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Polynuclear Aromatic Hydrocarbons (PAHs) in the Eastern Mediterranean Sea

K. YILMAZ*, A. YILMAZ*‡, S. YEMENİCIOĞLU*, M. SUR*, İ. SALİHOĞLU*, Z. KARABULUT*, F. TELLİ KARAKOÇ*, E. HATİPOĞLU*, A. F. GAINES*, D. PHILLIPS† and A. HEWER†

**Middle East Technical University (METU), Institute of Marine Sciences, P.O. Box 28, Erdemli, 33731, İçel, Turkey*

†Institute for Cancer Research, Haddow Laboratories, Cotswold Road, Belmont, Sutton, Surrey SM2 5NG, UK

PAHs have been monitored for several years in the eastern Mediterranean Sea as part of the MEDPOL Programme (UNEP, 1986; 1995). Figure 1 shows the location of the major sampling sites around the Mediterranean coast. Yılmaz *et al.*, (1991) have discussed how the distributions of dissolved and dispersed polyaromatic hydrocarbons measured in the eastern Mediterranean in 1989 were related to the local oceanography and how part of the observed concentrations were derived from phytoplankton.

For seawater analyses, 2.5 litres of seawater (or discharged waste) were extracted on board ship (or at the sampling location) with *n*-hexane. PAH concentrations were estimated by comparison of the fluorescence at 360 nm (excitation at 310 nm) with that of hexane solutions of chrysene (UNEP, 1986).

Sediments were obtained using a van Veen grab and were frozen at −20°C. Thawed samples were dried under vacuum at 40°C, or freeze-dried. Then, 0.2–0.5 g of dried sediment was refluxed with 20 ml of ethanol and ~0.75 g of potassium hydroxide for 90 min. Products were then extracted three times with 20 ml of hexane. PAHs in hexane were estimated by comparison of the fluorescence at 360 nm (excitation at 310 nm) with that of hexane solutions of chrysene (UNEP, 1992). In 1985–1986 the analysis of the sediments excluded the saponification step.

Biota were treated similarly to sediments. PAH concentrations were calculated from the equivalent chrysene fluorescence. Grey mullet were captured fresh from the METU and Mersin harbours. Blood was sampled from the caudal fin vein and livers were excised and homogenised. DNA was extracted from the samples and purified. DNA adduct concentrations were determined by ^{32}P post-labelling (Gill *et al.*, 1985; Gupta, 1984; Phillips *et al.*, 1987). Several livers were bulked and subsequently separated into seven samples after excision from grey mullet captured fresh from the open sea. The DNA adduct concentrations in the seven liver samples were determined. The variance was due to the post-labelling analysis and excess variance in the harbour samples was therefore due to sampling.

Tables 1 and 2 summarise the concentrations of PAHs in surface waters and sediments of the study area between 1985 and 1996. At the beginning of this period, an oil terminal in the Yumurtalık region (Fig. 1) connected Iraq to the eastern Mediterranean but this was not used between 1990 and 1997. Throughout the 10 year period, the north eastern Mediterranean coast has attracted summer tourism and a population influx, this increasing to 5.2 million in 1990 (Mersin Chamber of Commerce Press, 1995) and to approximately 10–12 million at present. Commercial shipping at Mersin, İskenderun and Cyprus has also been significant and currently exceeds 11 million tonnes a year at Mersin (Yercan, 1996); this includes tankers supplying oil refineries at Mersin and Cyprus. Nevertheless, Tables 1 and 2 serve as a baseline against which to compare environmental quality in future.

As demonstrated by Table 1, the surface waters of the eastern Mediterranean Sea do not suffer undue pollution by PAHs, the observed concentrations being similar to those noted in pristine surface waters off the coast of Antarctica which, in 1987, ranged between 0.15 and 4.65 $\mu g\,l^{-1}$ (Weber and Bicego, 1990). The mean of the eastern Mediterranean determinations recorded in May 1996 was slightly lower than usual but, generally, there has been little change in the PAH concentrations during the past 10 years. There has been a suggestion that higher evaporation leads to lower surface concentrations during summer periods (Sakarya, 1985).

In contrast, the pollution of surface sediments by PAHs appears to have increased during the 10 year period considered here (Table 2). Sediments containing ~0.5 $\mu g\,g^{-1}$ dry weight of PAHs have been deemed to be moderately contaminated and those possessing more than 10 $\mu g\,g^{-1}$ of PAHs highly contaminated (UNEP, 1994). Thus, for example, Lipiatov and Saliot (1991) observed PAH concentra-

‡Corresponding author.

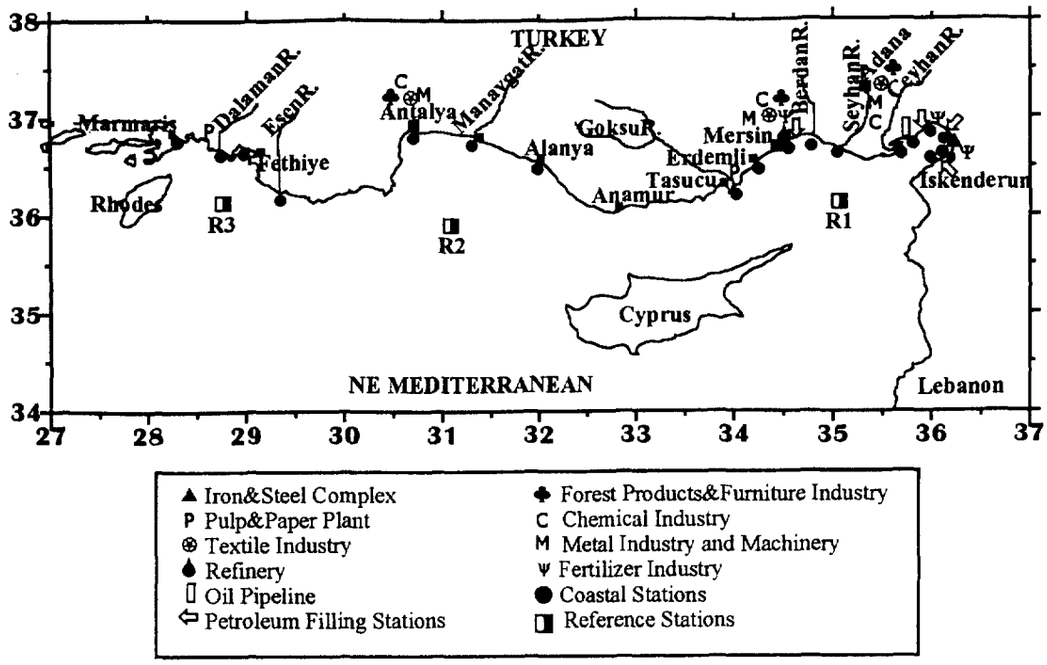

Fig. 1 The studied area and sampling locations.

tions in western Mediterranean sediments which rose from 0.18 μg g^{-1} dry weight in the open ocean to 2.4 μg g^{-1} in the Rhône River delta. The contrast between the clean eastern Mediterranean water and the polluted surface sediment suggests that the water column is being scrubbed continuously by particulates which eventually sediment out. The findings of Boulou-bassi and Saliot (1991) are relevant here, revealing the presence of high concentrations of PAHs in the fine particles dispersed in the Mediterranean water column.

There are several coastal discharges of domestic, commercial and industrial wastes in the region (Yılmaz *et al.*, 1992) and these generate point sources of pollution (Table 3). The eastern Mediterranean is a dynamic basin and the low concentrations of PAH prevailing in the open coastal waters show that the pollution is diluted rapidly, an extreme example being the dispersal in 3 months of 8000 tonnes of oil accidentally leaked from the Iraq pipeline at Yumurtalık in 1982 (Sakarya, 1985). City and river discharges have their highest volume in the spring, following the melting of the snow in the Toros mountains. The high incoming water volumes wash PAHs into the sea. By contrast, this is not true of factory discharges. The great range of PAH concentrations observed in the land-based discharges renders the calculation of average concentrations meaningless.

Table 4 records PAH concentrations recently observed in fish samples. Fish ingest, assimilate and

TABLE 1

PAH concentrations in the eastern Mediterranean Sea, 1985–1986 and 1995–1996 (μg l^{-1} in surface water).

Date	Stations	Min.–Max.	Mean ± SE
1985–1986	10	0.1–0.77	0.28 ± 0.07
July 1995	36	0.06–4.14	0.35 ± 0.05
Sept. 1995	34	0.01–1.36	0.20 ± 0.06
Oct. 1995	34	0.01–0.79	0.22 ± 0.03
May 1996	28	0.01–1.00	0.13 ± 0.04

TABLE 2

PAH concentrations (μg g^{-1} dry weight) in surface sediments.

Date	Stations	Min.–Max.	Mean ± SE
1985–1986	10	0.02–0.96	0.51 ± 0.10
1995	19	0.69–4.8	2.6 ± 0.3
1996	19	0.55–18.7	4.75 ± 1.0

TABLE 3

PAH concentrations (μg l^{-1}) in land-based discharges of waste, 1985–1996.

Nature of discharge	Minimum	Maximum
City of Mersin	0.5	625
City of Iskenderen	0.01	101
City of Adana	2.2	72
City of Antalya	1.8	4.5
Tarsus River	0.03	24
Seyhan River	0.15	35
Ceyhan River	0.3	88
Paper factory	40	1404
Fertiliser factory:		
Acidic discharge	0	108
Basic discharge	0	4451
Iron+steel factory	0	1390
Domestic waste	7	19

excrete PAHs (Malins and Hodgkins, 1981). Species such as the mullet (*Mugil* sp.), which ingest sediments and fish in such polluted waters as the busy harbours, maintain significant concentrations of PAHs in their tissues. Similar concentrations have been noted in Aegean fish (Saydam *et al.*, 1988). The observations in 1996 show the variance within a species to be rather large; nevertheless, species in two localities 55 km apart possessed very similar concentrations of PAH. It is to be hoped that future observations will show whether this phenomenon is of general occurrence.

Table 5 takes this analysis one stage further. The table shows the levels of aromatic DNA adducts recently observed in the liver and blood of grey mullet (*Mugil* sp.) inhabiting two eastern Mediterranean harbours: the small shallow, superficially clean (but in reality polluted) harbour of METU and the larger, highly polluted port of Mersin. The levels of aromatic DNA adducts determined by ^{32}P post-labelling (Gupta, 1985; Phillips *et al.*, 1987) cover a wide range and appear to be higher in liver than in blood. Thus, PAH concentrations were significantly higher in the liver than in the blood of *Mugil* sp. at METU in 1994 ($p<0.01$) and at Mersin in 1996, but not in 1994 ($0.01<p<0.025$).

In 1994, the levels of adducts in liver samples obtained from grey mullet inhabiting the METU harbour were significantly higher ($p\sim0.0005$) than those from the same species captured in open coastal waters. Even higher adduct concentrations were observed in livers from grey mullet in the highly polluted harbour at Mersin ($p\sim0.025$). Higher aromatic DNA adduct concentrations were observed in mullet livers taken from the two harbours in 1996.

Two species of grey mullet were distinguished in Mersin harbour, both of which had higher adduct concentrations than were observed in the less polluted harbour at METU ($p\sim0.005$). Some of the concentrations of aromatic DNA adducts found here are amongst the highest to have been observed in fish liver (cf. for example, Dunn *et al.*, 1987; Varanasi *et al.*, 1989; Dunn, 1991). These results suggest that when fish which ingest sediments are restricted to polluted localities, high levels of DNA adducts may form (but compare these data to the results of Kurelec *et al.* (1989)). The piscine biochemical response to PAHs is discussed elsewhere; it is, of course, essentially the same as the response of humans. Thus, although the concentrations of PAHs in Turkish eastern Mediterranean waters are generally low, discharges provide

TABLE 4

PAH concentrations ($\mu g\ g^{-1}$ dry weight) in the flesh of fish from the eastern Mediterranean Sea.

Year	*N*	Station	Fish species	PAH
1987	10	Mersin Harbour	*Mugil* sp.	10.0–14.5
1991	6	Turkish coast	*Mullus* sp.	1.1 ± 0.4
1991	2	Turkish coast	*Mugil* sp.	1.6 ± 1.2
1995	15	Mersin Sea	Mixed species	2.8 ± 0.5
1996	6	İskenderun Bay	*Mugil* sp.	8.7 ± 1.1
1996	7	İskenderun Bay	Shrimp	6.4 ± 1.0
1996	10	İskenderun Bay	*Upeneus moluccensis*	7.5 ± 1.1
1996	6	Karataş	*Mugil* sp.	10.7 ± 2.1
1996	6	Karataş	Shrimp	6.2 ± 0.9
1996	7	Karataş	*Upeneus moluccensis*	8.8 ± 1.5
1996	4	Karataş	*Solea solea*	4.6 ± 1.3

TABLE 5

Aromatic DNA adducts in grey mullet (mean $\pm$ SE/10^6 nucleotides).

Station	Date	Tissue	*N*	Adducts
METU Harbour[a]	1994	Liver	14	0.209 ± 0.018
METU Harbour[a]	1994	Blood	13	0.154 ± 0.010
METU Harbour[a]	1996	Liver	10	0.035 ± 0.023
Mersin Harbour	1994	Liver	12	0.488 ± 0.144
Mersin Harbour	1994	Blood	6	0.329 ± 0.092
Mersin Harbour[b]	1996[c]	Liver	14	1.3 ± 0.37
Mersin Harbour[b]	1996[c]	Blood	8	0.143 ± 0.028
Mersin Harbour[b]	1996[d]	Liver	6	2.58 ± 0.2
Mersin open sea	1994	Liver	7	0.104 ± 0.011

[a]In 1996, the harbour water and sediment contained $1.0\ \mu g\ l^{-1}$ and $8.0\pm2.2\ \mu g\ g^{-1}$ of PAHs (chrysene equivalent), respectively.
[b]In 1996, the harbour water and sediment (an ooze) contained $5.4\ \mu g\ l^{-1}$ and $219\pm10\ \mu g\ g^{-1}$ of PAHs (chrysene equivalent), respectively.
[c]*Lisa ramada*.
[d]*Oedolechiulus labeo*.

point sources of pollution. The waters and (especially) the sediments in the harbours and their neighbourhood are sufficiently polluted to present a hazard to the physiology of any fish which may assimilate the PAHs and such regions may pose a carcinogenic hazard to humans.

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Baseline Study on the Levels of Organic Pollutants and Heavy Metals in Bivalves from the Morrocoy National Park, Venezuela

RUDOLF JAFFÉ*§, IVAN LEAL†¶, JOSÉ ALVARADO†, PIERO R. GARDINALI* and JOSE L. SERICANO‡

**Southeast Environmental Research Program and Department of Chemistry, Florida International University, Miami, FL 33199, USA*

§Corresponding author.

¶Present address: Universidad Francisco de Miranda, Departamento de Química, Coro, Edo. Falcon, Venezuela.

†Departamento de Química, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

‡Geochemical and Environmental Research Group, College of Geosciences and Maritime Studies, Texas A&M University, College Station, TX 77845, USA

Bivalves have been extensively used as bioindicators of pollution in aquatic environments, particularly in coastal areas worldwide (e.g. Tavares *et al.*, 1988; Sericano *et al.*, 1990, 1993; Gold-Bouchot *et al.*, 1993; Jaffé *et al.*, 1995). The rationale behind the use of bivalves in monitoring programmes has been discussed in several scientific reports since the introduction of the 'Mussel Watch' concept (e.g. Goldberg *et al.*, 1978; Phillips, 1980; Farrington *et al.*, 1983; O'Connor *et al.*, 1994).

The present study reports the concentrations of selected organic and inorganic contaminants in the flat tree-oyster (*Isognomon alatus*) from one of the largest marine parks in Venezuela, the Morroccoy National Park, as an initial step to determine the present levels of contaminants and establish a baseline reference for