MYTITURK - SUB-REGIONAL SURVEYS FOR THE ASSESSMENT OF CONTAMINATION LEVEL OF AEGEAN AND MEDITERRANEAN COASTAL WATERS OF TURKEY USING CAGED MUSSELS EXISTING IN TURKISH COASTS

MEDITERRANEAN COAST

FINAL REPORT

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1. PREFACE

MYTITURK project is a continuation of the projects MYTILOS, MYTIMED, MYTIAD and MYTIOR which aimed to draw up a baseline report on chemical contamination and were carried out along the Mediterranean coastal regions. This research programme was initiated by IFREMER in 2003 and aims to investigate the sources, fate and effects of contaminants in the Mediterranean Sea in order to support the management of environmental issues. In the context of this project, the scientific work will assess contamination (Metals and organic pollutants) in the Mediterranean coastal seas in general and in particular along the coasts of Turkey (Aegean and Mediterranean Seas) using caged mussels (Mytilus Galloprovincialis and/or Brachydontes Donax) deployed at predetermined adequate locations. The stations have been chosen by taking in to account the type variety of inputs (city sewage, agricultural, industrial, riverine) to the sea.

Basic oceanographic parameters (salinity, temperature, pH) were measured during the period of retrieving the caged mussel. Contaminant analysis of the mussels from Mediterranean Sea will be carried out in the laboratories of the METU-IMS (Middle East Technical University-Institute of Marine Sciences) and in the IFREMER's laboratories,.

2. INTRODUCTION

Based on the framework Agreement for cooperation between UNEP and the Turkish Ministry of Environment and Forestry (MoEF) (Turkish Ministry of Environment and Urbanism) signed the 10/05/2006, UNEP agrees to co-operate with MoEF, Middle East Technical University-Institute of Marine Sciences (METU-IMS) and DEU-IMST with the project entitled "MYTITURK - sub-regional surveys for the assessment of contamination level of Aegean and Mediterranean coastal waters of Turkey using caged mussels existing in Turkish coasts".

The present activity of sub-regional surveys for the assessment of contamination level of Mediterranean coastal waters was approved at the 14'th Meeting of

Contracting Parties (Portoroz, Slovenia, November 2005) within the framework of MED POL Phase IV. The project has been included in the Programme and budget of MED POL approved at the 16th Meeting of the Contracting Parties (Marrakech, Morocco, 3-5 November 2009.

The objectives of the MYTITURK Project are:

a) investigation of the sources, fate and effects of chemical contaminants along the Aegean and Mediterranean coastal waters of Turkey;
b) evaluation of chemical contamination of the coastal waters in the context of Turkish National Coastal Marine Pollution Monitoring Programme, UNEP/MED POL Monitoring Activities and the European Water Framework Directive, relevant national and international legislation;
c) the protection of human and marine ecosystem.

2.1. The activities carried out with the support of this small-scale funding:

- DEU-IMST (in the Aegean Sea) and METU-IMS (in the Mediterranean Sea) participated in the cruises organised by IFREMER for the deployment and collection of caged mussels at selected locations along the coasts of Turkey.
- METU-IMS supplied the species Brachidontes.
- The caged mussels were deployed by R/V l'Europe (IFREMER) and retrieved by R/V Piri Reis (DEU-IMST). Scientists from METU-IMS participated these cruises during the Mediterranean leg.
- METU and DEU analysed mussels for (organic and metal) contaminants
- If necessary METU and DEU will participate in scientific and technical meetings and workshops to discuss the results of the project.

The expected results of the Project are the determination of selected hazardous substances (heavy metals, hydrocarbons and pesticides) in caged mussels after immersion of 3 months at the selected stations. The results of the project will provide information on the contaminant levels along the Turkish coasts. These data will be used to assess the quality of marine coastal environment andwill help to detect areas which are affected by pollutants.

3. CURRENT SITUATION

The concept of environmental pollution have started to develop in our country during the 70s. Mediterranean Action Plan (MED POL) was established by joint efforts of the Mediterranean countries, and the Office of UNEP / MAP Athens has been implemented in coordination with and the Middle East Technical University-Institute of Marine Sciences contribute actively from the date of the start of this study until 2009. The main objective of MED POL program was to determine trends of chemical contaminants, state of chemical pollution, pollution status in our seas and their sources by continuous monitoring, in accordance with EU criteria provide the necessary administrative and technical measures to be taken.

During the last quarter-century industrial complexes, oil filling plants and industrialization in coastal areas brought rapid growth of population. Again rapidly growing indoor-outdoor tourism activities concentrated at Coastal areas of the country, has created serious environmental problems. Especially, at semi-enclosed basins such as the Gulf of İskederun and Gulf of Mersin and wide and shallow continental shelf areas a significant increase in annthropogenic pollutants (industrial and domestic waste), have been created important changes in marine ecosystems. Pollution of Mersin Gulf coastal area, which receives domestic wastewater discharges and influenced of river, by organic matter and nutrients is very important. This area is heavily influenced by Seyhan River and Berdan Rivers. Pollution of Ceyhan river, vacated by the Gulf of Iskenderun by phosphorus, DIN and TSS is evident. High COD / BOD ratio observed during studies suggests that Ceyhan, there are a wide variety of sources (source diversity) of organic matter in the river water.

In order to determine the impact of Land-based pollutants in shallow coastal waters (continental shelf) eutrophication monitoring work carried out under national pollution monitoring program MEDPOL in the Gulf of Mersin. This work have shown that discharges of urban wastewater of Mersin (rich in phosphorus), and Seyhan-Berdan Rivers (rich in DIN) in to the Mersin Gulf coastal waters causes the formation of eutrophic conditions. Ammonia and phosphorus pollution at coastal waters of the gulf is obvious. Light transmittance in shallow coastal waters of the bay, which has a very weak interaction with open sea, is also very low. Secchi disk depth drop down to the ranges of 2-3 m. TRIX values of coastal waters are in the range of 4-6. The

measured pollution parameters and TRIX results indicate transformation of eutrophication in the waters close to shore and the continuity of that eutrophic conditions. Effects of Chemical pollutants increse on coastal marine ecosystem due to relatively long residence time in coastal waters of the gulf. Ranging from Mersin harbor to infront of the Seyhan delta light light penetration depth low and pollutant values are high, dissolved oxygen concentration falls below the value of sea-water saturation concentration. Low oxygen, is an indicator of transformation of the environment from autotrophic (produce oxygen) into heterotrophic (oxygen consumption) condition. Eutrophic in coastal waters of the region is expected to increase in the near future, for this reason water quality monitoring efforts in the region need to be continued. Before determining the Terrestrial sources of pollutants in breeding, selection of deep sea marine outfall discharge area, and bio-chemical treatment to be applied to domestic wastewater, bio-chemical properties of the receiving environment and the basic hydro-dynamic parameters must be determined. In summary, without a comprehensive and systematic research to protect and improve our natural resources is not possible to reveal a realistic approaches and solutions. .

Trend monitoring studies of heavy metals in sediments in the Eastern Mediterranean coast reveal that in mercury and chromium levels there observed no any tendency to change, but an upward trend, Cadmium and downward trend in copper observed. Overall, all the sediment samples show decreasing trend in ppDDE, ppDDT, ppDDD and Ar 1254 values, HCB, Dieldrin, Endrin, and Ar 1260 show an increasing trend. In the coastal and reference stations sediments there are an increase in aliphatic and aromatic petroleum hydrocarbon concentrations. Sediment samples taken from Tasucu, Iskenderun, Fethiye, Finike and Göksu regions have Pristane / Phytane ratio of 1.54, 1.13, 2.22, 1.15 and 1:10 respectively, which biogenic origin of oil contamination is indicated. Gulf of Iskenderun, Mersin and Antalya Bay samples have Pristane / Phytane ratio of 1:21, 1.34 and 1.54 respectively,and these regions suggest that the biogenic source of oil pollution.

An increase was observed in pp'DDD, pp'DDT Dieldrin concentrations in fish from Göksu, pp'DDE, HCB, Endrin, Ar 1254 pesticide derivatives does not change significantly. Overall, an increase in concentration of aliphatic petroleum hydrocarbon and a declining trend in aromatic petroleum hydrocarbon concentrations was

obtained. Pristane / Phytane ratio of Göksu fish is 1:48. This, indicates that oil pollution is of biogenic origin. pp'DDE, pp'DDD, Dieldrin, Endrin in fish samples from Mersin shows an increasing trend, pp'DDT Ar1254, R 1260 shows a decreasing trend. HCB levels have shown no tendency. In Mersin fish samples Pristane / Phytane ratio is 0.94 indicating petrogenic contamination.

4. ABBREVIATIONS, SYMBOLS AND UNITS

Parameters that were measured at the stations are:

Parameter	Symbol	Unit
Mytilus galloprovincialis	MG	
Brachydontes Donax	B	
Hexaclorobenzene	HCB	ng/g
Lindane	γ HCH	ng/g
Heptachlor	Hep	ng/g
Aldrin	Ald	ng/g
Dieldrin	Dield	ng/g
Endrin	End	ng/g
pp DDE		ng/g
pp DDD		ng/g
pp DDT		ng/g
Polychlorinated Biphenyls	Aroclor 1254	ng/g
Polychlorinated Biphenyls	Aroclor 1260	ng/g
Aliphatic Hydrocarbons	ALI	ng/g
Aromatic Hydrocarbons	ARO	ng/g
Naphthalene	Nap	ng/g
Acenaphthylene	Aceph	ng/g
Acenaphthene	Ace	ng/g
Fluorene	Fl	ng/g
Phenanthrene	Phe	ng/g
Anthracene	Ant	ng/g
Fluoranthene	Flu	ng/g
Pyrene	Pyr	ng/g
Chrysene	Chr	ng/g
Benzo a anthracene	BaA	ng/g
Benzo b fluoranthene	BbF	ng/g
Benzo k fluoranthene	BkF	ng/g
Benzo a pyrene	BaP	ng/g
Indeno pyrene	Inp	ng/g
Dibenzo (a,h) anthracene	DBA	ng/g
Benzo g,h,i perylene	BgP	ng/g
Mercury	Hg	ng/g
Cadmium	Cd	ng/g
Coper	Cu	µg/g
Zinc	Zn	µg/g

5. IMPLEMENTATION PLAN AND TIME TABLE

	Month	2011									2012		
		4	5	6	7	8	9	10	11	12	1	2	3
	Activity												
1.	Preparation of the methodology, chemicals and equipment	X											
2.	Deploymentof caged mussels	X											
3.	Retrieve of caged mussels				X								
4.	Analysis of samples					X	X	X	X	X	X	X	
5	Preparation of progress report						X						
6.	Preparation of Final and financial Report												X

6. METHODS AND MATERIALS

The objective of this study is to evaluate the chemical contaminant levels at the coastel waters which are under the influence of different land based sources. For this purpose mussels *M. galloprovincialis* and/or *Brachydontes* species are used as bioindicators. The physiology and accumulation ability of these species are well studied and can be found almost everywhere in the Mediterranean Sea further more these species are tolerable to a wide range of temperature and salinity and is resistant to dehydration (transport). The caging technique allows the selection of the area of study thus, comparable results can be obtained.

Active biomonitoring consisted of deployment of mussel cages (Figure 1) at preselected locations (Table 1; Figure 2) for about 3 months period, during which mussels accumulate contaminants. After retrieving the cage, accumulated contaminants levels in organism flesh measured. Caging method enables to control the age and sexual condition of organisms.

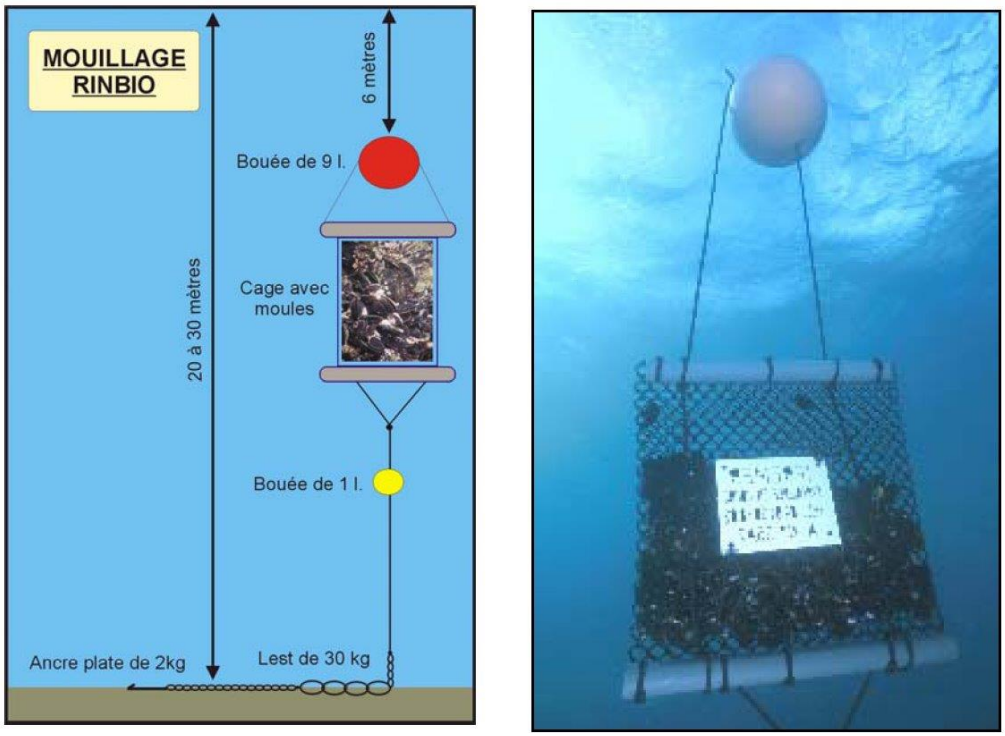

Figure1. Mussel cages used in this study.

The amount of accumulated contaminants is strongly related to the biological cycle, including age and sexual mating stage whereas, the seawater conditions (salinity, temperature, trophic level, etc...) are also affect not only bio-disponibility and contaminant speciation but also the metabolism and growth of targeted mussels. If the concentrations in tissues are linked to the ambient concentrations of available contaminants, the bio-accumulation factor (ratio between soft tissues concentration and available contaminants in the water) depends on the trophic level.

6.1. Placing, duration of immersion and recovery

The deployment of mussel cages were performed by R/V l'Europe (IFREMER) on April 2011 and retrieve was performed by R/V Piri Reis (Dokuz Eylül University) on

July 2011. Mussels "*Mytilus galloprovincialis* (MG)" was collected from an aquaculture farm in the outer part of Izmir Gulf and "*Brachydontes* (B)" were collected from Mediterranean coasts of Turkey from their natural habitat. About 1 kg of the collected organisms (*Brachydontes)* was reserved for the measurement and determination of base line contaminant levels (naturally existed).

Nine stations on the coasts of Mediterranean Sea was selected for the deployment of mussel cages (Figure 2). The station locations are chosen among the regions which are influenced by different character of input (riverine input, industrial effluens, seawage etc..) namely: Marmaris Gulf, Fethiye Gulf, Antalya Gulf (2 stations), Anamur Coast, Goksu Delta, Mersin Gulf, Iskenderun Gulf (2 stations). For stations positions see Figure 2 and Table 1. Maximum depth of the stations were 38 meters and their location were far away from trawling sites. During the collection of cages we discovered that some of the cages were missing and we could not obtain any sample from station Iskenderun-1 (see figure 2 for station location). Furtermore we got *Brachydontes* (B) samples from only one station (Iskenderun-2).

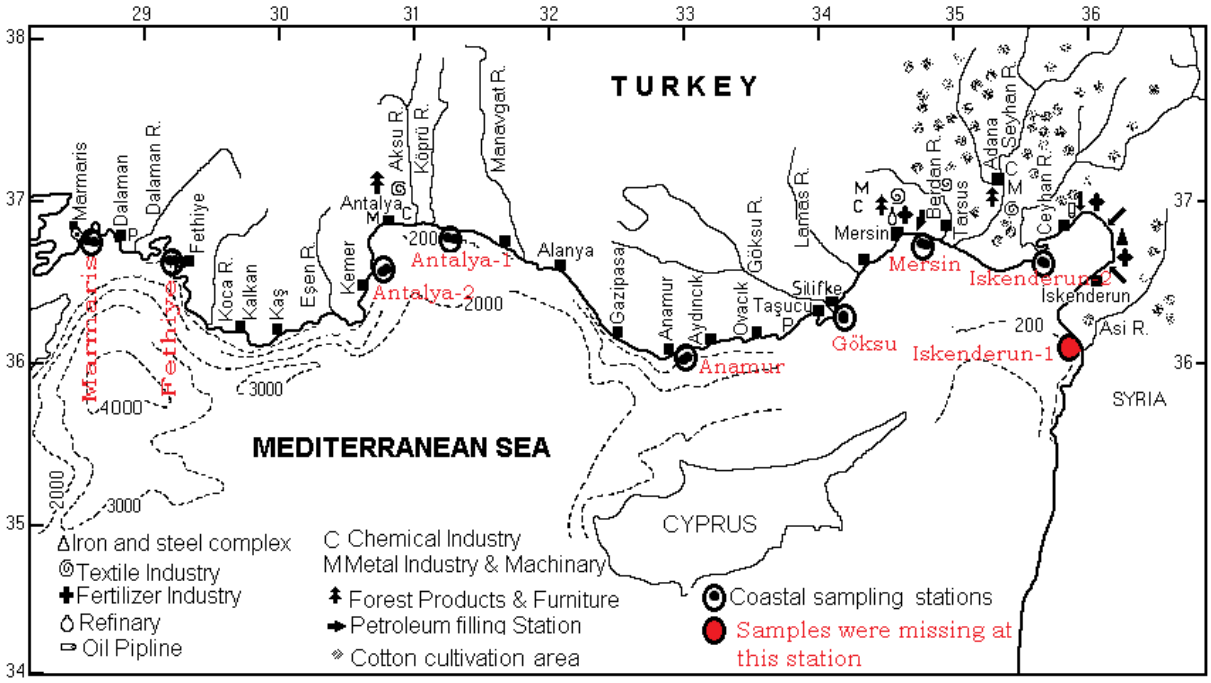

Fig. 2. Location of stations along the coasts of Mediterranean Sea.

Table 1. The coordinates of the stations

Location	Latitude (N)	Longitude (E)	Depth (m)
1) İskenderun 1	36^0 20’ 06.85” N	35^0 45’ 41.67” E	27 m
2) Iskenderun 2	36^0 38’ 09.97” N	35^0 41’ 00.78” E	19 m
3) Mersin	36^0 39’ 51.51” N	34^0 28’ 52.81” E	21 m
4) Goksu	36^0 18’ 31.77” N	34^0 05’ 57.91” E	15 m
5) Anamur	36^0 02’ 44.99” N	32^0 51’ 53.99” E	18 m
6) Antalya 1	36^0 47’ 20.51” N	31^0 12’ 31.93” E	16 m
7) Antalya 2	36^0 30’ 06.00” N	30^0 34’ 18.38” E	17 m
8) Fethiye	36^0 40’ 29.48” N	29^0 00’ 34.34” E	20 m
9) Marmaris	36^0 46’ 38.98” N	28^0 18’ 11.36” E	17 m

6.2. Mussel sample preparation

Mussel samples were prepared according to “UNEP/FAO/IOC/IAEA: Sampling of selected marine organisms and sample preparation for trace metal analysis. Ref. Method No. 7” and “UNEP/FAO/IOC/IAEA: Sampling of selected marine organisms and sample preparation for the analysis of chlorinated hydrocarbons. Ref. Method No. 12”.

6.3. Heavy Metal Analysis

Instrumentation: A GBC SensAA dual atomic absorption spectrophotometer equipped with hollow cathode lamp for each metal are used for the analysis of metals. Mercury concentration are measured by cold vapor technique by using GBC HG3000 hydride system and for flameless (graphite furnace) analysis GBC GF3000 graphite unit equipped with GBC PAL3000 autosampler are used . The instrumental conditions are those recommended in users handbook of the instrument.

6.4. Drying and digestion procedure of mussel samples:

Mussel samples were analyzed on dry weight basis. The samples were freeze dried by Freeze-Dryer (LABCONCO). 0.5-0.6 g of freeze dried sample was transferred into the teflon lined high pressure decomposition vessels (Milestone

StartE). Digestion was achieved by slow addition of appropriate amount (10 ml) of concentrated nitric + perchloric acid mixture and heated for 20 minutes under pressure. After cooling to room temperature, the digested samples were transferred to 50 ml capacity of volumetric flasks. The Teflon vessels were rinsed with distilled water twice and the solutions were combined. Then distilled-deionized water was used to make up the volume.

6.5. Mercury (Hg) analysis in mussel samples:

"UNEP/FAO/IOC/IAEA: Determination of total mercury in selected marine organisms by cold vapour atomic absorption spectrophotometry. Ref. Method No: 8" was used for mercury analysis. The measurements done by employing GBC HG3000 hydride generation system equipped with MC3000 vaporization unit. Tin(II) chloride was used as the reducing reagent. The analytical calculations were done by employing standard calibration curves. The validity of the method was controlled with reference material digested and analyzed at the same time with samples.

6.6. Copper, cadmium, zinc, analysis in mussel samples:

The samples are analysed by using the method "UNEP/FAO/IOC/ IAEA: Determination of total cadmium, zinc, lead and copper in selected marine organisms by flameless atomic absorption spectrophotometry. Ref. Method No: 11". 0.5-0.6 g of dried sample was transferred into the microwave digestion system vessels (Milestone StartE). Digestion was achieved by slow addition of appropriate amount (10 ml) of concentrated nitric + perchloric acid mixture and heated for 20 minutes under pressure. After cooling to room temperature, the digested samples were transferred to 50 ml capacity of volumetric flasks. The Teflon vessels were rinsed with distilled water twice and the solutions were combined. Then distilled-deionized water was used to make up the volume.The validity of the method was controlled with reference material digested together with samples.

6.7. Analysis of petroleum hydrocarbons (PH) and halogenated hydrocarbons (HH) in mussel samples

The methods used for the analysis of PH and HH in biota are: “Reference Method No: 12 Rev.2, UNEP/FAO/ IAEA/IOC: Sampling of selected marine organisms and sample preparation for the analysis of chlorinated hydrocarbons. UNEP, 1991”, “Reference Method No 6, UNEP/FAO/IOC/IAEA: Guidelines for monitoring chemical contaminants in the sea using marine organisms. UNEP, 1993”, “Reference Method No 57, UNEP/IOC/IAEA/FAO: Contaminant monitoring programs using marine organisms: Quality assurance and good laboratory practice. UNEP, 1990”.

6.8. Preparation of Samples for analysis:

For the PH analysis 4-5 g of freeze-dried sample were extracted in a microwave extraction system (1200W, temperature increases to 115ºC in 10 minutes and wait 20 minutes at this temperature) using 30 ml of methanol and internal standarts (n-C_{19}d40, n-C_{32}d66, Hexamethylbenzene, Cadalene, Naphthalene-d8) for recovery were added to the sample. After the extraction is completed, 5 ml 2 M KOH were added to the flask and the extraction was continued for 10 more minutes to saponify the lipids. The extract is transferred into a separatory funnel with 5 ml of water and extracted with 20 ml of hexane and 2 ml saturated NaCl solution. Then re-extracted again twice with 15 ml of hexane. All hexane extracts are combined, filtered through glass wool and dried with anhydrous sodium sulfate. The total lipid was determined in the aqueous phase. The hexane fraction was concentrated to 1 ml and transferred into the silicagel-alumina column which was pre-cleaned (with methanol and hexane) and dried.

4-5 g of dried biota sample were used for the analysis of halogenated hydrocarbons. The sample was extracted with a microwave digestion system (1200W, temperature increases to 115ºC in 10 minutes and wait 20 minutes in this temperature) using 30 ml hexane/acetone (90:10) by adding internal standarts (PCB29, PCB198, Endosulfan Id4, ε-HCH). After the extraction was completed, the extract was concentrated to about 15 ml with a rotary evaporator. Then the extract was dried with sodium sulfate and concentrated with nitrogen down to 1 ml. An appropriate volume of extract was taken to determine EOM (extractable organic

matter) gravimetrically. If the lipid content of the extract is more than 100-150 gr, sulfuric acid (about 5ml) was used for the removal of lipids. The samples were then transferred into florisil column which was precleaned with methanol and hexane and dried. Before fractionation, florisil was activated at 130°C for 8 hours and deactivated with 0.5 % water.

6.9. Gas Chromatography:

After the sample introduced in to the column, fractions were separated by eluting the sample with different solvent mixtures. The first fraction (saturated aliphatics) of petroleum hydrocarbons was eluted with 20 ml hexane, the second fraction (unsaturated and aromatic hydrocarbons) was eluted with 30 ml hexane: dichloromethane (90:10, v/v).

The first fraction (PCBs, pp' and opDDE, HCB, aldrin, heptachlor) was eluted with 70 ml of hexane, the second fraction (DDTs, DDDs, toxaphene, HCH isomers, chlordane) is eluted with 45 ml of hexane:dichloromethane (70:30, v/v), the third fraction (dieldrin, endrin ve endosulfan) is eluted with 70 ml dichloromethane for halogenated hydrocarbons. The fractions were first reduced to 15 ml by using Kuderna- Danish apparatus, then concentrated down to 1 ml under stream of N_2 gas and injected to gas chromatography.

The quality of the analytical data was assured using the reference material of IAEA-432 (mussel sample). Blanks were run periodically during the. The blank values of the analytical procedure always remained below the detection limits. The detection limits were 0.10–0.57 pgg^{-1} for OCPs, 2.4–4.5 pgg^{-1} for PCBs, 2.01-9.1 ngg^{-1} for aliphatics and 3.97-9.79 ngg^{-1} for PAHs.

6.10. Gas Chromotography Conditions for Petroleum Hydrocarbons:

Column 30m x 0.25mm, film thickness 0.25 µm
Carrier gas: Helium (99.99 % pure)
Inlet pressure: 13.728 kPa
Purge flow: 30 ml/min
Inlet temperature: 280ºC

Detector temprature: 250°C

Oven Temperature program: Initially 50 °C for 1 min, then increased to 200 °C with a velocity of 25 °C/ min, increased to a temperature of 316 °C with a velocity of 8 °C/ min held for 10 min.

MS Quad: 150ºC

MS Source: 230ºC

6.11. Gas Chromotography Conditions for Halogenated Hydrocarbons:

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

Carrier gas: Helium (99.99 % pure)

Inlet pressure: 13.728 kPa

Purge flow: 30 ml/min

Inlet temperature: 300ºC

Detector temprature: 250°C

Oven Temperature program: Initially 70 °C for 2 min, then increased to 150 °C with a velocity of 25 °C/ min, increased to a temperature of 200 °C with a velocity of 3 °C/ min and up to 280 °C with a velocity of 8 °C/min held for 10 min.

MS Quad: 150ºC

MS Source: 230ºC

7. RESULTS AND DISCUSSION

The contaminants (metals, petroleum hydrocarbons and halogenated hydrocarbons) concentrations determined in caged mussels from 8 stations along the Mediterranean coast of Turkey. The results are given in Tables 2, 3 and 4.

7.1. HEAVY METALS

The results of heavy metal concentrations were summarized in Table 2. For comparison of the results the bar graphics prepared for each metal were shown in Figures 3, 4, 5 and 6.

Table 2. Heavy metal concentrations measured in MG and B samples.

		STATION COORDINATES					
STATION	Total Depth	Lat N	Long E	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Hg (ng/g)
Iskenderun 1	27 m	36.331	35.761				
Iskenderun 2	19 m	36.631	35.683	2.99	5.95	237.27	31.46
Mersin	21 m	36.685	34.474	2.21	4.30	169.03	27.24
Goksu	15 m	36.309	34.099	2.38	4.61	237.22	24.75
Anamur	18 m	36.046	32.865	3.62	4.88	364.45	54.03
Antalya 1	16 m	36.789	31.209	4.04	5.10	225.83	53.63
Antalya 2	17 m	36.502	30.572	4.25	3.77	276.22	54.86
Fethiye	20 m	36.675	29.009	3.40	6.25	186.49	46.48
Marmaris	17 m	36.777	28.303	2.88	9.08	275.04	74.28
Iskenderun 2	Brachidontes	36.631	35.683	2,10	23,70	103,33	27,4

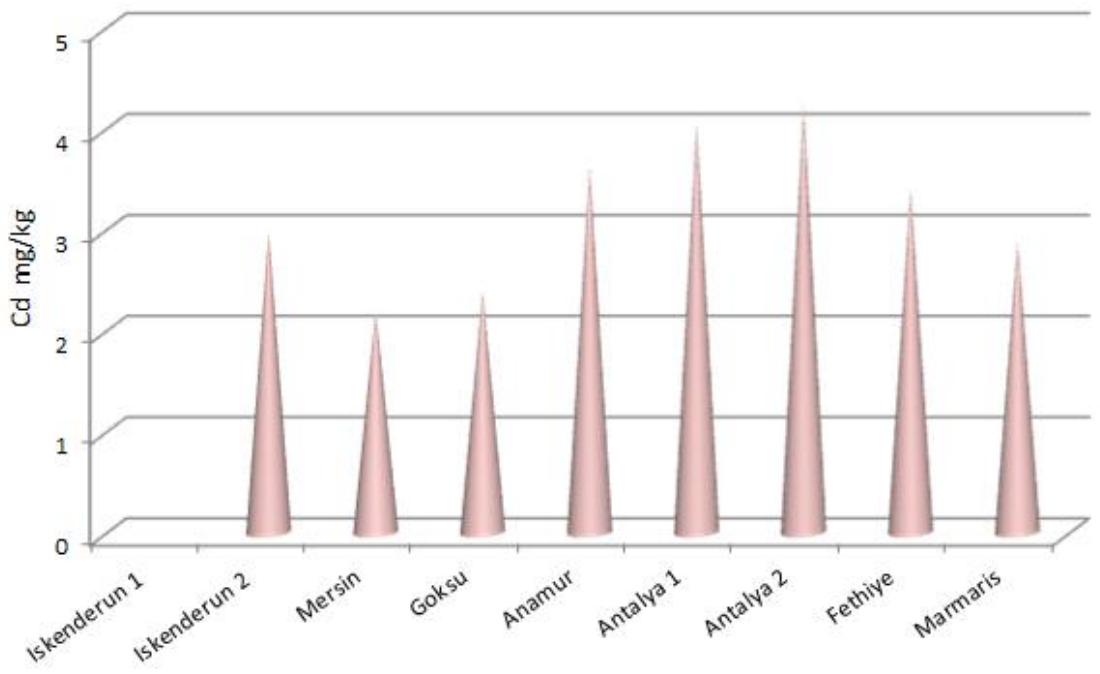

Figure 3. Cd concentrations in MG along Mediterranean coast of Turkey.

7.1.1 Cadmium:

The Cd concentrations obtained from different locations are shown in Figure 3. The highest cadmium concentrations were measured in samples from Golf of Antalya and the lowest concentrations were measured in those samples from Mersin and Göksu. Samples from Anamur ranked in the second order and Fethiye samples in the third with respect to their cadmium concentration. Marmaris and Iskenderun-2 samples contains almost same amount of cadmium.

As mentioned above the samples deployed at station Iskenderun-1 was missing. Further more we could get Brachydontes samples only from station Iskenderun-2 thus it is not possible to compare the results with those from other locations. If we compare the results from MG at same station the Cd concentration in both species is almost identical .

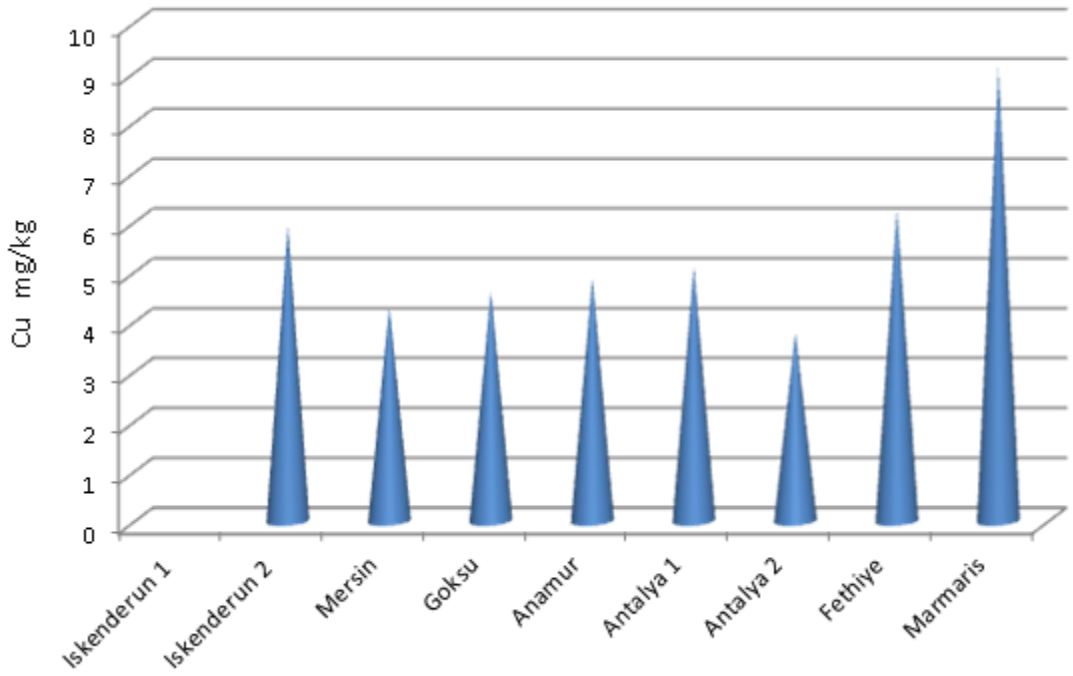

Figure 4. Cu concentrations in MG along Mediterranean coast of Turkey.

7.1.2. Coper:

The graphic of coper concentration versus locations is illustrated in Figure 4. The highest coper concentrations were measured in samples from Marmaris station and the lowest concentrations were measured in those samples from Antalya2. Samples

from Fethiye and Iskenderun2 contain almost identical amound os coper and ranked in the second order. Antalya1 samples ranked in the third order with respect to their coper concentration. Mersin, Göksu and Anamur samples contains almost same amount of coper.

If we compare the results from MG and B at same station (Iskenderun2) the Cu concentration in B is about 4 times higher than MG's.

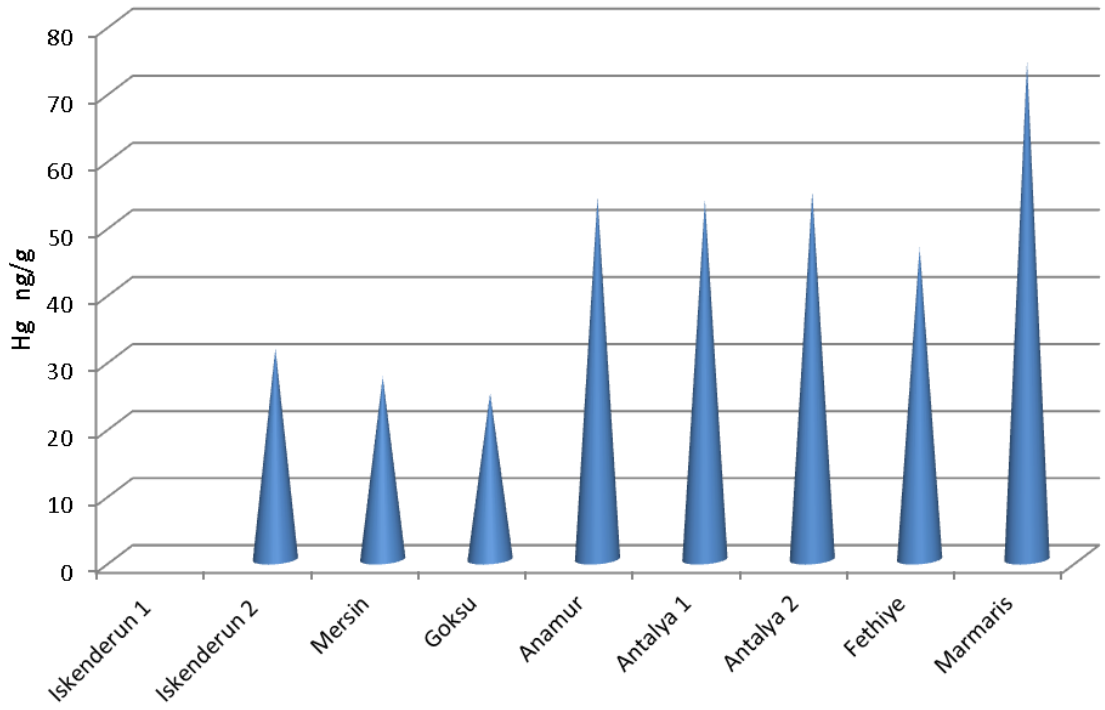

Figure 5. Hg concentrations in MG along Mediterranean coast of Turkey.

7.1.3. Mercury:

Mercury concentrations is drawn against sampling locations and the graph is given in Figure 5. As in the case of coper the highest mercury concentration measured in samples from Marmaris. Samples from Anamur, Antalya1 and Antalya2 rank in second order and contains almost identical amount of mercury. Samples from Fethiye rank in the third order in their mercury content and the lowest concentration was measured in the samples from Göksu stations. The mercury concentrations in the B samples are identical with those of MG samples from Iskenderun2 station.

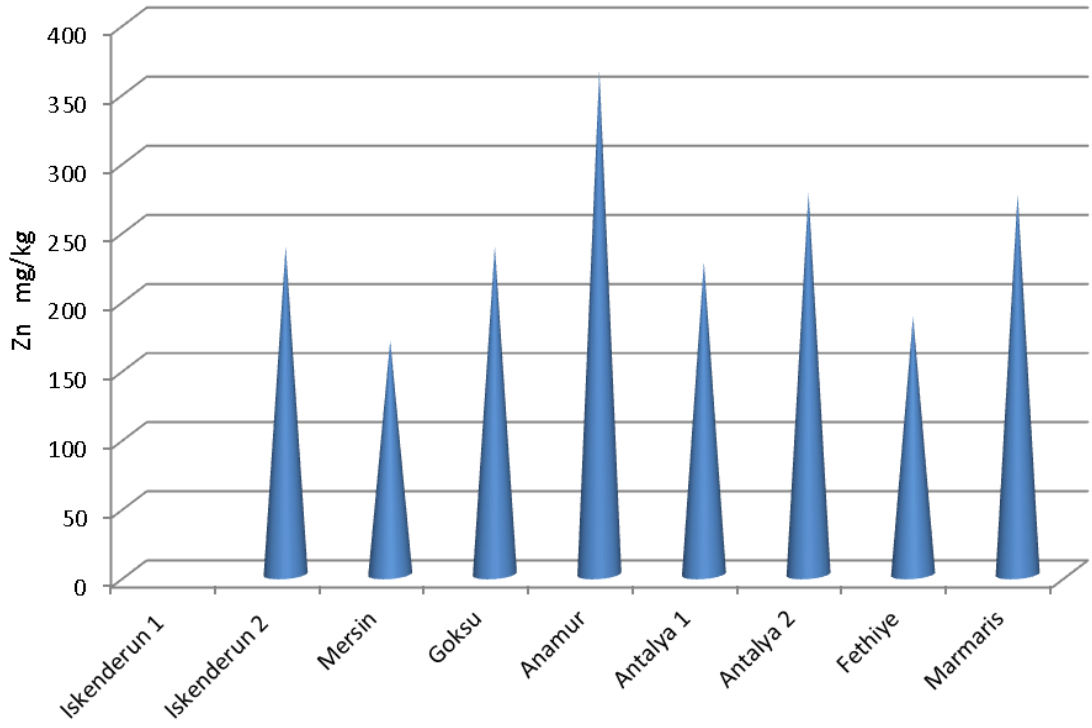

Figure 6. Zn concentrations in MG along Mediterranean coast of Turkey.

7.1.4. Zinc:

Zinc, one of the essential elements for organizms is highest in samples from Anamur. Antalya2 and Marmaris samples rank in second order while Antalya1 Iskenderun2 and Göksu samples rank in third order in their Zn content. The lowest Zn concentrations were measured in the samples from Mersin Bay and Fethiye Bay. The zinc concentration in B samples is almost half of the MG samples from same locations (station Iskenderun2) 103,33 mg/kg 237.27 mg/kg respectively.

7.2. ORGANIC POLLUTANTS

Mesured organic pollutants (petroleum hydrocarbons and PCB's) in the mussels are given in Table 3 and Table 4.

7.2.1. Total Aliphatic PH

For comparison the concentrations of total aliphatic hydrocarbons are drawn against locations as bar chart and are given in Figure 7. The highest total aliphatic hydrocarbon concentrations were measured in samples from Mersin Bay, mussels from Marmaris rank in the second order and Antalya1 station mussels in the third

order in their total aliphatic PH content. All these stations take place in the vicinity of commercial harbors. Further more there are petroleum storage tanks at the coastal side of Mersin station. Göksu mussels contain the lowest amount of aliphatic hyrdocarbons. A comparison between MG and B species showed that B species accumulate three times more aliphatic hydrocarbons 8045 ng/g (MG) vs 27152 ng/g (B) then did MG (Table 3).

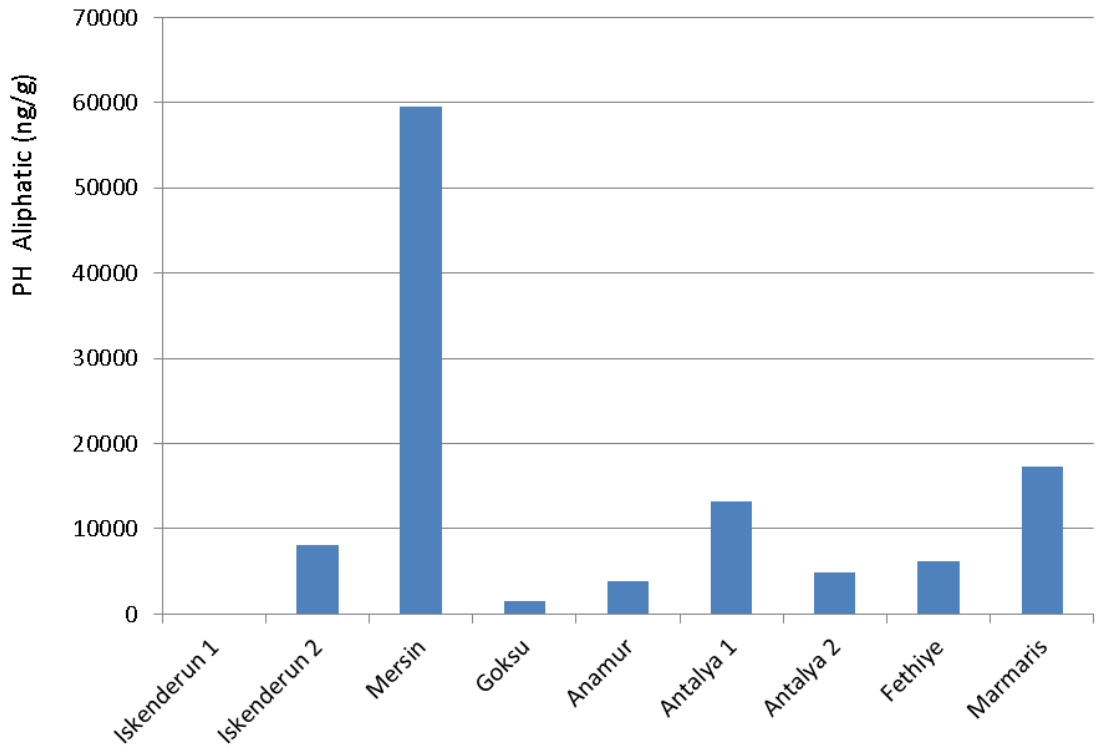

Figure 7. Aliphatic PH concentrations in MG along Mediterranean coast of Turkey.

7.2.2. Total Aromatic PH

The bar graph of measured total aromatic PH concentrations against locations are given in Figure 8. Mussels from Marmaris accumulated the highest amount of aromatic PH and mussels from Mersin Bay rank in the second order. Samples from Iskenderun2 accumulated considerable amount of aromatic PH and rank in the third order. As in the case of aliphatic PH Göksu mussels accumulated lowest amount of aromatic PH. Comparison between MG and B showed that both species accumulated almost identical amount of aromatic PH (4161 ng/g (MG) and 6501 ng/g (B)). In Figure 9 total PH (aromatic+aliphatic) is drawn against sampling locations. The concentration distribution of total PH is very similar to that of aliphatic PH.

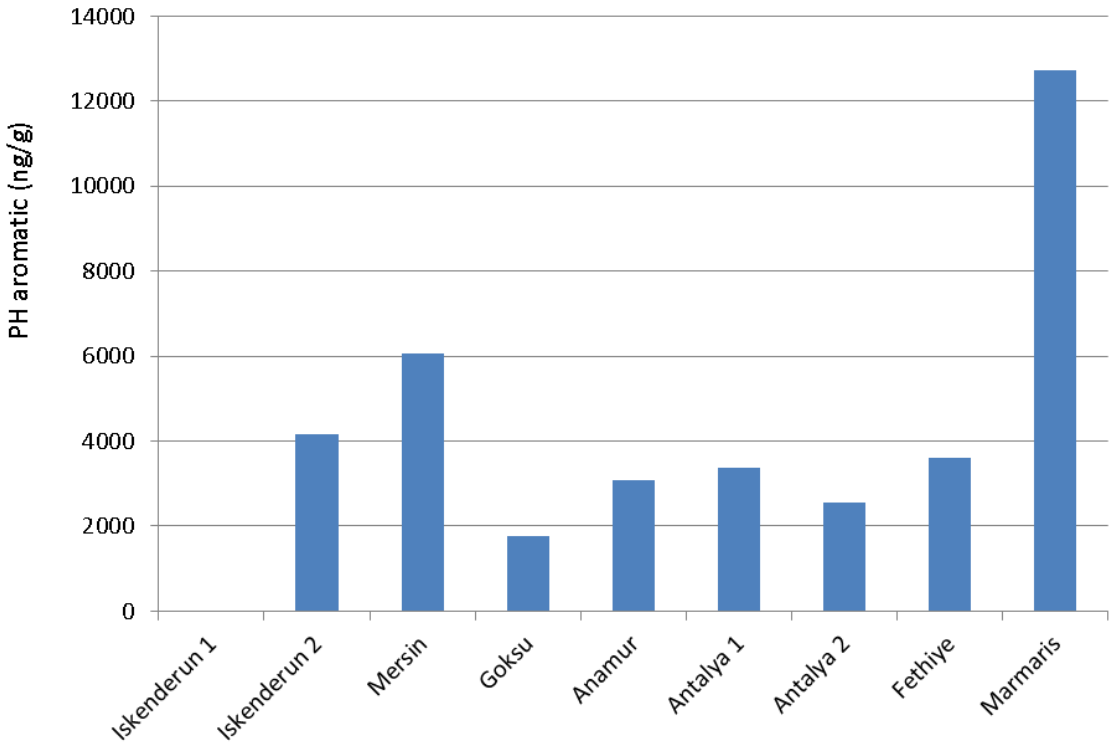

Figure 8. Aromatic PH concentrations in MG along Mediterranean coast of Turkey.

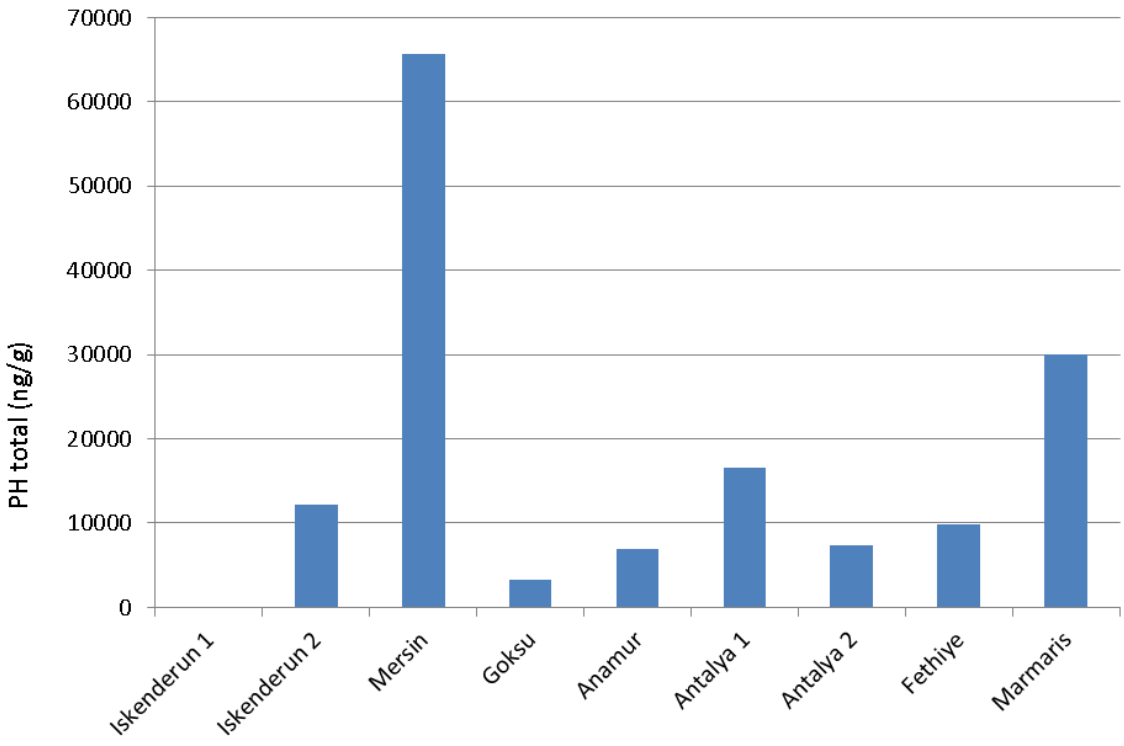

Figure 9. Total PH concentrations in MG along Mediterranean coast of Turkey.

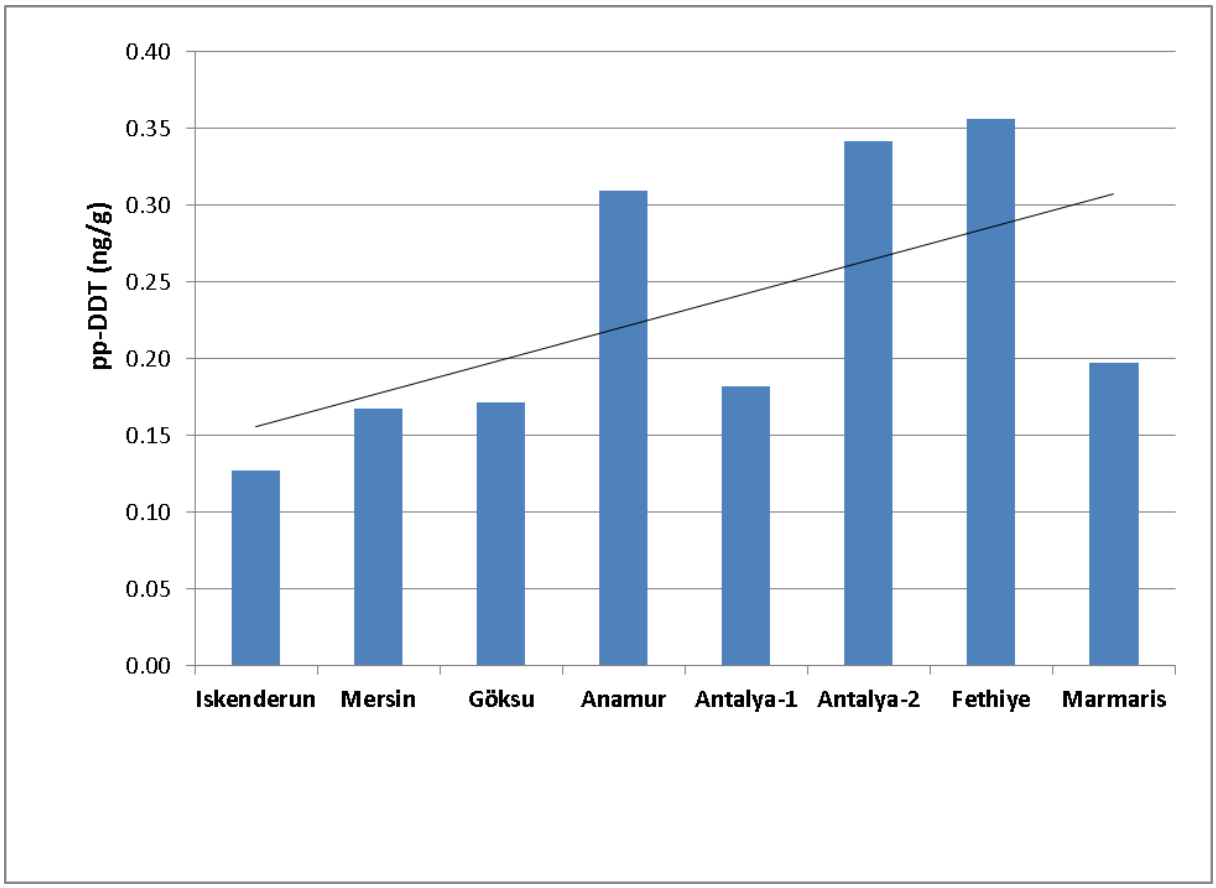

Figure 10. pp-DDT concentrations in MG along Mediterranean coast of Turkey.

7.2.3. PCB's

The results obtained from PCB's analysis of mussels are summarized in Table 4. The pp-DDT and pp-DDE concentrations are drawn against locations and are given in Figure 10 and Figure 11. When two graphics are compared they show opposite trends. If Marmaris excluded the highest concentrations of pp-DDT were measured at stations located in the western Mediterranean coasts of Turkey. Towards the stations located eastern Mediterranean coasts the concentration decrease and it reaches its lowest concentration at the most eastern Iskenderun2 station (Figure 10). When two species MG and B are compared, B contains about 4 times higher pp-DDT concentrations then that MG (Table 4).

The ppDDE concentrations is highest in mussels from stations located at eastern coasts (Iskenderun2 and Mersin) and decrease gradually towards the western coastal stations (Marmaris and Fethiye) (Figure 11). Again if we compare between

the pp-DDE of two species MG and B, it is obvious that pp-DDE concentration in B is higher than those MG more then 3 fold (about 4 times higher) (Table 4).

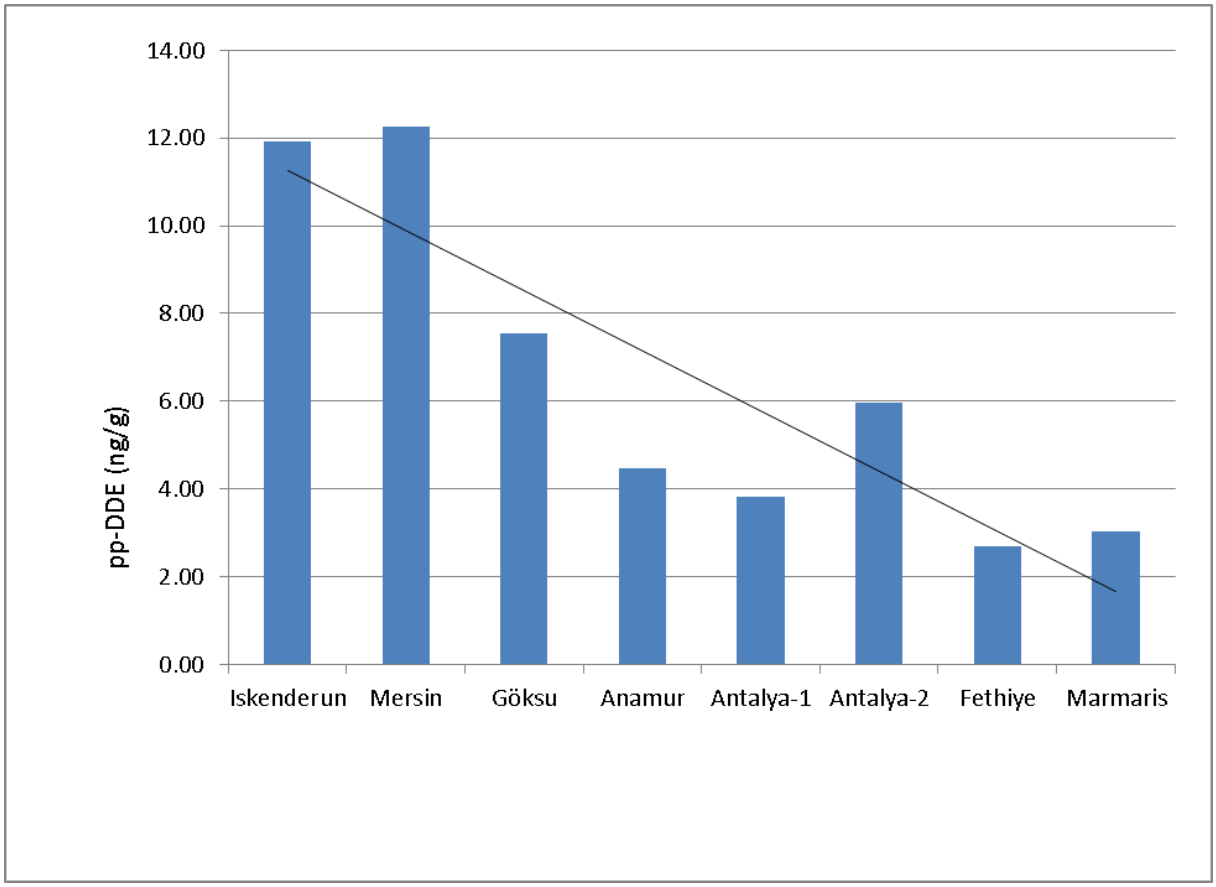

Figure 11. pp-DDE concentrations in MG along Mediterranean coast of Turkey.

8. CONCLUSIONS

During the last quarter-century industrial complexes, oil filling plants and industrialization in coastal areas brought rapid growth of population. Again rapidly growing indoor-outdoor tourism activities concentrated at Coastal areas of the region, has created serious environmental problems. Especially, at semi-enclosed basins such as the Gulf of İskederun and Gulf of Mersin and wide and shallow continental shelf areas a significant increase in annthropogenic pollutants (industrial and domestic waste), have been created important changes in marine ecosystems.

Findings during the long-term monitoring studies done under the MED POL in previous years reveal that Pristane / Phytane ratio of Mersin fish samples is 0.94

indicating petrogenic pollution in the region. During MYTITURK project studies the highest total aliphatic hydrocarbon concentrations in the mussels (MG) samples was measured from the Gulf of Mersin. Although, the highest aromatic PH was measured in samples from Marmaris, Gulf of Mersin rank in second order. In addition (to being limited connection with open sea) relatively long residence time of chemical pollutants in coastal areas (especially semi-enclosed basins, with a wide and shallow continental shelf areas, such as the, İskederun and Mersin bays), enhence their impact on marine ecosystems.

Prior to breeding of terrestrial sources of pollutants, selection of deep sea discharge area and the bio-chemical treatment to be applied of domestic wastewater before draining marine outfall, bio-chemical properties and the basic hydro-dynamic properties of the receiving environment must be determined and well documanted. In summary, without a comprehensive and systematic research to protect and improve our natural resources is not possible to reveal realistic approaches and solutions.

Table 3. Petroleum hydrocarbon concentrations (ng/g) along Mediterranean coast of Turkey.

Station	HEOM (µg/g)	n-C10	n-C12	1-methyl-naphthalene	1-ethyl-naphtahalene	n-C14	Ace-naphthalene	Acenaphthene	fluorene
Iskenderun 2	216	4867	234	54	13	66	124	34	44
Mersin	62	9957	280	64	124	120	365	225	423
Goksu	242	31	16	52	63	51	40	41	49
Anamur	636	142	42	0	0	0	0	69	27
Antalya 1	1259	10234	442	66	312	278	253	157	182
Antalya 2	519	1592	77	58	63	180	250	170	82
Fethiye	1330	1122	285	149	726	208	385	385	149
Marmaris	1012	5322	504	714	52	211	475	44	426
Iskenderun2 (B)	173	21168	821	95	206	256	286	358	213
Station	**n-C16**	**n-C17**	**pristane**	**phenanthrene**	**anthracene**	**n-octadecene**	**n-C18**	**phytane**	**2-methyl-phenanthrene**
Iskenderun 2	1081	309	108	1796	166	365	80	48	679
Mersin	262	244	104	187	180	176	79	322	501
Goksu	83	198	60	126	151	129	78	152	45
Anamur	121	274	123	137	498	188	167	69	204
Antalya 1	230	313	13	56	256	103	119	90	346
Antalya 2	289	395	192	203	268	249	98	68	152
Fethiye	421	502	109	149	198	228	470	278	149
Marmaris	1971	459	404	2905	399	1459	225	195	1897
Iskenderun 2 (B)	463	847	174	140	574	212	173	586	521
Station	**1-methyl phenanthrene**	**n-C20**	**3,6 dimethyl-phenanthrene**	**fluoranthene**	**n-C21**	**pyrene**	**n-C22**	**1-methyl-pyrene**	**n-C24**
Iskenderun 2	642	61	62	91	38	16	61	82	34
Mersin	164	1125	180	968	252	26	147	150	772
Goksu	195	87	158	63	139	269	42	102	71
Anamur	428	167	336	213	161	137	160	95	256
Antalya 1	495	47	252	193	135	471	57	54	45
Antalya 2	529	74	60	147	112	52	61	110	160
Fethiye	232	141	137	27	126	327	75	180	179
Marmaris	706	541	960	1607	291	39	383	303	489
Iskenderun2 (B)	606	0	369	306	610	1311	134	275	82

Table 3 cont'ed

Station	chrysene	n-C26	squalene	n-C28	perylene	n-C30	n-C32	n-C34	Total aliphatic	Total aromatic
Iskenderun 2	63	493	24	53	295	58	29	34	8045	4161
Mersin	474	40801	0	3845	1360	218	505	266	59547	6056
Goksu	71	72	50	0	329	113	104	61	1537	1755
Anamur	0	0	0	1126	937	194	345	353	3887	3081
Antalya 1	32	213	69	181	261	163	215	309	13255	3387
Antalya 2	56	358	97	162	580	122	266	172	4861	2565
Fethiye	79	1338	0	112	336	182	272	168	6211	3608
Marmaris	304	2776	0	746	1887	538	519	264	17297	12718
Iskenderun 2 (B)	143	159	219	127	1098	329	471	323	27152	6501

Table 4. PCB's concentrations (ng/g) along Mediterranean coast of Turkey.

Station	HEOM (µg/g)	alfa-HCH	HCB	beta-HCH	Lindane	Heptachlor	heptachlor exo epoxide	gama-Chlordane	alfa-Chlordane
Iskenderun	59.33	0.14	0.14	0.31	0.26	1.64	23.40	0.15	0.21
Mersin	64.67	0.04	0.11	0.06	0.05	1.04	28.05	0.62	0.11
Göksu	59.33	0.33	0.15	1.58	0.17	1.08	47.70	0.13	0.30
Anamur	36.00	0.09	0.20	0.27	0.47	1.61	15.49	0.14	0.33
Antalya-1	36.67	0.10	0.16	0.26	0.20	1.31	17.32	0.44	0.25
Antalya-2	56.33	0.10	0.18	0.74	0.39	1.76	88.63	2.09	0.36
Fethiye	30.67	0.04	0.33	0.22	0.61	1.74	22.15	0.27	0.37
Marmaris	59.00	0.15	0.66	0.26	1.64	2.81	16.30	0.34	0.59
Iskenderun (B)	60.00	0.00	0.42	1.97	1.72	0.00	22.19	12.44	0.68

Station	Dieldrin	pp-DDE	Endrin	pp-DDD	pp-DDT	AR1254	AR1260
Iskenderun	0.23	11.91	1.27	0.34	0.13	36.67	5.38
Mersin	0.11	12.26	0.45	0.13	0.17	21.59	3.92
Göksu	0.24	7.55	2.36	0.16	0.17	33.51	3.93
Anamur	0.23	4.48	0.66	0.17	0.31	127.43	2.71
Antalya-1	0.24	3.83	0.71	0.13	0.18	44.89	2.42
Antalya-2	0.26	5.97	0.79	0.16	0.34	44.47	6.89
Fethiye	0.33	2.69	3.05	0.19	0.36	31.37	2.54
Marmaris	0.60	3.02	1.39	0.28	0.20	33.04	5.22
Iskenderun (B)	0.91	38.81	1.56	0.99	0.54	138.30	3.97

9. REFERENCES

UNEP/FAO/IOC/IAEA: Sampling of selected marine organisms and sample preparation for trace metal analysis. Ref. Method No: 7

UNEP/FAO/IOC/IAEA: Determination of total mercury in selected marine organisms by cold vapour atomic absorption spectrophotometry. Method No: 8

UNEP/FAO/IOC/IAEA: Sampling of selected marine organisms and sample preparation for the analysis of chlorinated hydrocarbons. Ref. Method No. 12”

UNEP/FAO/IOC/ IAEA: Determination of total cadmium, zinc, lead and copper in selected marine organisms by flameless atomic absorption spectrophotometry. Ref. Method No: 11

UNEP/FAO/IOC/IAEA: Guidelines for monitoring chemical contaminants in the sea using marine organisms. Reference Method No 6.

UNEP/IOC/IAEA/FAO: Contaminant monitoring programs using marine organisms: Quality assurance and good laboratory practice. Method No 57.

UNEP/IOC/IAEA: Determination of DDTs and PCBs in selected marine organisms by packed column gas chromatography. Method No: 14

10. FINANCIAL REPORT

The expenditures mostly includes those chemicals necessary to perform the analysis and gases used by instruments (nitrogen, argon, dry air etc.). Some other expenditures are tavelling allowances and trvelling expences, a concentrating column (gold trap used for mercury analysis), purchase of a desktop computer.