	Anadolu Feneri	0.7	medium sand	1.5
23	Büyük ada(island)	1.4	medium sand	2.8
24	Tuzla-Shipyards	0.07	Silty sand	7.8

3.2.3.1 PAH concentrations in sediment

Total concentrations of the priority PAH in the sediments vary from 9.4 to 25000 ng g⁻¹ dw (Table 3.15 and Figure 3.16). Phenanthrene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, benzo[a]pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene were the most abundant PAH in the sediment (Table 3.14).

The results indicate that PAH contamination exists and the highest values are found in the shipyard areas. The maximum concentration of T-PAH occurred at station 24 (25000 ng g⁻¹ dw). The contribution of station 24 was found very high, when the individual PAH concentrations in the sediment were checked for all stations. For example the concentration of benzo(a)pyrene measured in station 24 was 2050 ng g⁻¹ dw, which is 14 to 1206 times higher than the other stations (Table 3.14). The similar calculations were carried out for each individual PAH, the results were between 3.4 to 11860 (except naphthalene 0.22) times higher than the rest of the sampling sites. The next highest T-PAH concentration was measured at station 6a (3100 ng g⁻¹ dw) which is a small creek mouth in a highly populated area. The lowest concentrations of PAH occurred at the entrance of the Black Sea at the stations of 12 in the Asian part.

Table 3.15 : The analysis results of PAH in the sediments (pg g⁻¹ dw).

Chemicals	Stations						ERL ^a	ERM ^b
	6	6a	12	23	24			
NAP	19300	700000 ^c	350	250	160000 ^c	160000	2100000	
ACL	3920	26000	130	15600	210000 ^c	44000	640000	
AC	7170	11000	20	70	94000 ^c	16000	500000	
FL	7740	49000 ^c	90	1000	170000 ^c	19000	540000	
PHE	53300	590000 ^c	350	62000	3100000 ^d	240000	1500000	
AN	25200	65000	120	17000	540000 ^c	85300	1100000	
FA	130000	420000	450	360000	4500000 ^c	600000	5100000	
PY	157000	520000	430	340000	5100000 ^d	665000	2600000	
BaA	95500	110000	350	140000	1800000 ^d	261000	1600000	
CHR	98300	87000	490	93000	2040000 ^c	384000	2800000	
BbFA	120000	114000	1700	92000	1800000			
BkFA	55800	59000	720	44000	970000			
BaP	150000	103000	1700	101000	2050000 ^d	430000	1600000	
IP	106000	87000	1300	57000	1200000			
BghiP	115000	120000	1100	51000	1300000			
DBahA	18300	13000	180	9000	190000 ^c	63400	260000	
T-PAH	1160000	3100000	9400	1400000	25000000 ^c	4022000	44792000	
CPAH	643900	573000	6440	536000	10050000			
CPAH %	55.5	18.5	68.5	38.3	40.2			
TEQ _{BaP}	190543	142170	2130	136130	2666400			

^aEffects Range Low

^bEffects Range Medium

^cValues are above ERL

^dValues are above ERM

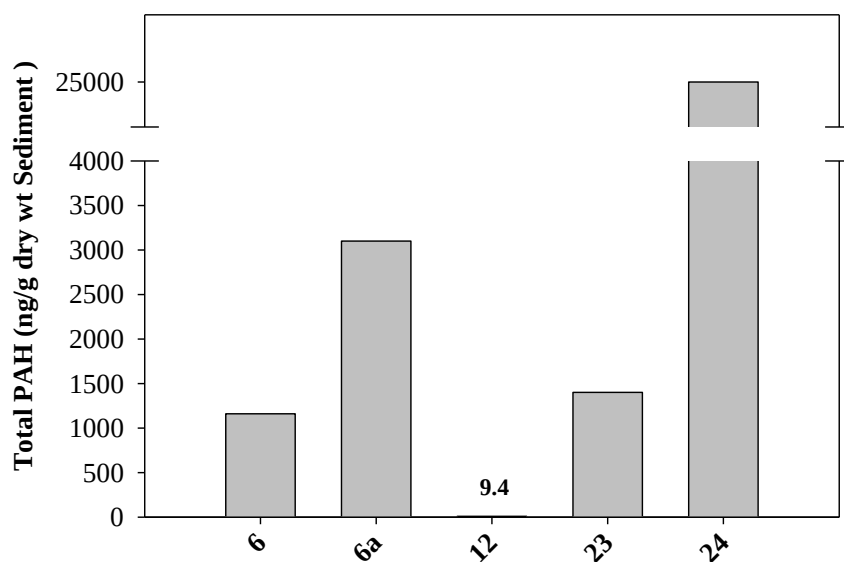


Figure 3.16 : Total concentrations of 16 EPA PAH in sediment (ng g⁻¹ dry wt sediment).

Total PAH concentrations of marine coastal areas in Turkey as well as with the other coastal areas are shown in Table 3.16. The comparison reveals that Istanbul Strait coastal sediments are more polluted compared to most areas in the Mediterranean basin (Baumard et al,1999; Cardellicchio et al., 2007; Bihari et al., 2006) and

Marmara Sea (Tolun et al., 2006; Ünlü and Alpar, 2006) except Cretan Sea (Gogou et al., 2000).

Table 3.16 : Worldwide concentrations of PAH in sediments (ng g⁻¹ dry wt.)

Costal Area	Concentration	References
France, Mediterranean Sea	36–6900 (Σ18 PAH)	Baumard et al.(1998)
Spain, Mediterranean Sea	2–8400 (Σ18 PAH)	Baumard et al.(1998)
Baltic Sea	9.5–1871 (Σ15 PAH)	Witt (1995)
Western Coast, Australia	1.0–3200 (Σ11 PAH)	Burt and Ebell(1995)
Danube Coastline, Black Sea	30.5–608 (Σ17 PAH)	Readman et al.(2002)
Turkey Coastline		
Izmit Bay, Marmara Sea	120-11400 (Σ14 PAH)	Tolun et al.(2006)
Gemlik Bay, Marmara Sea	50.8–13482 (Σ14 PAH)	Ünlü and Alpar (2006)
Istanbul Strait entrance, Black Sea	13.8-531 (Σ17 PAH)	Readman et al.(2002)
Istanbul Strait	1.1-3152 (Σ16 PAH)	Karacik et al.(2009)
Istanbul Strait	9.4-25000 (Σ16 PAH)	This study

The average total PAH concentration in the strait sediments calculated as 1417 ng g⁻¹ dry wt is higher than the average value reported for the Black Sea basin (Readman et al, 2002). The most polluted station 24 is not included the average because it is located in the Marmara Sea. On the other hand, when the PAH sediment concentrations at the Black sea entrance sites were compared with the values reported by Readman et al (2002), the levels in this study were found much higher. The survey sites reported in the previous studies in the Marmara Sea are industrial areas and enclosed seas where the water circulation is very limited, as a consequence, much higher PAH values were measured at those sites (Tolun et al., 2006; Ünlü and Alpar, 2006). The T-PAH concentration measured at Black Sea entrance station in this study is lower than most of the stations in the Istanbul Strait. The results of the first sampling study conducted at the three common stations of the Istanbul Strait were shown in Table 3.17. The order of magnitude is the same for station 6 and 12. Station 23, the island station, were found more polluted in terms of PAH. This could be the result of increasing touristic activates and recently built small port at the sampling site.

Table 3.17 : Comparations of total PAH in sediments (ng g⁻¹ dw).

Sampling Station	Previous Study(Karacik et al 2009)	This Study
6	3152	1160
12	1.1	9.4
23	144	1400

Calculated PAH molecular indices for the 2007 and 2009 sampling are shown in Table 3.18. Those indices show the predomination of pyrogenic PAH. Station 6 indicates a pyrogenic PAH source is similar to the previous studies. The small creek in Istinye Bay (st 6a) carry out the pyrogenic content through is creek bed. This could be the results of house heating and heavy traffic in the area. Station 12 had a very low concentration of PAH and the source is close to the petrogenic origin in both sampling period. The island station (st 23) is became more polluted by PAH and the source is became more petrogenic. Station 24 is both affected by petrogenic and pyrogenic source of PAH because of the heavy shipbuilding and repair activities at the area. The PAH molecular indices at the site indicate both affects. PHE/AN, BaA/(BaA+CHR) and FA/PY indicates pyrogenic origin and LMW/HMW indicates petrogenic origin at site 24.

Table 3.18 : The molecular indices calculations for the source identifications of PAH.

Stations	PHE/AN	FA/PY	BaA/(BaA+CHR)	LMW/HMW
6	2.12 - 3.9 ^a	0.83 – 0.9 ^a	0.49 – 0.53 ^a	0.88 – 0.18 ^a
6a	9.06	0.82	0.55	4.54
12	2.92 – 8.14 ^a	1.05 – 1 ^a	0.42 – 0.5 ^a	0.33 – 0.37 ^a
23	3.63 – 1.8 ^a	1.07 – 1.2 ^a	1.48 – 0.5 ^a	3.15 – 0.12 ^a
24	5.79	0.87	0.48	2.44

^a Previous study results (Karacik et al., 2009)

Table 3.15 shows the SQG values for PAH. Contamination levels for each individual PAH as well as T-PAH is higher than ERL and ERM for Phenanthrene, Pyrene, Benzo(a)anthracene, Benzo(a)pyrene in station 24. This could be due to the intensive shipbuilding and repairing activities at the site. ERL values (Naphthalene, Fluorene and Phenanthrene) are also exceeding in station 6, which is similar to previous study (Karacik et al., 2009).

Carcinogenic PAH (CPAH) (US EPA, 1993; Naz, 1999) were found in the Istanbul Strait sediment. Total concentration of CPAH in the sediments varied from 6.4 to 10050 ng g⁻¹, and the contribution was up to 68.5 % of total PAH (Table 3.14). Station 24 is the highest CPAH concentration and station 12 is the lowest concentrations. Total toxic benzo[a]pyrene equivalent (TEQ_{BaP}) was also calculated by using the toxicity equivalency factor (TEF) values proposed by US EPA (1993) (Table 3.14). TEF values for seven carcinogenic PAH. These PAH include

benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd) pyrene and TEFs for those PAH are 0.1, 0.1, 0.1, 1, 0.01, 0.1 and 0.1 respectively. The calculations were made according to the equation 3.4.

$$TEQ_{BaP} = \sum_{i=0}^n C * TEF \quad (3.4)$$

Where; TEQ_{BaP} is the Total Toxicity Equivalence based on benzo[a]pyrene (BaP) , TEF is Toxicity equivalency factor of the individual PAH and C is Concentration of the individual PAH in the sample.

Table 3.15 is show the TEQ_{BaP} levels calculated from all sediment samples. The maximum values of Total TEQ_{BaP} were $2666 \text{ ng g}^{-1} \text{ dw}$ at stations of 24 and the minimum values $2.1 \text{ ng g}^{-1} \text{ dw}$ at station 12 indicating the infulnace of shipbuilding activites and urban sites.

3.2.3.2 PCB concentrations in sediments

Total PCB concentrations showed (Figure 3.17, Table 3.19) large variation in sediments and ranged from $0.04 \text{ ng g}^{-1} \text{ dw}$ (site 23) to $520 \text{ ng g}^{-1} \text{ dw}$ (site 6).

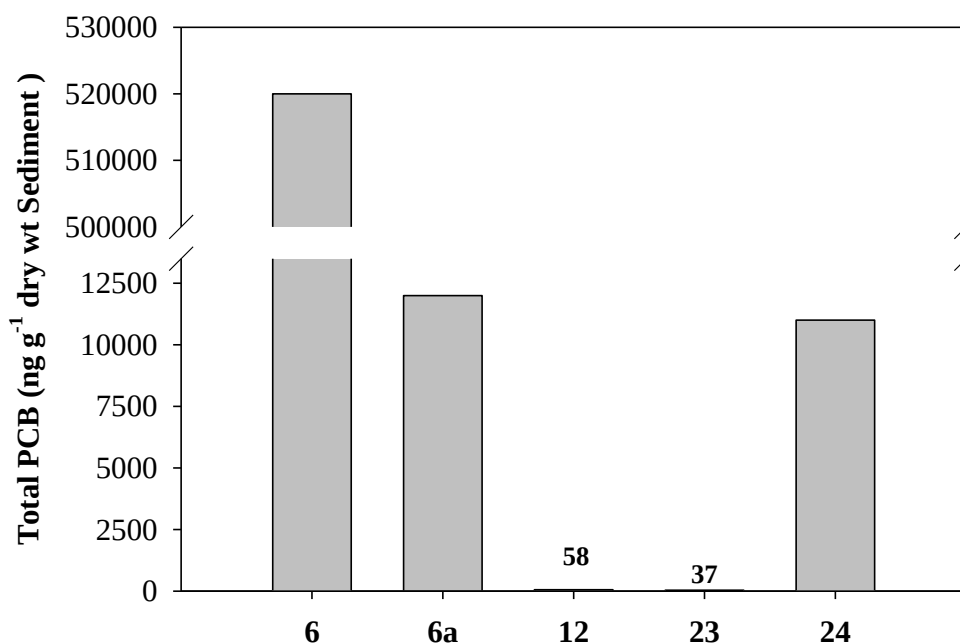


Figure 3.17 : Total concentrations of PCB in the sediment.

Very low levels of total PCB were detected in the sediments at sites 12 and 23. In the other stations, indicator PCB especially PCB 138, 153 and 180 were the dominant congeners. In addition to the site-specific pollutant sources at site 6, the stream

entering to that site presumably responsible also for this extremely high total sediment PCB concentration. The analysis results of site 6a representing the contribution of stream to site 6 obviously reveals that fact.

Table 3.19 : The analysis results of PCB in the sediments ($\text{pg g}^{-1} \text{ dw}$).

Chemicals	Stations					
	6	6a	12	23	24	23 Soil
Indicator PCB						
PCB #28	600	820	9	nd	1000	135
PCB #52	7000	450	10	nd	730	347
PCB #101	71600	850	11	7	1200	2012
PCB #138	116000	2400	nd	12	1800	4957
PCB #153	166000	2500	nd	7	1600	8195
PCB #180	109000	3100	19	nd	800	9282
Non-ortho PCB						
PCB #77	580	70	nd	nd	270	70
PCB #81	nd	nd	nd	nd	10	1.6
PCB #126	130	10	nd	nd	30	28
PCB #169	20	nd	nd	nd	nd	2.4
Mono-ortho PCB						
PCB #105	3600	220	9	nd	980	430
PCB #114	680	20	nd	nd	60	37
PCB #118	19100	590	nd	11	1800	1449
PCB #123	770	30	nd	nd	40	37
PCB #156	12000	470	nd	nd	310	384
PCB #157	1200	50	nd	nd	80	46
PCB #167	5800	170	nd	nd	150	187
PCB #189	2400	70	nd	nd	30	104
T-PCB	520000	12000	58	37	11000	27700

3.2.3.3 OCP concentrations in sediment

Among the 28 OCP compounds, trans-heptachloroepoxide, aldrin and mirex were not detected in any of the sediment samples (Figure 3.18 Table 3.20). Total sediment OCP concentration ($450 \text{ ng g}^{-1} \text{ dry weight}$) at site 24 was found much higher compared to the concentrations measured at the other sites ($1.0 \text{ ng g}^{-1} - 20 \text{ ng g}^{-1}$), showing the role of shipyard industry again in the OCP pollution.

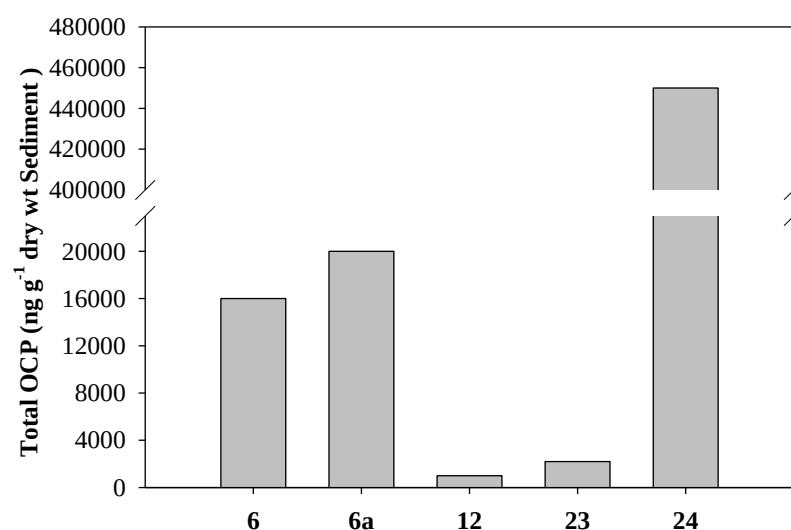


Figure 3.18 : Total concentrations of OCP in the sediment.

Table 3.20 : The analysis results of OCP in the sediments (pg g⁻¹ dry wt).

Chemicals ^a	Stations				
	6	6a	12	23	24
α-HCH	60	1700	30	30	780
β-HCH	650	3200	80	260	19000
γ-HCH	50	310	nd ^b	10	920
δ-HCH	10	190	nd	10	390
ε-HCH	nd	50	nd	nd	120
PeCB	90	200	nd	nd	580
HCB	250	530	nd	nd	670
PCA	10	580	nd	nd	1400
OCS	0	nd	10	nd	40
4,4'-DDT	810	3100	300	270	82000
2,4'-DDT	150	490	240	70	20000
4,4'-DDD	6300	2100	110	440	19000
2,4'-DDD	5300	770	110	130	9200
4,4'-DDE	2200	2700	60	910	240000
2,4'-DDE	220	90	10	20	4600
t-CHL	20	90	nd	nd	4200
c-CHL	10	80	nd	nd	1400
OXC	nd	nd	nd	nd	120
Heptachlor	nd	nd	nd	nd	370
c-HE	10	70	nd	nd	2300
t-HE	nd	nd	nd	nd	nd
Aldrin	nd	nd	nd	nd	nd
Dieldrin	120	680	20	30	12400
Endrin	20	90	nd	nd	240
(END)-I	nd	1400	30	nd	23500
(END)-II	10	1200	20	nd	11000
MOC	nd	30	nd	nd	50
Mirex	nd	nd	nd	nd	nd
T-OCP	16000	20000	1000	2200	450000

β and γ isomers of HCH and DDT related compounds were the dominant compounds in sediments; DDT related compounds contribute for 81-91 % of all stations except

station 6a. (END)-I and (END)-II were found much higher in sites 6a and 24 compared to the other sites. The usage of OCP, including aldrin, endrin, DDT, dieldrin, HCHs, heptachlor, chlordane, and toxaphene, was prohibited in Turkey between 1971 and 1989. However, those results obtained in this study and some related monitoring studies (for example Kolonkaya, 2006) show that they are still being used illegally in some parts of Turkey.

3.2.3.4 Water pollutant concentrations from the sediment data

Sediment-based aqueous concentrations of the sites (C_{w-sed}) were calculated by Equation (3.5)

$$C_{w-sed} = C_{sed} f_{oc}^{-1} K_{oc}^{-1} \quad (3.5)$$

where C_{sed} is the pollutant concentration in the sediment, f_{oc} is the organic carbon content and K_{oc} is the sediment organic carbon–water partition or sorption coefficient calculated by using the approximation given by Karickhoff (1981) (Eq. 3.6). K_{ow} values were taken from Mackay et al (2006) and Huckins et al (2006).

$$K_{oc} = 0.41 K_{ow} \quad (3.6)$$

For calculations, it was assumed that the equilibrium existed between pollutants in organic phase of the sediments and in the water phase.

C_w values calculated by using sediment concentrations of pollutants were presented in Table 3.21. The water concentrations estimated from sediment pollutant concentrations and K_{oc} values (C_{w-sed}) of PAH and OCP were higher as those estimated from SPMD levels (C_{w-spm}) probably due to much higher concentrations of pollutants in the pore water with regard to overlying water.

Table 3.21 : Estimated water concentrations (C_w - pg L^{-1}) from sediments.

Chemicals	Stations				
	6	6a	12	23	24
NAP	994000	4200000	23500	9100	2180000
ACL	47000	36600	2000	130000	644000
AC	104000	18000	410	670	353000
FL	62000	46000	900	3500	346000
PHE	174000	223000	1500	143000	2630000
AN	88000	26400	550	42300	487000
FA	95000	36100	430	188000	846000
PY	126000	48300	450	192000	1060000
BaA	14200	1900	69	14500	71400
CHR	16400	1700	110	11000	88300
BbFA	24000	2700	440	13000	96300

Table 3.21 (continue): Estimated water concentrations (C_w - $\mu\text{g L}^{-1}$) from sediments.

BkFA	4300	520	72	2400	19100
BaP	8100	650	120	3900	28700
IP	4000	380	62	1500	12100
BghiP	1700	210	22	550	5200
DBahA	700	56	9.0	230	1800
T-PAH ($\mu\text{g L}^{-1}$)	1800	4640	31	760	8870
PCB #28	160	25	3.0	nd ^b	72
PCB #52	1040	7.8	2.0	0.1	28
PCB #101	4050	5.6	0.8	0.2	18
PCB #138	850	2.0	nd	0.1	3.4
PCB #153	2710	4.7	nd	0.1	6.6
PCB #180	910	3.0	0.2	nd	1.7
PCB #77	23	0.3	nd	nd	2.8
PCB #81	nd	nd	nd	nd	0.2
PCB #126	3.3	nd	nd	nd	0.2
PCB #169	0.1	nd	nd	nd	nd
PCB #105	110	0.8	0.3	0.1	7.5
PCB #114	28	0.1	nd	nd	0.7
PCB #118	750	2.7	nd	0.3	18
PCB #123	29	0.1	nd	nd	0.4
PCB #156	110	0.5	nd	nd	0.8
PCB #157	16	0.1	nd	nd	0.3
PCB #167	110	0.4	nd	nd	0.7
PCB #189	200	0.7	nd	nd	0.6
T- PCB	11100	54	6.4	0.9	160
α -HCH	850	2720	600	280	2810
β -HCH	11400	6580	1810	3200	87200
γ -HCH	1230	880	nd	120	5760
δ -HCH	63	200	nd	51	890
ϵ -HCH	nd	130	nd	nd	660
PeCB	70	19	1.7	1.1	120
HCB	68	17	nd	nd	49
PCA	4.6	27	nd	nd	150
OCS	0.4	nd	0.8	nd	0.9
4,4'-DDT	330	150	160	79	8700
2,4'-DDT	47	18	100	15	1600
4,4'-DDD	1350	53	32	66	1080
2,4'-DDD	540	9.0	14	9.3	240
4,4'-DDE	190	27	6.9	57	5340
2,4'-DDE	72	3.4	3.9	5.0	390
t-CHL	12	5.2	nd	nd	560
c-CHL	6.9	4.8	nd	nd	190
OXC	nd	nd	nd	nd	13
Heptachlor	nd	nd	nd	nd	13
c-HE	24	29	nd	nd	2240
t-HE	nd	nd	nd	nd	nd
Aldrin	nd	nd	nd	nd	nd
Dieldrin	240	170	45	47	6800
Endrin	57	25	nd	nd	150
(END)-I	nd	230	54	nd	8500
(END)-II	28	290	49	nd	5700
MOC	6.5	4.7	6.8	nd	17
Mirex	nd	nd	nd	nd	nd
T-OCP	16600	11600	2880	3930	139200

On the other hand, black carbon which is resistant to thermal or chemical degradation under the conditions applied in the TOC method may be responsible for

the underestimation of K_{oc} and thereby overestimation of C_{w-sed} especially for PAH. (Ribeiro et al.,2008; Obst et al.,2011; Allan et al.,2012). The values C_{w-spm} and C_{w-sed} were similar -particularly for PAH- in site 12 where the polluted waters rather than sediments were more effective for the accumulation of pollutants in SPMD. The differences between the C_w 's of PAH were much more significant for sites 6, 6a and 24 and of OCP for site 24. The reason is likely that SPMD reflect the concentration of pollutants in the flowing water, whereas, the water concentrations estimated from sediments is much related with the pore water and/or overlying water concentrations because SPMD were generally deployed 2-3 meters above the sediment (when possible). T-PCB water concentrations calculated from the sediment data indicate the effect of polluted sediments in station 6. The disadvantages to estimate water concentrations from bed sediment concentrations were explained by Gale et al (1997) as inhomogeneous distribution of pollutants in the sediments, the use of K_{oc} values that do not account for the specific sediment organic carbon composition or quality, and the assumptions of sorption equilibrium and instantaneous mixing with the water column. For these reasons, it seems that the use of SPMD data is more realistic than using sediment data to estimate water pollutant concentrations.

3.2.4 Mussels

Both transplanted and local mussels were used for the second sampling study. Station 12 does not have a local mussel population due to the frequent salinity changes and predator activates by seastars, crabs and mollusks (like *Rapana venosa*). Local mussels could not also be collected from Station 24, since they had much higher sampling size (>5cm).

3.2.4.1 PAH concentrations in mussels

The mussel analysis data show that T-PAH concentrations accumulated in the mussel tissues ranged from 28.1 to 323 ng g⁻¹ ww for 7 days, 21.6 to 886.5 ng g⁻¹ ww for 21 days exposure time and 34.7 to 202 ng g⁻¹ ww for local mussels (Table 3.22, Figure 3.19). Phenanthrene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene and benzo(j)fluoranthene are the dominant PAH in all sites and both transplant and local mussels. Maximum T-PAH concentration in mussels was measured at station 24 and the values are also quite high at station 6a in local mussels. The lowest concentration

of T-PAH was found at station 12. Lower molecular weight (LMW) PAH were dominant at all stations.

Characteristic values of molecular indices in mussels were calculated to find the origin of PAH. PAH in mussels at station 6,12 and 23 mainly came from petrogenic source according to FA/PY (2.4, 2.2 and 3.6), BaA/(BaA+CHR) (0.14, 0.17 and 0.21) and LMW/HMW (8, 9.6 and 21) ratio which is similar to the results obtained for the BR sorbent data. Station 6a and 12 have a pyrolytic PAH source. Even though Station 24 is a shipyard area, the source analysis of PAH indicate that more pyrolytic activities exist in the area. The BR sorbent results to determine the origin of PAH is similar for stations 12 and 23 petrogenic.

Table 3.22 : The analysis results of PAH in the mussel ($\mu\text{g g}^{-1}$ wet w) exposures of 7 and 21 days, local mussel and control mussels.

Chemicals	Stations											Control
	6(7d)	6(21d)	6(Local)	6a(Local)	12(7d)	12(21d)	23(7d)	23(21d)	23(Local)	24(7d)	24(21d)	
NAP	438	3107	465	2635	403	525	700	993	687	493	659	1377
ACL	53	40	67	301	66	nd	316	223	116	235	556	332
AC	165	597	550	2812	141	171	202	372	130	2635	5957	194
FL	1072	1217	1496	n.d	715	857	1651	1463	1404	2808	4075	1175
PHE	9097	8041	7836	43430	8249	7393	15344	15462	11319	32378	82126	11712
AN	nd	nd	344	13148	nd	nd	42	82	41	5113	12649	nd
FA	5779	6030	8047	33858	3879	3387	13522	9331	8061	86411	240635	5388
PY	3018	2470	3305	63223	1737	1669	5053	2582	2273	98450	242526	3115
BaA	1564	1213	1467	8200	1413	836	1554	770	1783	19577	67136	2494
CHR	6990	7383	7140	18410	5821	4127	9588	5901	6710	40642	121689	8070
BbFA	3751	2315	2443	6430	2483	1198	2934	771	716	12235	42278	3539
BkFA	1831	1280	1212	3315	1351	687	1427	502	781	7252	19970	1928
BaP	695	536	656	2875	458	222	477	248	249	6536	23589	932
IP	1186	624	457	1328	751	264	712	303	223	3551	10317	899
BghiP	771	448	326	2245	485	217	427	313	224	3691	9879	882
DBahA	144	74	55	252	104	38	78	41	33	847	2506	168
T-PAH	36554	35375	35866	202462	28056	21591	54027	39357	34749	322854	886547	42205
CPAH	16161	13425	13430	40810	12381	7372	16770	8536	10495	90640	287485	18030
CPAH %	44.2	38.0	37.4	20.2	44.1	34.1	31.0	21.7	30.2	28.1	32.4	42.7
TEQ _{BaP}	1613	1160	1291	5012	1126	566	1243	546	670	11289	39027	1916

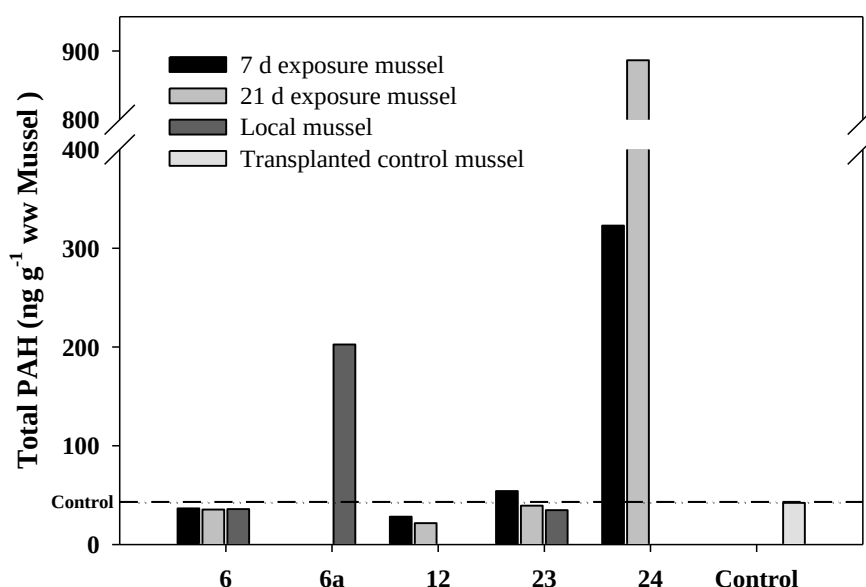


Figure 3.19 : Total concentrations of 16 EPA PAH in mussel ($\text{ng g}^{-1} \text{ ww}$).

Figure 3.19 shows that the total concentration of PAH in the mussel tissue. Depuration of the T-PAH could be observed at station 12 and 23 compared to the control mussels. Similar results were observed in BR sorbent data for station 12 and 23. The high level of T-PAH in the mussel tissues at the shipyard area indicate that transplant mussels still in the accumulation phase and could accumulate more pollutants.

Concentration of carcinogenic PAH, especially BaP in the mussels was found high at station 24 after 7 and 21 days of exposure time. The maximum admissible concentration of BaP in shellfish and mussel tissue is $2 - 10 \text{ ng g}^{-1} \text{ ww}$ according to European Regulations (EC1881/2006). The value of BaP (6 and $23 \text{ ng g}^{-1} \text{ ww}$) was exceeding the limit established by the law at station 24. It seems that consuming mussel from that area is revealing the risk for human health.

Although, the T-PAH levels are in the same order of magnitude, comparison of the first and second sampling data shows that T-PAH concentrations were 2 to 1.7 times higher at station 6 and 23 during the first sampling time. This could be the result of seasonal change. The local mussels collected from station 23 were more away from the coastline during the second sampling campaign. This 50 meter differences could affect the pollution levels in mussels, which could come from the land sources. Station 6 was effected by the fresh water income from the istinye creek. The seasonal

changes on the flow rate changes also the amount of pollutant carried by the creek. This may be the results of the difference between first and second sampling at station 6.

3.2.4.2 PCB concentrations in mussels

The concentration of the individual PCB congeners in the mussel samples were presented in Table 3.23 and Figure 3.20. Mussel analysis data show that T-PCB concentrations accumulated in the mussels ranged from 1.22 to 2.11 ng g⁻¹ ww, 0.97 to 3.18 ng g⁻¹ ww and 1.59 ng g⁻¹ ww for 7 and 21 days exposures and for local mussels respectively. The highest value was observed at station 6 and the lowest was at the Black Sea entrance of the strait (station 12). The most abundant PCB congeners in mussel samples were indicator PCB representing 76.2-80.7% of the total amount of PCB in all stations. The lowest percentile for indicator PCB was found in the island local mussel samples. The PCB pattern found in mussels showed a predominance of PCB-153 followed by PCB-138 and PCB-101 for indicator PCB. PCB-77 was dominant for non-ortho PCB, whereas PCB-118 and PCB-105 exhibited higher values for mono-ortho PCB.

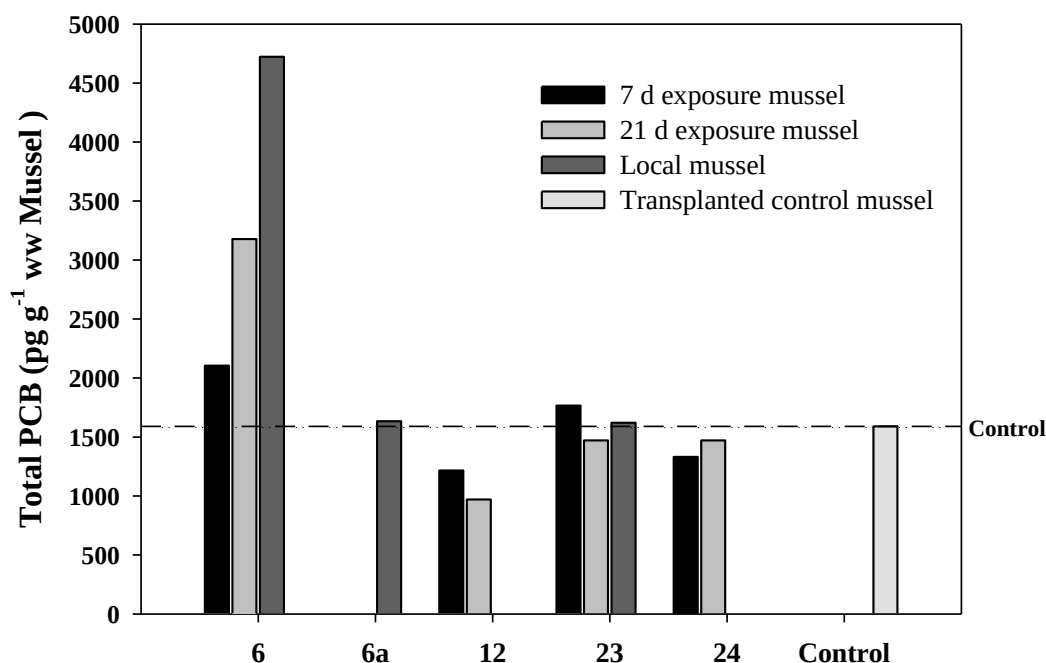


Figure 3.20 : Total concentrations of PCB in the mussels (pg g⁻¹ ww).

Except station 6 and 12, all PCB levels were found similar to the control mussel values. Depurations of PCB are visible at station 12, which is the clean site compared

to the other stations. Comparing the data from the first sampling indicate big differences at station 23. T-PCB concentration was reduced from 35.9 ng g⁻¹ ww to 1.6 ng g⁻¹ ww in this second sampling. This could be due to the local releases/spills during the first sampling period.

Table 3.23 : The analysis results of PCB in the mussel (pg g⁻¹ ww) exposures of 7 and 21 days, local mussel and control mussels.

	Stations											
Chemicals	6(7d)	6(21d)	6(Local)	6a(Local)	12(7d)	12(21d)	23(7d)	23(21d)	23(Local)	24(7d)	24(21d)	Control
Indicator PCB												
PCB #28	101	106	225	244	76	125	192	183	205	199	183	133
PCB #52	114	188	240	198	65	62	125	144	192	161	144	107
PCB #101	299	531	723	215	128	104	202	178	233	176	178	180
PCB #138	403	586	908	225	234	165	289	230	229	183	230	274
PCB #153	659	980	1538	382	415	291	531	404	326	311	404	488
PCB #180	99.8	154	177	53	42	28	47	34	51	43	34	65
Non-ortho PCB												
PCB #77	14	16.8	26	28.9	9.5	8.4	17.6	19.2	26	24	19	15
PCB #81	1.5	1.5	1.8	1.4	nd	1	1.8	2	2.5	1.1	2	1.3
PCB #126	1.6	2	2.9	1.6	1.4	0.9	1.9	2.2	2.7	1.3	2.2	1.9
PCB #169	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.3
Mono-ortho PCB												
PCB #105	86.1	118	162	64	53.8	41	78.8	66.4	88	52	66	74
PCB #114	7.1	9.5	14.1	5.6	4.6	3.7	7	4.8	6.3	4.6	4.8	6.3
PCB #118	244	378	536	173	146	112	216	163	212	141	163	186
PCB #123	5.8	8.3	11.9	3.8	4.5	3	9.1	3.7	5	3.1	3.7	10
PCB #156	33	48.1	73	18	15.7	10.6	21	15.7	21	15	16	21
PCB #157	7.6	9.9	17	5.5	4.4	2.8	5.5	5	5.3	4.5	5	6
PCB #167	24.3	35	59.3	13.8	14.4	9.8	19.7	14.3	14	11	14	19
PCB #189	3.9	5.3	7.8	2	2.3	1.2	2.5	1.9	2.1	1.7	1.9	2.5
T-PCB	2105	3177	4723	1634	1216	970	1766	1471	1621	1332	1471	1590
WHO-TEQ _{PCB}	0.214	0.221	0.330	0.212	0.108	0.107	0.213	0.211	0.314	0.110	0.231	0.212

3.2.4.3 OCP concentrations in mussels

Total OCP concentrations analyzed in the mussels ranged from 7.7 to 14.3 ng g⁻¹ ww, 7.0 to 38.2 ng g⁻¹ ww and 10.9 ng g⁻¹ ww for 7 and 21 days exposures and local mussels respectively (Table 3.24, Figure 3.21). The minimum and maximum values were detected at deployment sites of 12 and at the polluted site 24. OCS, t-HE, and mirex (except station 6) in all mussel samples were undetectable. Station 6 and 6a shows a high OCP concentration in local mussel population while transplanted mussels OCP levels were relatively lower than that of the control mussels. (DDE + DDD) /DDT ratio in those sites (33.7 and 32.2) indicates a historical DDT contamination. The similar local mussel OCP concentrations in 6 and 6a stations show that source of the OCP in the coastal area was the small creek entering the bay. Stations 12 and 23 indicate a depuration of OCP in the mussels. 4,4'-DDT and 2,4'-DDT were not detected at station 12. (DDE + DDD) /DDT ratio in the mussels are 16.7-4.0 at station 23.

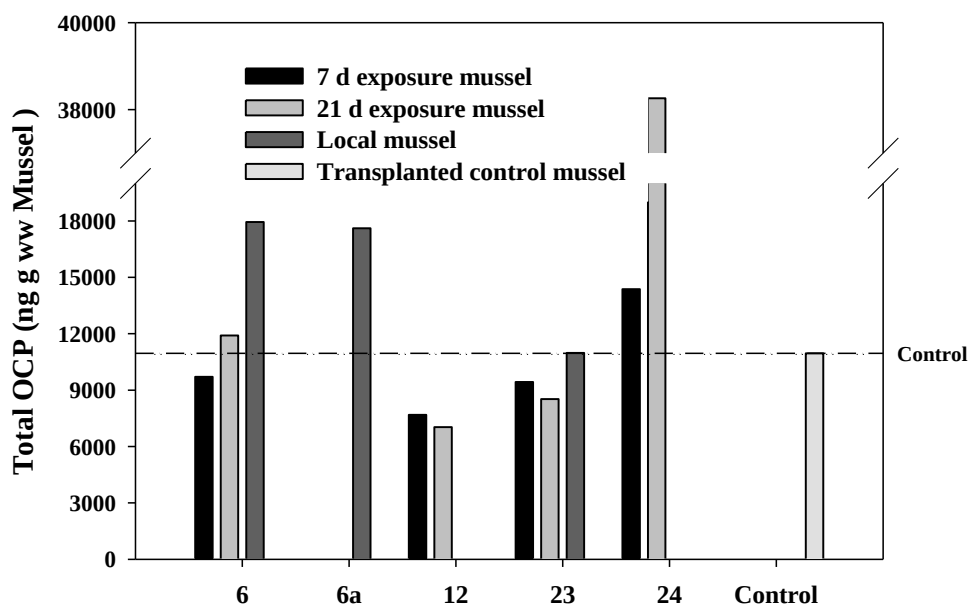


Figure 3.21 : Total concentrations of OCP in the mussels.

(DDE + DDD) /DDT ratio in the mussel samples were found between 30.5 and 24.8 at station 24. DDT related compounds contribute for 82 -68 % of the total OPCs concentration at site 24 for 7 and 21 days of exposure time. High OCP concentration levels were also found in sediments and passive samplers.

Table 3.24 : The analysis results of OCP in the mussel (pg g⁻¹ ww) exposures of 7 and 21 days, local mussel and control mussels.

Chemicals	Stations											Control
	6(7d)	6(21)	6(Local)	6a(Local)	12(7)	12(21d)	23(7d)	23(21d)	23(Local)	24(7d)	24(21d)	
α-HCH	89	80	283	80	13	26	15	44	33	nd	nd	97
β-HCH	2834	3754	5577	3372	2160	2472	1791	2682	2866	1541	1351	2950
γ-HCH	38	53	69	59	25	40	31	34	36	22	35	40
δ-HCH	nd	nd	2.8	nd	14	59	26	nd	45	nd	nd	33
ε-HCH	nd	nd	12	nd	34	84	16	nd	30	nd	nd	40
PeCB	18	21	29	30	12	14	14	19	14	29	31	18
HCB	38	31	59	29	22	24	34	55	24	36	22	37
PCA	4.6	5.5	10	48	4.7	4.1	12	11	13	13	14	5.5
OCS	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4,4'-DDT	nd	nd	74	nd	nd	nd	262	nd	1203	56	448	170
2,4'-DDT	19	94	250	235	nd	nd	145	nd	295	319	562	62
4,4'-DDD	2394	2754	4393	3194	2144	1804	2576	1827	2089	6418	16743	3090
2,4'-DDD	636	761	1049	1303	557	496	690	604	618	1501	3335	802
4,4'-DDE	3298	3876	5288	2986	2477	1786	3444	2847	3252	3391	4750	3269
2,4'-DDE	105	132	200	93	77.6	62	102	95	87	150	256	117
t-CHL	21	17	26	38	12	12	24	24	37	29	35	19
c-CHL	17	30	37	49	12	13	19	27	32	20	13	21
OXC	7.8	11	16	16	5.4	6.7	6.8	11	9.3	6.4	7.9	7.3
Heptachlor	6.7	3.5	9.0	1.9	nd	nd	nd	1.9	nd	2	nd	nd
c-HE	27	37	59	50	21	25	26	32	34	27	32	28
t-HE	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Aldrin	2.7	1.3	3.4	2.4	nd	nd	nd	nd	1	9.3	28	1.4
Dieldrin	105	145	267	286	66	65	103	128	155	236	313	97
Endrin	16	26	54	13	12	13	23	21	32	21	26	26
(END)-I	19	47	121	3701	11	12	64	50	60	402	6493	13
(END)-II	nd	23	50	2005	2.9	10	9.3	8.2	8.1	138	3766	6
MOC	1.2	1.1	nd	16	1.4	nd	0.7	nd	4	5.1	nd	9.2
Mirex	6	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
T-OCP	9704	11903	17938	17607	7684	7027	9432	8522	10977	14370	38261	10956

3.2.4.4 Mussel bioconcentration and bioaccumulation factors

Bioconcentration is the uptake of chemicals by the organisms from the surrounding water. It is expressed as bioconcentration factor (BCF) and can only be measured under laboratory conditions (Mackay and Fraser, 2000; Arnot and Gobas, 2006). BCF is the ratio (in L kg^{-1} wet weight) of chemical concentration in the organism C_B (by diet), to the freely dissolved chemical concentration in the water C_{WD} . It is shown as in Equation 3.6.

$$\text{BCF} = C_B / C_{WD} \quad (3.6)$$

Bioaccumulation is the uptake of chemicals from the ambient water by all possible exposure routes (diet, dermal, respiration etc.). The bioaccumulation factor (BAF) is the ratio of the concentration of chemical in the organism C_{BA} (by all exposure routes) to that in the water, similarly to that of BCF (Mackay and Fraser, 2000). BAF is calculated from Equation 3.7.

$$\text{BAF} = C_{BA} / C_{WD} \quad (3.7)$$

The BCF and BAF should not be mixed and are not exchangeable quantities (Arnot and Gobas, 2006). In this study, freely dissolved chemical concentrations in the water were calculated from SPMD data and the chemicals in the transplanted mussel were used to find out BAF. Individual chemicals BAF values were given on table 3.25 and table 3.26. The missing values are not detected values in SPMD or mussels.

Table 3.25 : BAF values of PAH calculated from SPMD water concentration.

Stations	6	6a	12	23	24
Chemicals	BAF (L kg^{-1})				
NAP		175		320	
ACL	233	274		269	1853
AC	2985	1223	950	1005	1805
FL	580		536	542	1405
PHE	2062	2068	2549	2034	11567
AN		3984		482	5500
FA	2513	3983	2419	2744	22918
PY	7057	8003	7257	7172	22666
BaA	22887	17447	39810	22647	71421
CHR	23816	20456	19652	22696	52908
BbFA	27235	29227	24449	38550	84556
BkFA	18551	23679	16357	19308	57057
BaP	53600	23958	44400	124000	76094
IP	28364	13551	18857		79362
BghiP	74667	18708			82325
DBahA		14824		11333	83533

Quantitative Structure Activity Relationships (QSARs) are models used to predict the toxicity of chemicals. They are mostly used to calculate BCFs and BAFs of chemicals (Arnot and Gobas, 2003).

Calculated PHE BAF values range from 236 to 5587 by using QSAR models reported in the literature (Yakan, 2013). BAF values of the present study are range from 2034 to 11567 for PHE (Table 3.25).

Table 3.26 : BAF values of OCP calculated from SPMD water concentration.

Stations	6	6a	12	23	24	Arnot and Gobas, 2006	
Chemicals	BAF (L kg ⁻¹)					QSARs model	
α-HCH	2051	1101	614	1243		2510	150
β-HCH	28877	13488	14541	16763	6433	2068	121
γ-HCH	1896	1052				1578	90
δ-HCH						3695	228
ε-HCH						4660	295
PeCB	1055	866	1142	2098	1616	28158	2113
HCB	746	429	1086	2619	775	67236	5480
PCA	1833	645		2313	2483	49340	3905
OCS						198609	17947
4,4'-DDT					3446	48395	3823
2,4'-DDT	9400	5000			20071	61038	4929
4,4'-DDD	22950	5507	24378	33833	38052	83176	6918
2,4'-DDD	20568	5429	20667	40267	30318	157471	13919
4,4'-DDE	76000	21329	45795	142350	69853	176848	15805
2,4'-DDE	41250	21581	44214	94600	54468	57597	4626
t-CHL						40663	3159
c-CHL		12615	21333	18133		40663	3159
OXC						49340	3905
Heptachlor						120116	10347
c-HE	10027	5511	7656	9500	9969	7558	500
t-HE						7558	500
Aldrin						214585	19534
Dieldrin			11679	12800	17389	12257	850
Endrin	3757				2640	11128	764
(END)-I	4710	4158		10660	4995	17362	1244
(END)-II		13019			18552	12741	886
MOC						1200052	128706
Mirex						40663	3159

Individual BAF values of OCP were shown in table 3.26. QSARs models were applied from literature to predict BAF values of OCP chemicals (Arnot and Gobas, 2006). The range of BAF values, that calculated from SPMD and mussel data, are in the same range of QSAR model made by Arnot and Gobas (2006).

3.2.5 Neutral red retention assay (NRR)

Neutral red retention (NRR) assay was applied in this study, as a biomarker to determine the effects of pollutants on the mussels. Lysosomal membrane stability of blood cells decreases by the effect of neutral red dye and this induce leaking of cell content (Dailianis et al.,2003).

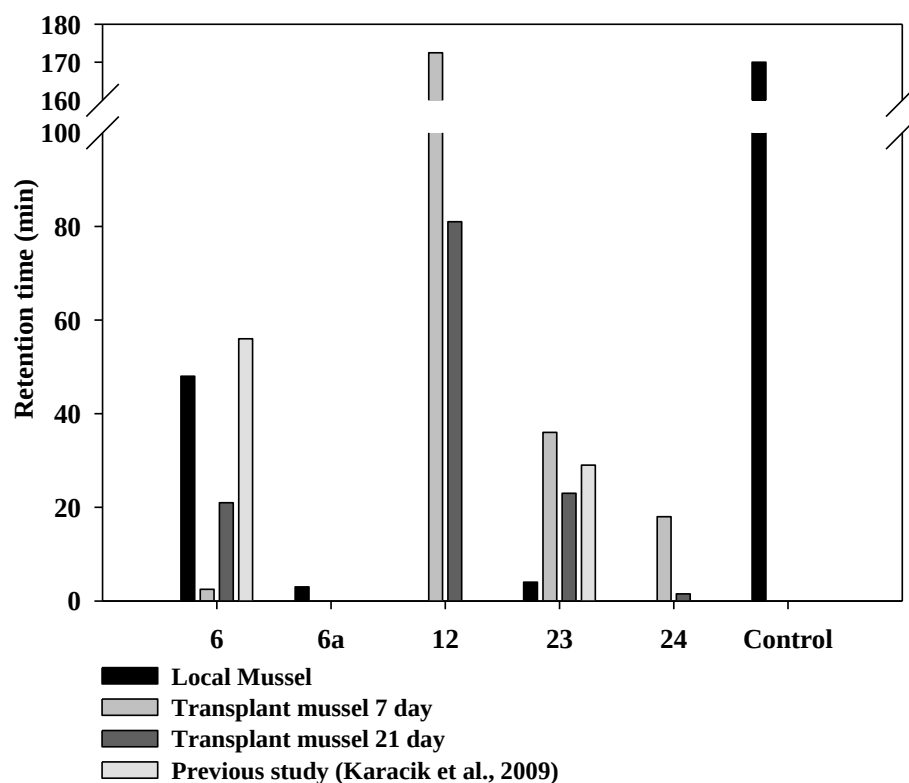


Figure 3.22 : Lysosomal stability retention times (min) of mussels (*Mytilus galloprovincialis*).

The results indicate that station 12 has the highest retention time 172 min. (Figure 3.22). Station 24 and 6a have the lowest retention times. The results show that the higher chemical concentrations in the mussels result in the lower the retention time.

3.2.6 SPMD and BR sorbent exposed to the sediments (pore water sediment experiment)

The concentration of organic pollutants in the SPMD and BR sorbent exposed to the sediments in laboratory conditions increased rapidly in the first seven days and then the rate of uptake relatively diminished by the end of exposure period (Table 3.27). During the exposure period, perhaps some fraction of the organic pollutants were associated with the colloidal organics. Thus, most probably, the dissolved form of the

pollutants in the interstitial water were uptaken firstly and then the uptake rate of SPMD depended on the diffusion rate of the chemicals from particles or from the colloidal form to the interstitial water. The pollutants sequestered by SPMD in the sediment were generally higher than it was by those in the water. This is especially evident in sites 6a and 24. A possible reason may be the accumulation of sediment/pore-water accommodated soluble fractions in SPMD. These results also indicate that, in some of the sites, the release of pollutants from the sediments to the pore water and then to reach the overlying water and SPMD was not very efficient during the exposure period.

Table 3.27 : The analysis results of T-PAH, T-PCB and T-OCP in the sediment pore water (pg g^{-1} Passive Sampler) exposures of 7 and 21 days for SPMD and 21 days for BR sorbent.

Chemicals	Stations														
	6			6a			12			23			24		
	(7)	(21)	BR(21)	(7)	(21)	BR(21)	(7)	(21)	BR(21)	(7)	(21)	BR(21)	(7)	(21)	BR(21)
T-PAH	52000	81000	1209897	5500000	9500000	2648643	9000	13000	50581	11000	21000	33984	1300000	2500000	1922709
T-PCB	18000	25000	49244	1600	3000	2762	600	700	15	1000	1100	54	6100	12000	30939
T-OCP	6700	6200	18330	8500	16000	22074	2200	2400	2771	1700	4400	6665	100000	230000	124150

4. CONCLUSIONS AND RECOMMENDATIONS

In the first stage, the detailed distribution and source of POP in the Istanbul Strait were determined by sampling sediment and mussels along the Strait area. PCB, PCDD and PCDF were detected in all samples, showing their ubiquity in coastal areas. The sediment and mussel concentrations of those chemicals in the Istanbul Strait are comparable to other areas around the world, and when dioxin-like compounds were considered, high contamination levels were detected in sediment samples collected from three stations, although the TEQ values did not exceed the safe limits. In general, sediments collected from urbanized sites including the bayous and river mouths within the strait and from locations where the heavy ship traffic/port activities occur exhibited the highest levels of contaminants. Although the sediment and mussel PCB concentrations showed a positive correlation, the contaminant accumulation exhibited different patterns, sediment PCB levels showed big differences depending on the sampling area whereas mussel PCB levels were more or less in the same order of magnitude except at the island station. This study provided evidence for the levels of pollutants regarding to PCB and PCDD/F and contributes to the mapping of these pollutants in the Mediterranean region. This work also provided the first data on contamination status of OCP in sediments and mussels in the Istanbul strait. The results indicated that there still existed a variety of OCP in the strait ecosystem. The pollution in the middle parts was more pronounced comparing to the both endings of the strait showing the influence of the local sources in the system. Among OCP determined in sediments and mussels in the present study, residual levels of DDTs were predominant, followed by HCHs and other OCP. The highest levels of β -HCH and 4-4'-DDE in shellfish was due to their resistance to microbial degradation and thereby long half life. The DDT congener pattern in mussel tissue suggests no current local source of the pesticide, as DDT metabolites predominated in tissue samples, rather than the parent compound. The levels of OCP measured in sediments and mussels can be considered as relatively low when compared to reported data from similar studies elsewhere in Asia and the rest of the

world. None of the OCP concentrations exceeds the ERM values although some concentrations measured at some inner stations were higher than ERL limit values. On the other hand, for mussels, both HCH and DDT concentrations (total) measured were well below those legal limits for human health set for fish and fisheries products. Thus, the results suggest that the OCP under investigation in sediments and in mussels may not pose serious hazards at most of the strait stations.

In the second stage, Passive sampling systems were used together with transplant and local mussel samples as well as sediment samples. SPMD and BR sorbent have proven useful in effective sampling the dissolved fraction of PAH, PCB and OCP from water and from sediment pore water on a time-integrated basis. Water concentrations estimated by using SPMD data seem more reliable compared to the estimations made by using the sediment data. Since the uptake in SPMD can be affected by water temperature, turbulence and biofouling, the application of PRC to overcome those problems in the monitoring sites provided reliable assessment of the targeted compounds in the water column and pore-water. Water concentration of pollutants calculated by NLS method is more useful since it used all PRC. The pollutants in SPMD buried in the sediments were generally higher than those for SPMD in the water, due to the fact that the uptake in the sediments is membrane controlled whereas the uptake in the sediment is aqueous-film controlled. Estimation of water concentrations by using pollutant concentrations accumulated by SPMD was found more reliable than using sediment data when the disadvantages/advantages of the two systems were considered.

BR sorbent is used as passive sampler first time in this study. Although, the sampling mechanisms are different, sampling results from BR sorbent are similar with SPMD. In general, BR sorbent has much better sampling capacity for PCB, OCP and HMW PAH. Further research using with PRC in the BR sorbent could allowed us to calculate water concentration of pollutants.

Transplanted mussel data show similar trend with the passive samplers. Depurations of the pollutants are visible in clean sites. On the other hand, mussels are more sensitive to temperature, salinity and seasonal changes as well as local predators.

It can be concluded that bioassays like NRR assay appear to be useful for measuring potential toxicity in polluted coast line. The approach of using bioassays combined

with passive sampling such as SPMD and BR sorbent and transplanted mussels is suitable for evaluating the effects of pollutants in the marine environment.

The data obtained from this study provided relevant information for future risk assessment and passive sampling studies. Also it can be used to develop a proper pollution monitoring model.

For further research plan, calibration and analyte recovery methods should be developed for BR sorbents by using performance reference compounds.

Passive samplers are good alternatives for water sampling. European Union regulations indicate very low levels of pollutants in the water. Conventional methods are not enough to measure ultra low-level of pollutants in water samples. SPMD and BR sorbents show a good potential for sampling of pollutants in the marine environment. Further studies should be performed for practical uses of BR sorbent in the field.

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APPENDICES

APPENDIX A: Chemicals

APPENDIX A

Table A.1 : The analysis results of PAH, PCB and OCP in the sediment pore water (pg g⁻¹ Passive Sampler) exposures of 7 and 21 days for SPMD and 21 days for BR sorbent.

Chemicals	Stations														
	6			6a			12			23			24		
	(7)	(21)	BR(21)	(7)	(21)	BR(21)	(7)	(21)	BR(21)	(7)	(21)	BR(21)	(7)	(21)	BR(21)
NAP	5517	n.d.	5338	4520676	7445021	nd	n.d.	n.d.	30683	637	1124	n.d.	26850	16002	n.d.
ACL	346	397	1120	37085	63592	65560	140	476	n.d.	187	231	n.d.	4736	7065	6929
AC	2272	3302	14678	28855	64505	86074	1576	1251	n.d.	1485	1601	n.d.	113098	199693	79113
FL	1714	2490	7476	104209	224416	195472	632	536	2611	645	1312	n.d.	67930	65083	24621
PHE	5559	9974	111979	480031	897924	936976	2396	2201	4003	2568	5285	n.d.	300940	437041	244956
AN	1363	2655	29460	43162	91676	90953	225	331	327	163	330	1016	48021	90615	36761
FA	9971	15158	254075	139373	300321	406441	1681	3374	1615	2801	5031	6111	244383	565595	357345
PY	13863	27205	204824	142163	312797	417437	989	1718	735	1545	2912	4379	319172	774961	353620
BaA	1616	2752	89002	8671	20340	62397	113	286	629	231	380	2788	28498	64169	104218
CHR	2596	4339	89801	12345	29135	103206	338	802	1177	417	845	2641	69657	153044	166139
BbFA	2145	4016	100873	4222	8751	59627	317	625	2087	301	588	3311	18704	43581	120384
BkFA	1510	2521	48309	2818	6252	34786	135	360	1165	164	321	2013	12203	28319	63535
BaP	1546	2742	103726	3092	6868	62184	69	201	2373	112	208	3803	13592	31190	129445
IP	1086	1735	70793	1591	3315	53240	160	245	1732	115	263	3968	5226	10125	106598
BghiP	863	1508	65503	2251	5282	64736	81	245	1150	63	138	3333	5172	10096	103706
DBahA	188	326	12940	334	591	9554	128	59	294	11	110	621	1299	2708	25339
T-PAH	52000	81000	1209897	5500000	9500000	2648643	9000	13000	50581	11000	21000	33984	1300000	2500000	1922709
Indicator PCB															
PCB #28	214	302	151	422	961	879	43	35	n.d.	29	49	n.d.	218	430	270
PCB #52	1847	2538	2262	174	376	364	40	0.6	4	50	53	n.d.	423	895	600
PCB #101	4846	6942	9253	205	335	243	19	59	n.d.	156	141	7	993	1841	2552

Table A.1 (continue): The analysis results of PAH, PCB and OCP in the sediment pore water (pg g⁻¹ Passive Sampler) exposures of 7 and 21 days for SPMD and 21 days for BR sorbent.

PCB #138	2853	3970	9968	212	339	276	174	217	n.d.	175	202	8	1023	1854	5406
PCB #153	4596	6740	14170	330	506	302	194	206	n.d.	262	343	3	1823	3256	9208
PCB #180	1183	1670	7740	67	122	210	53	62	n.d.	79	106	n.d.	777	1503	9607
Non-ortho PCB															
PCB #77	50	71	93	13	34	52	4.7	2.8	4	6.5	8.6	6	32	70	65
PCB #81	n.d.	n.d.	n.d.	n.d.	n.d.	3	n.d.	n.d.	n.d.	n.d.	2.0	n.d.	2.7	4.5	6
PCB #126	n.d.	n.d.	12	n.d.	n.d.	3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.7	7.1	17
PCB #169	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8
Mono-ortho PCB															
PCB #105	330	489	750	31	92	111	14	15	n.d.	58	27	12	188	387	579
PCB #114	35	57	93	1.2	7	10	0.7	1.3	n.d.	4.4	2.1	n.d.	13	20	54
PCB #118	1409	1975	2811	95	224	225	33	48	n.d.	150	105	13	493	986	1408
PCB #123	35	58	81	4	11	6	2	1.1	n.d.	3.0	2.4	n.d.	10	16	46
PCB #156	213	338	1022	21	32	37	11	15	n.d.	21	21	n.d.	62	126	710
PCB #157	30	n.d.	127	0.8	2.3	9	1.4	n.d.	n.d.	0.6	2.2	n.d.	11	21	63
PCB #167	133	187	549	15	23	25	8	12	8	13	13	7	40	67	222
PCB #189	n.d.	52	161	n.d.	n.d.	6	4	n.d.	n.d.	n.d.	5.2	n.d.	12	19	118
T-PCB	18000	25000	49244	1600	3000	2762	600	700	15	1000	1100	54	6100	12000	30939
α-HCH	322	318	476	3024	5461	4732	20	41	112	9	23	80	136	330	127
β-HCH	1383	885	1354	1089	2209	2035	902	1432	771	562	1106	523	1309	3271	803
γ-HCH	352	150	72.8	377	486	146	132	17	72	n.d.	307	93	303	375	1385
δ-HCH	62	34	16.4	88	161	124	14	8	16	0.7	4.4	24	64	199	89
ε-HCH	n.d.	n.d.	n.d.	39	82	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	26	64	n.d.
PeCB	96	301	121	198	501	373	30	31	n.d.	12	18		144	305	198
HCB	178	609	223	325	616	706	11	63	111	2.0	85	627	273	470	315
PCA	33	45	54.5	38	61	114	16	11	40	16	37	n.d.	36	5.1	23
OCS	n.d.	n.d.	6.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12	n.d.	n.d.	n.d.	23
4,4'-DDT	526	284	10909	221	226	3254	427	233	1053	85	672	2881	1287	1404	19909

Table A.1 (continue): The analysis results of PAH, PCB and OCP in the sediment pore water (pg g⁻¹ Passive Sampler) exposures of 7 and 21 days for SPMD and 21 days for BR sorbent.

2.4'-DDT	126	127	212	49	26	166	72	44	90	58	140	95	243	395	5575
4.4'-DDD	1977	1751	2456	662	1418	2453	120	165	213	204	461	513	76618	181959	68368
2.4'-DDD	660	529	952	197	406	695	n.d.	63	44	48	100	104	14033	33673	16231
4.4'-DDE	663	719	1094	432	841	2096	426	258	198	616	1244	1582	3752	8291	8920
2.4'-DDE	47	45	44.2	12	33	70	4.3	5.9	10	15	24	42	313	681	552
t-CHL	n.d.	n.d.	17.7	n.d.	2.7	43	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
c-CHL	n.d.	n.d.	11.1	n.d.	45	36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	27
OXC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Heptachlor	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
c-HE	15	41	18.2	55	121	98	n.d.	16	5	4.6	12	16	11	22	13
t-HE	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Aldrin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dieldrin	174	125	178	261	499	707	n.d.	21	37	1.1	51	75	569	1432	760
Endrin	22	83	33.3	n.d.	29	60	n.d.	n.d.	n.d.	n.d.	10	n.d.	128	128	64
(END)-I	39	122	42.2	932	2113	2449	n.d.	n.d.	n.d.	37	54	n.d.	219	573	408
(END)-II	11	n.d.	30.2	434	1001	1535	18	n.d.	n.d.	n.d.	17	n.d.	83	65	236
MOC	5.3	n.d.	7.7	15	22	181	7.5	10	n.d.	2.5	10	10	4.4	32	124
Mirex	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
T-OCP	6700	6200	18330	8500	16000	22074	2200	2400	2771	1700	4400	6665	100000	230000	124150

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▪ Okay O.S., **Karacık B.**, Başak S., Henkelmann B., Bernhöft S. and Schramm K-W., (2009): PCB and PCDD/F in sediments and mussels of the Istanbul Strait (Turkey), *Chemosphere*, 76, 2, 159-166.

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