J. Black Sea/Mediterranean Environment
Vol.15: 165- 178 (2009)

Oil pollution in the Black Sea marine organisms during 2003-2006: mussel, shellfish, and algae

Karadeniz deniz organizmalarında 2003-2006 yıllarında petrol kirliliği: midye, deniz salyangozu ve deniz algleri

Kasım Cemal Güven*, Filiz Nesimigil, Selin Cumalı

*Istanbul Aydın University, İnönü Cad., 40, Sefaköy, Istanbul, Turkey.

Abstract

Oil pollution was investigated in mussel, shellfish and 3 green, 1 brown and 2 red algae collected different part of the Black Sea coast of Turkey. The oil pollution was found in the samples collected from the east part of the Black Sea were found more polluted than west and middle part of the Black Sea coast of Turkey.

The maximum oil pollution levels in the mussels samples collected in 2005-2006 are similar as 106.01-107.33 µg/L wet weight.

Oil pollution found in mussel, *Rapana venosa* and algae were found high in east part of the Black Sea coast of the Black Sea. The maximum oil level in *R.venosa* was found as 15.80 µg/g in Yeşilırmak River mouth. The high pollution of algae samples were found as 141.83 µg/g in *Enteromorpha compressa* collected from Samsun Harbour.

In generally high concentration of oil in the Turkish Black Sea coast have been found in harbour samples. Limited water exchanged in harbour is the main cause of the oil contamination.

In generally oil pollution in algae was higher than in mussel and in *R. venosa.*

Keywords: The Black Sea, oil pollution, mussel, shellfish, algae.

***Corresponding author:** kcguven@yahoo.com.tr

Introduction

Oil is almost inevitable pollutant for sea. Oil enters to marine from many sources as shipping traffic, oil production, pipline breaks, illegal discharge of tanker ballast water, tanker accident, refinery and from air, incompletely burned fuel, automobile exhausted gas, wood-burning etc. Oil pollution especially polyaromatics (PAHs) are important. Marine organisms were taken up oil from the sea and it incorporated in their body (Murray et al. 1991, Baumard et al. 1998). It is a health risk from consumption of sea food contamined by oil derived carcinogens PAHs.

Petroleum is a complex mixture and contents thousands aliphatic and aromatic group compounds. Every crude oil contents the similar homologous series but not the same concentration. Thus crude oils are not markedly in chemical composition.

Contamination of marine water by petroleum cause acute or chronic toxicity for marine organisms. It was accumulated by bivalves the whole and cane be used as bioindicator for pollution. It affects productivity and quality of marine organisms.

Mussel is filter feeding organism, accumulated and released of oil in 1-2 days and transformed in 13-18 days (Lee et al. 1972, Fossato and Canzonier 1976, D'Adamo et al. 1997, Rantamaki 1997. The first report on transformation of PAH compounds as 1-methylnaphtalene and anthracene by mussel were demonstrated by Tomruk and Güven (2008).

The paper published on oil pollution in mussel were collected from coastal area are: from Germany, France, Spain (Baumard et al. 1998 a,b), Spain (Hernandez 1995), in northern Adriyatic Sea (Notar and Leskovsek 2000), in Dardanelle, Turkey (Güven et al. 2003), in native and caged mussel, (Piccardo et al. 2001) and in tanks (D'Adamo et al. 1997).

Oil pollution in marine organisms after tanker accidents or Gulf War was:

Amoco Gadiz	April 1978 in English Channel (Dauvin 1998)
Exxon Waldes	24.March.1989 Prins William Sound, Alaska (Baker et al. 1989, Saxton et al. 1993)
Aegean Sea	03.Dec.1992 in Gallicia Coast (Porte et al. 2000)
Nassia	14.March.1994 in Bosphorus (Güven et al. 1995, 1998)
Sea Empress	15.Feb.1996 in Milford Haven West Wales (Leonard et al. 1998, Batten et al. 1998)
Gulf War	1990-1991 in Arabian Gulf (Tawfiq and Olsen 1993)

There are not found a literature on shellfish.

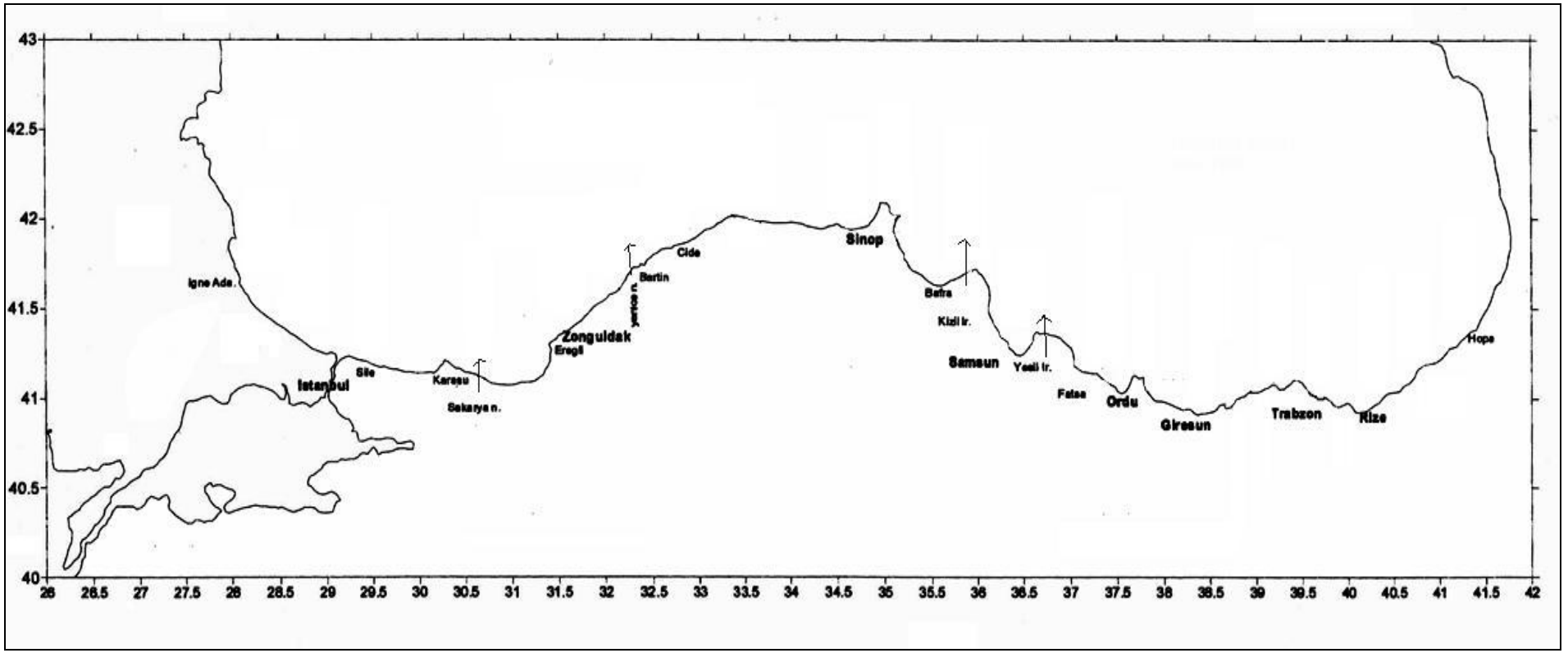
The oil pollution in algae were investigated by various authors (George 1961, Clarck and Blumer 1967, Youngblood et al. 1971, Clarck and Finley 1974, Farrington and Tripp 1977, Rossi et al. 1978, Mironov et al. 1981, Knutzen and Sortland 1982, Peckol et al. 1990, Güven et al. 1996, Binark et al. 2000, Erakın and Güven 2008).

In this work oil pollution in *Mytilus galloprovancialis, Rapana venosa* and six algae collected from the Black Sea were investigated during 2003-2006.

Material and Methods

The sampling stations in the Black Sea are shown in Figure 1.

Figure 1. Sampling station



Mussel:	*Mytilus galloprovincialis* Lamarck, 1819
Shellfish:	*Rapana venosa L.*
Algae*:*	*Ulva rigida* J. Agardh
	Enteromorpha compressa (Linnaeus) Nees
	Chlodophora coelothrix (Kutzing)
	Cystoseria barbata (Stackhouse) J. Agardh
	Corallina granifera Ell.et Sool
	Laurencia obtusa J. Agardh

Extraction technique from mussel and shellfish

20-40 g (wet/weight) samples were mixed with the same amount sodium sulfate anhydrous and extracted with DCM in Soxhlet apparatus at 8 h. The extracts were filtered and dried over sodium sulfate anhydrous, distilled at 40 ^{o}C. The residue was saponified with 5 ml (5%) potassium hydroxide in ethanol solution. It was heated under reflux at 2 h in water bath then; 50 ml water is added and extracted with 30 ml pentane. The organic phase was separated and distilled. The residue was taken with DCM, dried over sodium sulphate anhydrous, filtered and distilled at 40 ^{o}C. The residue was taken with hexane and the volume was adjusted 10 ml. Its intensity was measured by ultraviolet spectrofluorometer (UVF).

Extraction of algae

100g wet weight alga was extracted with 50 ml DCM at 8 h in Soxhlet apparatus. The extract was distilled at 40 ^{o}C and the residue was dried over anhydrous sodium sulphate then distilled at 40 ^{o}C. The residue was taken with hexane and the volume adjusted to 10 ml then analyzed similar to mussel by UVF.

Standard curve of oil

The standard curve was plotted with Russian crude oil as a reference while it was mainly transported via the Black Sea. The concentrations of reference crude oil were 0.25-1.5 µg/ml in hexane. The fluorescence intensity was measured by ultraviolet spectrofluorometer (UVF) (Shimadzu 1501) at 310/360 nm (ex/em). The calibration curve was plotted and its equation was taken from apparatus.

The solvents: Dichloromethane (DCM), hexane and chemicals sodium sulfate anhydrous are Merck products (Darmstadt, Germany).

Russian crude oil was obtained from TÜPRAŞ refinery.

Results

Oil pollution of mussel

1. The results on oil pollution in mussels collected of Turkish coast in the Black Sea are shown in Table 1-3.

Table 1. Oil pollution of mussel collected west part of the Black Sea (µg/g, wet weight).

Year / Stations	İğneada 1	İğneada 2	Yeniköy	Karaburun	Kıyıköy
23.08.2003	37.6	23.5	2.9	9.3	10.0
04.08.2004	4.21	3.67	2.47	3.29	1.62

The oil pollution was found higher in 2003 than 2004 samples collected from İğneada.

Table 2. Oil pollution of mussel in the station in Turkish coast of Black Sea in 2005 (µg/g, wet weight).

Station	April	Sept.
İğneada St. 1	-	46.21
İğneada St. 2	27.54	46.17
İğneada St. 3	17.37	31.61
Karaburun	-	2.34
Zonguldak 1	17.80	67.74
Zonguldak 2	-	31.61
Cide	44.31	31.41
Bafra	57.56	-
Sinop	42.39	14.80
Samsun Harbour	47.85	43.57
Giresun Harbour	36.34	49.45
Ordu	63.22	82.78
Trabzon Harbour	65.85	104.28
Rize Harbour	38.00	41.52
Hopa Harbour	107.33	46.17

-was not determined

The highest oil pollution was found in April 2005 in Hopa Harbour and in September 2005 in Trabzon Harbour.

Table 3. Oil pollution of mussel in the station in Turkish coast of the Black Sea in September, 2006 (μg/g, wet weight).

İğneada 1	17.66
İğneada 2	37.81
İğneada 3	-
Zonguldak	106.01
Bartın	60.71
Sinop Harbour	27.94
Samsun Harbour	104.01
Ordu Harbour	27.91
Giresun Harbour	36.65
Trabzon Harbour	42.05
Rize Harbour	42.27
Hopa Harbour	55.71

The oil pollution was found high in sample collected in Zonguldak and Samsun Harbour at similar level.

2. *Oil pollution of Rapana venosa*

Oil pollution level in *R. venosa* samples collected from river mouth and İğneada-Rize coasts are shown in Tables 4 and 5.

Table 4. Oil pollution of *Rapana venosa* in April, 2005.

Sakarya River mouth, Karasu	3.17
Kızılırmak River mouth, Bafra	15.75
Yeşilırmak River mouth, Çarşamba	15.80

Oil pollution of *R.venosa* was found high in Yeşilırmak and Kızılırmak River mouth. The lowest oil pollution was found at the mouth of Sakarya River.

Table 5. Oil pollution of *Rapana venosa* collected from between İğneada and Rize coasts in September 2006 (µg/g, wet weight).

İğneada 1	6.10
Zonguldak	3.83
Cide	3.97
Sinop Harbour	2.00
Samsun Harbour	80.10
Ordu	2.64
Ordu Harbour	26.02
Rize Harbour	3.88

Oil pollution level of *R.venosa* was found high in Samsun Harbour.

3. Oil pollution of algae

Oil pollution of algae is shown in Tables 5-6.

Table 6. Oil pollution of algae in April, 2004 (µg/g, wet weight).

Algae	Stations	Level
Corallina rubrum	Cide 1	18.61
	Cide 2	29.20
Chlorodophora coelothrix	Bafra	141.83
	Rize Harbour	97.57
Ulva rigida	Sinop	78.81
	Samsun 1	4.61
	Samsun 2	9.15
	Vakfıkebir	62.52
Ceramium rubrum	İğneada	6.91
	Giresun	25.55

Table 7. Oil pollution of algae in 2005 (µg/g, wet weight).

Algae	Stations	April	September
Ceramium rubrum	İğneada	7.37	5.98
Ulva rigida	İğneada	18.45	4.95
Corallina granifera	Cide	-	4.93
Ulva rigida	Sinop	4.83	4.40
Chlodophora coelothrix	Bafra	-	6.89
Ulva rigida	Samsun	35.51	6.68

The oil pollution of *Ulva rigida* was found high in Samsun sample.

Table 8. Oil pollution in alga collected in April, 2006 (µg/g, wet weight).

Algae	Stations	April	September
Ceramium rubrum	İğneada	6.91	-
Chlodorophora coelthorix	İğneada	-	8.51
Cystoseria barbata	Cide	29.20	-
Corallina granifera	Cide	18.61	-
Ulva rigida	Sinop H.	78.81	-
Enteromorpha compressa	Sinop H.	-	10.08
Gelidium latifolium	Sinop H.	-	1.30
Enteromorpha compressa	Samsun H.	141.83	16.23
Chlodophora coelthorix	Samsun H.	-	7.07
Ulva rigida	Giresun H.	-	2.25
Enteromorpha compressa	Trabzon H.	62.52	-
Enteromorpha compressa	Rize H.	95.57	-
Cystoseria barbata	Hopa H.	-	35.22

H.: Harbour

There are no data on oil concentration in mussel and *R.venosa* samples collected from Turkish Black Sea coast. Also oil contamination level in algae collected east part of Şile (Middle and east part of Turkish Black Sea coast) were not reported up to date.

Discussion

1. Mussel

Oil pollution in mussel collected west part of the Turkish Black Sea coast was found high in İğneada samples. The oil contamination range in mussels (wet weight, µg/g) are: 1.62- 57.6 in west part of the Turkish coast of the Black Sea and 2.34- 107.38 in 2005 and 17.66- 106.01 in 2006 sample collected from the middle and east parts of the Turkish coast of the Black Sea. The maximum oil pollution levels in the mussels samples collected in 2005-2006 are similar as 106.01- 107.33.

When compared the results of the east part of the Black Sea, Bosphorus with Dardanelles mussel samples were found the former were more polluted than the later.

2. Rapana venosa

The comparison of the oil pollution *Rapana venosa* collected Yeşilırmak River mouths was found more polluted than the sample collected from Samsun and Ordu Harbour.

3. Algae

Oil pollution in algae was found high in April 2006 in the sample of *Enteromorpha compressa* collected from Samsun, Trabzon and Rize Harbour, and of *Ulva rigida* in Sinop Harbour.

Oil pollution of algae in sea area of Turkey was first made after tanker accident occurred in 1994 as in Ceramium rubrum 290.00 μg/g Karaburun in the Black Sea, and in *Cystoseria barbata* 90.80 μg/g in Bosphorus (Güven et al. 1998) and *Cystoseria barbata* in Bosphorus sample 91.11 μg/g; *Ceramium rubrum* 196.76 μg/g (Binark et al. 2000).

In the present work the maximum level of oil pollution of algae was found in *Enteromorpha compressa* collected from Samsun Harbouras 141.83 μg/g. When compared the results of earlier and present work showed that the pollution of algae were high in all examined time.

Conclusions

In general high concentrations of oil in the Turkish Black Sea coast have been found in harbour samples. By comparing the data of oil concentration it can be concluded that oil concentration increases generally intensity of shipping traffic. Limited water exchanged in harbour is the main cause of the oil contamination.

-Oil pollution in mussel was found high in east part of the Black Sea.

-Oil pollution level was found for *R. venosa* sample collected also high in east part of the Black Sea.

-Oil pollution level for algae was also found high east part of the Black sea.

These results showed that oil pollution level in the east part of the Black Sea was higher then middle and east part of the Black Sea. The main

causes of the petroleum pollution in the east part of the Black Sea are location of loading stations in this area: for Russian and Kazakhstan oil as Novorossiyst, Subsa and for Caspian oil as Batum and Kulevi. All stations are located in the east part of the Black Sea. It is the main cause of the high pollution in sea water and also marine organisms.

Carcinogenic hydrocarbon in marine food is an important subject for human health. Public health authorities should be urged to establish laboratories for continuous surveys of the pollution level encountered in commercial sea food. Fish and shelf fish tainted by oil will again be fit for human consumption after a period from two weeks two several months.

Özet

Karadeniz Türkiye sahillerinde 2003 ile 2006 yılları arasında midye, deniz salyangozu ve 6 deniz algi üzerinde petrol kirliliği araştırılması yapılan bu çalışmada Karadeniz'in doğu kısmındaki örneklerde kirliliğin daha fazla olduğu bulunmuştur. Özellikle limanlar üzerindeki örmeklerde bulunan petrol kirliliği miktarının yüksek olduğu saptanmıştır.

Acknowledgment

The authors are thankful to Prof. Dr. E. Doğan, the Director of Institute of Marine Science and Management, Istanbul University for providing the necessary research facilities.

References

Baker, B., Campella, B., Gist, R., Lowry, L., Nickerson, S., Schwartz, C. and Stratton, L. (1989). Exxon Waldes oil spill: the first 8 weeks. Alaska fish and Game 21: 3-37.

Batten, S.D., Allen, R.J.S. and Wotton, C.O.M. (1998). The effects of the sea empress oil spill on the plankton of the Southern Irish Sea. *Mar. Poll. Bull.* 36: 764-774.

Baumard, P., Budzinski, H. and Garrigues, P. (1998a). PAHs in Arcachon Bay, France: Origin and biomonitoring with caged organisms. *Mar. Poll. Bull.* 36: 577-586.

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

Binark, N., Güven, K.C., Gezgin, T. and Ünlü, S. (2000). Oil pollution of marine algae. *Bull. Environ. Contam. Toxicol.* 64: 866-872.

Clark, R.C Jr., Finley, J.S. (1974). Analytical techniques for isolating and quantifying petroleum parafin hydrocarbons in marine organisms. NBS spec. Publ. 409, Marine Pollution Monitoring (Petroleum), Prooceeding of a Symposium and Workshop held at NBS, Gaithersburg, Maryland, May 13-17, pp 209-212.

Clark, R.C., Blumer, M. (1967). Distribution of n-paraffin in marine organisms and sediment. *Limnol Oceanog.* 12: 79- 87.

D'Adamo, R., Pelosi, S., Trotta, P. and Sansone, G. (1997). Bioaccumulation and biomagnification of polycyclic aromatic hydrocarbons in aquatic hydrocarbons in aquatic organisms. *Mar. Chem.* 56: 45-49.

Dauvin, J-C. (1998). The fine sand *Abra alba* community of the Bay of Morlaix twenty years after the Amoco Cadiz oil spill. *Mar. Poll. Bull.* 36: 669-676.

Erakın, S. and Güven, K.C. (2008). The volatile petroleum hydrocarbon in marine algae around Turkish coasts. *Acta. Pharm. Sci.* 50: 167-182.

Farrington, J. W. And Tripp, B. W. (1977). Hydrocarbon in western North Atlantic surface sediments. *Geochim Cosmochim Acta* 41: 1627-1641.

Fossata, V.U. and Canzonier, W.J. (1976). Hydrocarbon uptake and loss by the mussel *Mytilus edulis*. *Mar. Biol.* 36: 243-250.

George, M. (1961). Oil pollution in marine organisms. *Nature* 192: 1209.

Güven, K.C., Çetintürk, K., Küçük, M., Alpaslan, M. and Tekinay, A.A. (2003). Oil, phthalates and biotoxin analyses of mussels (*Mytilus galloprovincialis*) collected from Dardanelles. *Turkish J. Marine Sciences* 9: 83-95.

Güven, K.C., Okuş, E., Ünlü, S., Doğan, E. and Yüksek, A. (1998). Oil pollution of marine organisms after Nassia tanker accident in the Black Sea, Bosphorus and the Sea of Marmara. *Turkish J. Mar. Sci.* 4: 3-10.

Güven, K.C., Ünlü, S., Okuş, E. and Doğan E. (1995). Oil contamination of *Mytilus galloprovincialis* after the Nassia accident. *Turkish J. Mar. Sci.* 1: 67-79.

Hernandez, J..E., Machado, L.T., Corbella, R. and Rodriguez, M.A. (1995). N-Alkanes and polynuclear aromatic hydrocarbons in fresh-frozen and precooked-frozen mussels. *Bull. Environ. Contam. Toxicol.* 55: 461-468.

Knutzen, J., Sortland, B. (1982). Polycyclic aromatic hydrocarbons (PAH) in some algae and invertebrates from moderately polluted parts of the coast of Norway. *Water Res.* 16: 421-428.

Lee, R.F., Sauerheber, R. and Benson, A.A. (1972). Petroleum hydrocarbons: uptake and discharge by the marine mussel *Mytilus edulis*. *Sciences* 17: 244-346.

Leonard, D.R.P., Law, R.J. and Kelly, C.A. (1998). Responding to the sea empress oil spill. Internatinal symposium on marine pollution 5-9 Oct., Monaco

Mironov, O.G., Shchekaturina, T.L., Tsimbal, I.M. (1981). Saturated hydrocarbons in marine organisms. *Mar. Ecol. Prog. Ser.* 3: 303-309.

Murray, A.P., Richardson, B.J. and Gibbs, C.F. (1991). Bioconcentration factors for petroleum hydrocarbons, PAHs, LABs and biogenic hydrocarbons in the blue mussel. *Mar. Poll. Bull.* 22: 595-603.

Notar, M. and Leskovsek, H. (2000). Polycyclic aromatic hydrocarbons in mussel from the Northern Adriatic Sea. *Fresen. Environ. Bull.* 9: 427-434.

Peckol, P., Levings, S.C., Garrity, S.D. (1990). Kelp response following the World Prodgiy oil spill. *Mar. Poll. Bull.* 21: 473- 476.

Piccardo, M.T., Coradeghini, R. and Valerio, F. (2001). Polycyclic aromatic hydrocarbon pollution in native and caged mussels. *Mar. Poll. Bull.* 42: 951-956.

Porte, C., Biosca, X., Pastor, D., Sole, M. and Albaiges, J. (2000). The Aegean Sea oil spill. 2. temporal study of the hydrocarbons accumulation in bivalves. *Environ. Sci. Technol.* 34: 5067-5075.

Rantamaki, P. (1997). Release and retention of selected polycyclic aromatic hydrocarbons (PAH) and their methylated derivatives by the common mussel (*Mytilus edulis*) in the brackish water of the Baltic Sea. *Chemosphere*. 35: 487-502.

Rossi, S.S., Rommel, G.V. and Benson, A.A. (1978). Hydrocarbons of Macrocystis pyrifera blades. *Phytocehmistry* 17: 1431- 1432.

Saxton, W.L., Newton, R.T., Rorberg, J., Sutton, J. and Johnson, L. E. (1993). Polycyclic aromatic hydrocarbons in seafood from the Gulf of Alaska following a major crude oil spill. *Bull. Environ. Contam. Toxicol.* 51: 515-522.

Shabana, M., Gonaid, M., Salama, M.M. and Abdel-Sattar, E. (2006). Phenylalkylamine alkaloids from *Stapelia hirsuta L. Natural Product Research 20: 710-714.*

Tawfiq, N.I. and Olsen, D.A. (1993). Saudi Arabia's response to the 1991 Gulf oil spill. *Mar. Poll. Bull.* 27: 333-343.

Tomruk, A. and Güven, K.C. (2008). Biotransformation of 1-methylnaphtalene and anthracene in mussels (*Mytilus galloprovincialis* Lamarck, 1819). 17: 256-259.

Youngblood, W.W., Blumer, M., Guillard, R. L. and Fiore, F. (1971). Saturated and unsaturated hydrocarbons in marine benthic algae. *Mar. Biol.* 8: 190-201.

Received: 01.05.2008
Accepted: 02.06.2008