

### 3.3 SELECTED ORGANIC POLLUTANTS

#### 3.3.1 Petroleum hydrocarbons

##### 3.3.1.1 Sources and inputs

The input of petroleum hydrocarbons into the marine environment ranges from diffuse chronic inputs (terrestrial run-off and natural seeps) to large point source releases (e.g. tanker spills). Deliberate release of oil into the world's oceans from marine operations or land-based activities is a relatively more important pollution source than accidents involving single massive inputs of oil (Table 3.3.1.1).

In 1977, Le Lourd estimated that the amount of oil released into the Mediterranean was between 0.5 and 1 million tonnes per year, with half being discharged from the coast and half in the open sea. Other authors (Longé, 1980) evaluated this quantity as 1.7 million tonnes, which is probably overestimated.

Based on the 350 million tonnes of oil crossing the Mediterranean each year (Smith, 1975) it can be assumed that the quantity of oil entering the Mediterranean through local tanker practices is around  $330 \times 10^3$  tonnes. Even a figure of  $500 \times 10^3$  tonnes has not been considered unreasonable by IMO (UNEP, 1984).

The input of petroleum hydrocarbons from land-based industrial discharges into the Mediterranean has been conservatively estimated at 20,000 tonnes per year (Rouit, 1975).

The overall input of oil from different industrial sources is estimated at 110,000 tonnes.

Urban inputs can be computed by using the estimates of Eganhouse and Kaplan (1981) of 1,014 tonnes per year per person for urban populations and 398 tonnes per year per person for rural areas. If we take into account the Mediterranean population distribution given by Henry (1977) we get a total input of 160,000 tonnes of oil per year.

Combustion products are estimated from atmospheric fluxes given by Ho *et al.* (1983) at 35,000 tonnes per year, including dry and wet deposition.

The resulting value of 0.6 million tonnes (Table 3.3.1.2) falls within the Le Lourd estimates.

##### 3.3.1.2 Environmental levels

###### Seawater:

- i) Dissolved/dispersed petroleum hydrocarbons (DDPH): taking into account that the Mediterranean has: a surface of  $2.96 \times 10^6$  square kilometers; a yearly input of 0.6 million tonnes of petroleum hydrocarbons; most of the input in the nearshore areas; a mean residence time in the top 100 meters of one year (Burns *et al.*, 1985); we can reach an estimate of the order of  $0.2 \mu\text{g/L}$  of total petroleum compounds for the top 100 meters of the open Mediterranean.

Western Mediterranean: Samples collected nearshore frequently show concentrations above  $10 \mu\text{g/L}$ , particularly if they were taken close to industrialized

areas or river mouths. From the Spanish coast between Castellon and Cartagena results showed concentrations between 0.06 and 8.26  $\mu\text{g/L}$  as mean values at each station. In Mar Piccolo, Taranto, Italy, concentrations ranging from 0.1-36  $\mu\text{g/L}$  have been reported (Strusi, pers. comm.). Mean values are 3.26, 7.42 and 7.98  $\mu\text{g/L}$  from three sampling occasions.

Adriatic: Most of these studies have dealt with the Rijeka Bay area, although recently data from Sibenik and Split have also been obtained. Concentrations from these areas range from 0.1  $\mu\text{g/L}$  or below in unpolluted zones, to 50  $\mu\text{g/L}$  in polluted parts.

Central Mediterranean: The only concentrations reported from sampling offshore are those reported by Monaghan *et al.* (1974). From nearshore areas (Libyan coast) Gerges and Durham (1983) report concentrations between 0.6 and 28  $\mu\text{g/L}$ . The highest values (10 - 28  $\mu\text{g/L}$ ) are reported from areas far from major industrial activities. Similar concentrations ranging from 0 (unpolluted) to 27.6  $\mu\text{g/L}$  (polluted) were reported in a study carried out by the Marine Fisheries Research Center, Tripoli (MFRC, 1981). From the coastal waters around Malta, concentrations between 0.02 and 0.29  $\mu\text{g/L}$  have been reported (UNEP, 1980). Values ranging from 0.1 to 2.6  $\mu\text{g/L}$  are reported from Greek coastal waters, while concentrations in the range 1 to 2.6  $\mu\text{g/L}$  were reported from harbour areas. However, some studies in areas quite far from major land-based industrial activities, such as off-shore in the Aegean Sea, show concentrations exceeding 10  $\mu\text{g/L}$ . Sakarya *et al.*, 1985 reported values between 0.14 and 1.39  $\mu\text{g/L}$  from the Aegean Sea. From Turkish waters, data ranging from 0.02 to 40  $\mu\text{g/L}$  are reported (Sunay *et al.*, 1983; Sakarya *et al.*, 1985). Concentrations of around 1.5  $\mu\text{g/L}$  are reported from coastal waters southwest of Mersin (Sunay *et al.*, 1983). However, the same authors report concentrations of 2.0 to 6.0  $\mu\text{g/L}$  from off-shore areas between Turkey and Cyprus. Concentrations up to 7.0  $\mu\text{g/L}$  were reported from the industrialized Iskenderun Bay (Sunay *et al.*, 1983). Sakarya *et al.*, 1985 reported concentrations ranging between 0.11 and 1.0  $\mu\text{g/L}$  from the northeastern Mediterranean coast off Turkey. Concentrations between 10 and 20  $\mu\text{g/L}$  have been reported from areas close to harbours, oil refineries, river mouths, etc. in Israel. High concentrations of dissolved hydrocarbons were found south of Cyprus (25-40  $\mu\text{g/L}$ ) and southeast of Crete (10 to above 40  $\mu\text{g/L}$ ), although more recently concentrations ranging between 2.6 and 8.1  $\mu\text{g/L}$  were reported from Limassol Bay, Cyprus and levels from 4.2 to 13.6  $\mu\text{g/L}$  from Larnaca Bay, Cyprus, (unpublished report to IOC, 1984). Several reports are available on the oil contamination of coastal waters off Egypt (Aboul-Danab and Halim, 1981, 1981a; Wahby and El Deeb, 1981; El Samra *et al.*, 1983). Concentrations up to 30-40  $\mu\text{g/L}$  have been reported in areas influenced by various industrial activities (Aboul-Dahab and Halim, 1981, 1981a; Wahby and El Deeb, 1981). The same authors report concentrations below 10  $\mu\text{g/L}$  and usually below 5  $\mu\text{g/L}$  in offshore waters. One study of the petroleum hydrocarbon content of the waters reaching the Mediterranean from the Suez Canal has been reported by El Samra *et al.*, 1983. This study showed that the water contained 0.5 - 14  $\mu\text{g/L}$ .

- ii) Pelagic tar: Available data on pelagic tar from the Mediterranean show that between 1969 and 1983 mean concentrations in the Mediterranean ranged from 0.5 to 130  $\text{mg m}^{-2}$  and that the Ionian Sea was the most tar polluted area in the Mediterranean Sea. The data also suggest that normal values for offshore areas are up to 5  $\text{mg m}^{-2}$ , while in nearshore waters, concentrations can be much higher and range between 10 and 100  $\text{mg m}^{-2}$ . Measurements of pelagic tar conducted after 1980 indicate that there may have occurred a reduction in tar quantity especially in the Eastern Mediterranean during the past few years.

Table 3.3.1.1

Inputs of petroleum hydrocarbons in the marine environment  
(million metric tonnes per year)  
(from IMCO, 1981; Baker, 1983; US Nat. Acad. Sci., 1985)

	Best estimate		Probable range		US Nat. Acad. Sci., 1985	
Transportation	1.49		1.00-2.60		1.47	
Tanker operation		0.71		0.44-1.45		0.70
Drydocking		0.03		0.02-0.55		0.03
Marine terminals		0.02		0.01-0.03		0.02
Bilge and fuel oil		0.32		0.16-0.60		0.30
Tanker accidents		0.02		0.02-0.04		0.02
Production platforms	0.05		0.04-0.07		0.05	
Atmospheric	0.30		0.05-0.50		0.3	
Municipal, industrial wastes, run-off	1.40		0.70-2.80		1.18	
Natural seeps/erosion	0.03		0.03-2.60		0.25	
<b>Total</b>	<b>3.27</b>		<b>1.82-8.57</b>		<b>3.25</b>	

Table 3.3.1.2

Inputs of petroleum hydrocarbons in the Mediterranean  
(10<sup>3</sup> tonnes per year)

Source	Estimate
Spilled oil from tankers, ballasting and loading operations, bilge and tank washings	330
Land based discharges, run-off	160
Municipal	110
Industrial	
Atmospheric deposition	35
<b>Total</b>	<b>635</b>

Estimated data from various sources

**Beaches:** The data on tar on Mediterranean beaches show considerable variation and mean quantities were found to range between 0.2 and 4388 g/m (Golik, 1986). Measurements on tar on beaches in Cyprus and in Israel conducted during a 10-year period (Golik, 1985; Demetropoulos, 1985) suggest a similar reduction of the quantities of tar in the Eastern Mediterranean. These findings show a drastic decrease in the amount of tar on beaches.

**Sediments:** Along the French coast between Fos-sur-Mer and Monaco, Mille *et al.* (1983) reported concentrations of aliphatic and aromatic hydrocarbons ranging between 20 and 950 µg/g. Comparable results have been reported by Albaiges *et al.* (1983) in sediments collected along the Spanish coast outside harbours, oil terminals and river mouths (1-62 µg/g of aliphatics and 2 - 66 µg/g of aromatics). In Mar Piccolo, Taranto, Italy, average concentrations of 14.7 µg/g aliphatic and aromatic hydrocarbons were found at 8 stations at depths from 1 to 10 meters (Strusi, 1984 personal communication). Similar results have recently been reported for the East Adriatic coast. From the eastern Mediterranean, results are available from Cyprus and Turkey. From Cyprus concentrations of 0.114 to 1.35 µg/g are reported in sediment samples collected at 90m depth. From Iskenderun Bay, Turkey, average sediment concentrations of 0.24 µg/g were reported by Sunay *et al.* (1983).

### 3.3.1.3 Levels in seafood

Few studies have been carried out on the uptake of petroleum hydrocarbons in organisms from the Mediterranean.

#### (a) Mussels

Risebrough *et al.* (1983) used the technique employed in the Mussel Watch project in a study of petroleum hydrocarbons in molluscs from the Ebro delta. Mussels (*Mytilus galloprovincialis*), oysters (*Ostrea edulis*), and clams (*Venus gallinae*) were selected as the indicator organisms.

The levels found were generally in the order of 100 - 300 µg/g. These concentrations were equivalent to those in mussels in the most polluted harbours and bays in California.

From Mar Piccolo, Taranto, Italy, a study has been reported on the levels of hydrocarbons in mussels (Strusi, 1984 personal communication). The results, which are given as wet weight concentrations, range from 0.5-10.1 µg/g with an average of 2.7 µg/g.

In another study by Albaiges *et al.* (1983), relatively high concentrations of petroleum hydrocarbons were found in bivalves from the Spanish Mediterranean coast (190 - 215 µg/g DW) (Table 3.3.1.3). A study by Ballester *et al.* (1982) of mussels from a drilling platform in the Ebro river delta showed concentrations of up to 20-30 µg/g of n-alkanes.

#### (b) Fish

Petroleum concentrations of tissues of three species of fish (*Mullus barbatus*, *Merluccius merluccius*, *Trachurus trachurus*) have been reported by Albaiges *et al.* (1985). This study showed that baseline levels in muscle tissues for the area between

Barcelona and the French border were 1.5 - 12 µg/g and 1.7 to 8.4 µg/g DW of saturated and aromatic hydrocarbons respectively. Higher concentrations were found in fish off Barcelona and the Ebro river. The results are summarized in Table 3.3.1.3. In this study, it was also shown that hydrocarbons are largely accumulated in liver and in adult species.

From the coast of Turkey, notably from Iskenderun Bay, a study of the concentration of PAH in fish has been carried out (Sunay *et al.*, 1983). The average concentrations in muscle and liver were 0.13 and 0.79 µg/g, respectively.

Albaiges *et al.* (1983) found lower concentrations of petroleum hydrocarbons in tissue samples of pelagic fish from the Spanish Mediterranean coast than in bivalves from the same area (Table 3.3.1.3).

Table 3.3.1.3

Hydrocarbons in biota samples from the Spanish Mediterranean Coast  
(in µg/g dry wt) (Albaiges *et al.*, 1983 and 1985)

Species	Samples	Area fraction (UCM)	Saturate fraction (crude oil eq.)	Aromatic
<i>Mytilus</i>	10	Palamós	106-190	not analyzed
		Barcelona	500-3200	"
		Ebro Delta	8-216	"
<i>Mullus</i> sp. (muscle)	14	Palamós	12.6	4.4
		Barcelona	22.2	9.3
		Ebro Delta	5.8	11.1
<i>Merluccius</i> sp. (muscle)	14	Palamós	1.5	1.7
		Barcelona	0.2	3.9
		Ebro Delta	0.2	2.4
<i>Trachurus</i> sp. (muscle)	14	Palamós	11.2	4.2
		Barcelona	1.4	10.9
		Ebro Delta	5.4	3.7
<i>Engraulis</i> sp. (muscle)	19	Barcelona	7.7	7.8

### **3.3.2 Organohalogen compounds**

#### **3.3.2.1 General facts on organohalogen compounds**

Organohalogen is a group of organic compounds which are substituted with halogens i.e. chlorine, bromine, fluorine or iodine. Approximately 20% of these are pesticides while the rest are miscellaneous compounds used, produced or by-produced by the industries. By far the majority of environmental information available refers to chlorinated hydrocarbons and especially to chlorinated pesticides. Little interest has been shown to industrial compounds with the exception of polychlorinated biphenyls (PCB).

Organohalogen compounds include:

##### **1. DDT and its metabolites**

DDT is the abbreviation for p,p'-dichloro-diphenyl trichloroethane. Dehydrochlorination gives the metabolite DDE and dechlorination the metabolite DDD.

##### **2. Hexachlorocyclohexane (HCH)**

The gamma-isomer known as lindane is the one normally used as an agricultural pesticide.

##### **3. Aldrin/Dieldrin/Endrin**

Aldrin is an alicyclic chlorinated hydrocarbon and is therefore less resistant to oxidation than the aromatics, being rapidly converted to the epoxide, dieldrin, which is also used as a pesticide. Endrin is a stereoisomer of dieldrin and is one of the most toxic of the chlorinated pesticides.

##### **4. Hexachlorobenzene (HCB)**

Hexachlorobenzene is a fully chlorinated compound formed when all the hydrogen atoms in benzene are substituted by chlorine atoms. It is used as a general fumigant and especially as a fungicide in grain storage.

##### **5. Heptachlor/Heptachlor epoxide**

In the environment it is degraded or metabolized and is more commonly found as its epoxide. It is used as an insecticide and it also occurs in technical chlordane.

##### **6. Polychlorinated biphenyls (PCB)**

PCB are a group of aromatic organochlorine industrial products similar in structure to chlorinated hydrocarbon insecticides such as DDT. PCB are produced commercially by the chlorination of biphenyl with anhydrous chlorine. Impurities found in commercial PCB can include polychlorinated naphthalenes (PCNs) and polychlorinated dibenzofurans (PCDFs).

### 3.3.2.2 Sources and inputs

#### Production and use:

**Chlorinated pesticides:** There are no sales or production statistics for the Mediterranean countries. In the implementation of MED POL X of MED POL Phase I consumption figures were collected for the 1973/1976 period which are shown in Table 3.3.2.1. However, Cyprus, Egypt, Greece, Israel, Italy, Libya and Turkey reported to FAO that in 1985 no chlorinated pesticides were used in their countries for agricultural purposes.

**Polychlorinated biphenyls:** PCB have been produced industrially since 1929 and were or are manufactured in many industrial countries, including some Mediterranean countries. PCB are nowadays used primarily in the electrical industry in capacitors and transformers. In the past they were far more widely used, for example in hydraulic systems, in the formulation of cutting and lubricating oils, and in pesticides, paints, plastics and inks (Geyer *et al.*, 1984).

Table 3.3.2.2 includes the trade name of PCB manufactured in Mediterranean countries and production figures.

#### Inputs into the sea:

PCB concentrations in air averaged  $0.23 \text{ ng/m}^3$  in a 1975 and  $0.07 \text{ ng/m}^3$  in a 1977 cruise (Villeneuve, 1985). These levels are of the same order of magnitudes as those found in the Central Pacific ( $0.2\text{-}0.3 \text{ ng/m}^3$ ), the Antarctic ( $0.1\text{-}0.25 \text{ ng/m}^3$ ) and Bermuda ( $0.2\text{-}0.65 \text{ ng/m}^3$ ). Over Rijeka the dominant components were PCB (1.3 to 12 ng/L Aroclor equivalent), followed by DDT (0.6 to 1.7 ng/L), DDE (0.1 to 1.3 ng/L), DDD (0.04 to 0.3 ng/L) and Dieldrin (0.02 to 0.1 ng/L). In the other regions, the PCB ranged from 0.03 to 1 ng PCB/ $\text{m}^3$ .

Comparison of atmospheric and riverine input rates of organohalogen compounds to the World Ocean made recently by GESAMP (1989) shows that pollution of the marine environment by these substances through the atmosphere is more important than that through river discharges.

Beside atmospheric deposition, halogenated hydrocarbons reach the marine environment through agricultural run-off, rivers and discharge of industrial and municipal wastes. Project Med X of MED POL-PHASE I which was concerned with the sources and amounts of pollutants entering the Mediterranean Sea from land-based sources estimated a total load of organochlorine pesticides of about 90 t/a (range 50-200) carried by surface run-off, either directly or through rivers. This project does not include polychlorinated biphenyls. The results are summarized in Table 3.3.2.3 and suggest that the minimum input occurs in Area VII 2.9 t/a (3%) and the maximum in Area II 14.9 t/a (17%). However, the reliability of the data for Area II are questionable since France provided no agricultural use data.

Table 3.3.2.1

Pesticide consumption by agriculture in the Mediterranean watershed (excluding Albania, Algeria, France, Malta, Monaco, Morocco, former Yugoslavia, 5 regions of Italy) (UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, 1984 - modified).

Kind of Pesticide	Cyprus (1976)	Egypt (1975 /76)	Consumption (t active ingredient per year)							Tunisia (1973/74)	Turkey (1976)	Total	estimated area treated (10 <sup>3</sup> -km <sup>2</sup> )
			Greece (1973)	Israel (1974)	Italy <sup>1</sup> (1975)	Lebanon (1973)	Libya (1974)	Spain <sup>2</sup> (1976)	Syria <sup>2</sup> (1976)				
Organochlorine compounds	14.9	743.3	85.5	132.3	2972.4	35.3	5.8	323.2	65.8	39.0	1266.8	5684.3	216.8
- DDT and related compounds	11.2	169.3	-	10.3	866.4	-	-	12.7	36.7	-	864.1	1970.7	29.1
- BHC and lindane	0.6	21.9	-	25.0	1563.7	-	1.7	122.3	9.1	36.0	163.0	1943.3	126.6
- Cyclodienes (aldrin, dieldrin, endrin, etc.)	0.1	98.7	-	0.8	-	-	2.0	99.2	6.3	3.0	81.2	291.3	15.4
- Other organochlorine compounds	0.3	453.4	85.5	96.5	542.3	-	2.1	89.0	13.7	-	158.5	1444.3	44.4

1 Except Piemonte, Valle d'Aosta, Lombardia, Trentino, Alto Adige and Umbria regions  
 2 Mediterranean watershed only

Table 3.3.2.2

Manufacturers, Trade Names of PCB and 1980 production figures  
(after Geyer *et al.*, 1984)

Country	Manufacturer	Trade name	Production (m.tonnes)
France	Prodelec	Phenoclor,	6557 <sup>a</sup>
Italy	Caffaro	Pyralene	1479
Spain	Cross, S.A.	Fenoclor, Apirolio	1241

<sup>a</sup> Includes T 60 which is 100% triphenyl

Table 3.3.2.3

Estimated annual pollution loads of organochlorine pesticides  
in the regional Mediterranean sea areas

Mediterranean Region	Pollution load tonnes/year	% of total
I	6.4	7
II	14.9	17
III	10.4	12
IV	12.1	13
V	14.0	16
VI	6.1	7
VII	2.9	3
VIII	7.4	8
IX	6.7	7
X	9.1	10

Data from Project X of MEDPOL - PHASE I

### 3.3.2.3 Environmental levels

**Seawater:** The concentrations of DDT total, HCH total, PCB and in certain cases dieldrin found by various authors in different seawater samples (film, particulate matter, dissolved phase, and non defined "seawater" samples) collected from various sites in the Mediterranean Sea are summarized in Table 3.3.2.4. For mean concentration of PCB in open Mediterranean seawater, the data reported by Villeneuve *et al.* (1981) span a range of 0.2 to 19 ng/L, with an average of 21.1 ng/L. Elder (1976), found the highest concentrations of PCB in water samples from the coast of the Golfe du Lion, with lower concentrations in the coastal waters to the east and north. The highest value (38 ng/L), was found at the mouth of the Rhône

suggesting that the Rhône is an important source of PCB for northwestern Mediterranean coastal waters. In the Northern Adriatic coastal waters in 50 samples analyzed between 1977 and 1978 most concentrations were below the detection limits of 0.05 ng DDT/L and 0.1 ng PCB/L (Picer & Piccer, 1979). Lindane levels off-shore in the eastern basin ranged from 0.06 to 0.12 ng/L. The higher concentrations were observed near terrestrial run-off and river inputs. Particulate matter had higher concentrations than the seawater dissolved phase. The contamination by polychlorinated biphenyls and hexachlorobenzene (HCB) in sea waters of the Tiber River estuary was studied in 1976 and 1977 by Puccetti and Leoni (1980). PCB were found to be present in 85 samples out of 86 at a mean value of 0.297 µg/L in 1976, and of 0.135 µg/L in 1977. In contrast, HCB was identified in only 16% of the analysed samples.

**Sediments:** The concentration of PCB in open sea sediments in the Mediterranean was in the 0.1 - 15850 µg/kg range. The concentrations of DDT total, HCH total, PCB and in one case dieldrin found by various authors in sediment samples collected from various sites in the Mediterranean Sea are summarized in Table 3.3.2.5. The contamination by chlorinated biphenyls and hexachlorobenzene in sediments of the Tiber river estuary was studied in 1976 and 1977 by Puccetti and Leoni (1980). All samples were found to be polluted with PCB, but HCB was not found in the sediment samples. Levels of PCB, DDTs and HCHs were measured in sediments taken from the central Mediterranean (area IV and VI). HCH was usually 1 ng/g; DDT total ranged from 1 ng/g to 27.5 ng/g; PCB generally ranged from ca. 1 ng/g to 80 ng/g (Amico *et al.*, 1982). The highest levels, particularly with PCB, were found in the area of the straits of Messina and along the northern coast of Sicily. The exceedingly high levels of PCB observed within the Augusta Harbor compare closely with those (360-470 ng/g) found for the Japanese Port of Taganoura, regarded as highly polluted (Rhead, 1975). The contamination of the Bay of Naples and adjacent marine area sediments by chlorinated hydrocarbons was assessed using grab and core sediment samples collected in July 1980 (Baldi *et al.*, 1983). Inside the Bay of Naples, PCB attain very high levels (3200 ng/g d.w.). Outside the Bay, levels of PCB though lower, never fall below 10 ng/g. Concentrations of DDT total (mainly as DDE) are lower than 20 ng/g in all, except two samples taken just outside Naples harbour and three from near the Sarno River. In the cores, concentrations of DDT total decrease to non-detectable values at depths greater than 25 cm (Baldi *et al.*, 1983).

Persistent chlorinated hydrocarbons in more than 100 grab and core sediment samples (1976-1984) collected from open and coastal waters of the Northern Adriatic were analysed over a nine-year period (Picer N. and Piccer M., 1979; Piccer M. *et al.*, 1981; Piccer M. and Piccer N., 1982; Piccer N. *et al.*, 1985; Piccer M. and Piccer N., 1985). Istrian coastal water sediment samples from the Pula area show a significantly higher concentration of DDT total and especially PCB in comparison with those from the well-known tourist Porec area. Relatively high concentrations of pollutants were also found in some samples collected close to sources of pollution in the Rijeka bay. But the results show that a great part of Rijeka bay sediments as well as those from the open Northern Adriatic are relatively free of chlorinated hydrocarbons contamination.

Table 3.3.2.4

Chlorinated hydrocarbons in surface film (S.F.), seawater (S.W.),  
seawater-dissolved phase (S.W.D.F.), and particulate matter (P.M.)  
from the Mediterranean Sea (ng/l)

Area	Matrix	Pollutant	Mean	Minimum	Maximum	References
II	S.F.	HCH <sub>total</sub> PCB Hexachlorobenzene	4.4 2.0	- ND	- 2.8	Burns & Villeneuve (1982) Burns <i>et al.</i> (1985)
II	S.W.	HCH <sub>total</sub> PCB Hexachlorobenzene	8.9 8.5 0.4	1 ND ND	14 38 1.0	Elder (1976); Elder <i>et al.</i> (1976); Burns & Villeneuve (1982); Chabert&Vicente (1981); Marchand <i>et al.</i> (1985); Monod & Arnoux (1979)
II	S.W.D.P.	HCH <sub>total</sub> PCB	0.5 0.3	0.3 -	0.7 -	Burns <i>et al.</i> (1985)
II	P.M.	HCH <sub>total</sub> PCB	0.03 0.7	0.01 -	0.08 -	Burns <i>et al.</i> (1985)
III	S.W.	PCB	21.1	0.2	19	Elder <i>et al.</i> (1976); Villeneuve <i>et al.</i> (1981)
IV	S.W.	DDT <sub>total</sub> HCH <sub>total</sub> PCB	12.4 6.3 2.3	9.0 5.9 0.2	15.7 6.6 11.6	Elder <i>et al.</i> (1976); Leoni <i>et al.</i> (1976) Villeneuve <i>et al.</i> (1981)
IV	S.W.	PCB	210	50	548	Pucetti & Leoni (1980)
V	S.F.	DDT <sub>total</sub> PCB Dieldrin	1.9 51 0.1	ND 0.9 ND	25.5 597 0.9	Picer <i>et al.</i> (1981); Picer & Picer (1982) Picer, N. <i>et al.</i> (1985)

Table 3.3.2.4 (continued)

Area	Matrix	Pollutant	Average	Minimum	Maximum	References
V	S.W.	DDT <sub>total</sub>	5.1	ND	95	Fossato <i>et al.</i> (1982) Fossato (1983); Fossato <i>et al.</i> (1986); Fossato & Dolci (1985); Picer, N. <i>et al.</i> (1985); Picer & Picer (1982);
		HCH <sub>total</sub>	0.8	0.1	7.0	
		PCB	4.1	ND	17	
		Dieldrin	0.03	ND	0.07	
V	S.W.	HCH <sub>total</sub>	48	1	77	Elezovic <i>et al.</i> (1980)
V	P.M.	DDT <sub>total</sub>	0.6	ND	2.4	Fossato (1983); Fossato <i>et al.</i> (1982) Fossato <i>et al.</i> (1986); Fossato & Dolci (1985)
		HCH <sub>total</sub>	0.4	0.1	1.2	
		PCB	3.3	0.7	9.1	
V	S.W.D.P.	DDT <sub>total</sub>	0.5	-	-	Fossato (1983); Fossato <i>et al.</i> (1982); Fossato <i>et al.</i> (1986); Fossato & Dolci (1985)
		HCH <sub>total</sub>	1.2	-	-	
		PCB	2.0	-	-	
VI	S.W.	PCB	1.8	1.7	1.9	Villeneuve <i>et al.</i> (1981)
VII	S.W.	HCH <sub>total</sub> PCB	0.07	-	-	Elder <i>et al.</i> (1976); Villeneuve <i>et al.</i> (1981) Villeneuve & Burns (1983)
			0.9	0.2	1.7	
VIII	S.W.	DDT <sub>total</sub> HCH <sub>total</sub> PCB	0.9	0.4	1.5	Elder <i>et al.</i> (1976); Fytianos <i>et al.</i> (1985)
			0.05	0.01	0.12	
			1.5	0.2	2.8	
X	S.W.	HCH <sub>total</sub> PCB	0.09	0.06	0.12	Villeneuve <i>et al.</i> (1981); Villeneuve & Burns (1983)
			0.4	0.1	0.8	

- = No available data  
ND = non detected (under detection limit)

Table 3.3.2.5

Chlorinated hydrocarbons in sediments from the Mediterranean Sea  
(µg/kg dry weight)

Area	Pollutant	Mean	Minimum	Maximum	References
I	DDT <sub>total</sub>	2.7	0.4	11.0	Cousteau (1979); Elder <i>et al.</i> (1976) Villeneuve & Burns (1983)
	HCH <sub>total</sub>	0.3	0.2	0.3	
	PCB	34.6	0.3	323	
II	DDT <sub>total</sub>	8.2	0.4	200	Arnoux <i>et al.</i> (1981a); Arnoux <i>et al.</i> (1981b); Arnoux <i>et al.</i> (1981c); Burns <i>et al.</i> (1985); Cousteau (1979); Chabert & Vincente (1981); Marchand <i>et al.</i> (1976); Marchand (1983); Marchand <i>et al.</i> (1985); Mond & Arnoux (1979)
	HCH <sub>total</sub>	225	0.1	1880	
	PCB	85.5	0.2	15850	
	Hexachlorobenzene	5.6	ND	32	
III	DDT <sub>total</sub>	11.0	1.2	40.0	Cousteau (1979); Elder <i>et al.</i> (1976); Villeneuve & Burns (1983)
	HCH <sub>total</sub>	1.6	0.9	2.1	
	PCB	7.4	0.1	14	
IV	DDT <sub>total</sub>	4.3	0.2	27	Amico <i>et al.</i> (1982); Baldi <i>et al.</i> (1983); Cousteau (1978); Elder <i>et al.</i> (1976); Monod & Arnoux (1979); Pucetti & Leoni (1980); Villeneuve & Burns (1983)
	HCH <sub>total</sub>	1.8	0.1	27	
	PCB	102	0.6	3200	
V	DDT <sub>total</sub>	6.8	ND	47.8	Cousteau (1979); Donazzolo <i>et al.</i> (1983); Fossato (1983); Picer & Picer (1982); Picer <i>et al.</i> (1985); Picer & Picer (1985, unpublished results); Picer <i>et al.</i> (1978b); Picer <i>et al.</i> (1981); Picer N. <i>et al.</i> (1985); Villicic <i>et al.</i> (1979)
	HCH <sub>total</sub>	1.1	0.1	4.6	
	PCB	24.1	ND	332	
	Hexachlorobenzene	7.2	-	-	
	Dieldrin	0.1	ND	0.7	
VI	DDT <sub>total</sub>	10.3	0.1	35.5	Amico <i>et al.</i> (1982); Cousteau (1979); Elder <i>et al.</i> (1976); Villeneuve <i>et al.</i> (1981); Villeneuve & Burns (1983)
	HCH <sub>total</sub>	0.7	0.1	2.6	
	PCB	38.1	0.8	347	

Table 3.3.2.5 (continued)

Area	Pollutant	Mean	Minimum	Maximum	References
VII	DDT <sub>total</sub>	0.2	0.1	0.4	Cousteau (1979); Villeneuve & Burns (1983)
	HCH <sub>total</sub>	1.1	0.2	2.2	
	PCB	0.8	0.1	1.1	
VIII	DDT <sub>total</sub>	128	0.3	1893	Cousteau (1979); Dexter & Pavlou (1973); Villeneuve <i>et al.</i> (1981); Villeneuve & Burns (1983)
	HCH <sub>total</sub>	0.6	0.4	0.8	
	PCB	155	0.6	775	
IX	DDT <sub>total</sub>	12.0	0.4	29.0	Balkas <i>et al.</i> (1979); Bastürk <i>et al.</i> (1980); Cousteau (1979); Villeneuve <i>et al.</i> (1981); Villeneuve & Burns (1983)
	HCH <sub>total</sub>	0.2	0.2	0.3	
	PCB	1.5	ND	3.0	
X	DDT <sub>total</sub>	2.7	ND	780	Cousteau (1979); Villeneuve & Burns (1983); Villeneuve <i>et al.</i> (1981)
	HCH <sub>total</sub>	0.7	-	-	
	PCB	2.2	0.6	51.1	

Dexter and Pavlou (1973) measured PCB and pesticide residues in surface sediment samples collected in Saronikos Gulf. In terms of the maximum concentrations and geographical extent of significant benthic deposits, the Keratsini area can be considered only moderately contaminated in comparison with some American outfalls.

From July 15 to December 7, 1977, the research vessel Calypso gathered samples of sediments at 141 locations distributed in 12 Mediterranean countries (Cousteau, 1979). The results of the 457 analyses of sediment samples for polychlorinated biphenyls and DDTs are included in Table 3.3.2.5. Several years later Villeneuve and Burns (1983) analysed measurements of lindane content in the same samples for lindane and noted that concentrations were highest near the mouth of rivers draining major agricultural areas such as the Rhône, Ro, Danube and Ebro, and near agricultural areas of northern Italy, Sicily and Northern Africa. Core samples showed that most of the lindane was contained in the first 3 to 4 cm of sediment.

**Non-edible biota:** Elder and Fowler (1977) sampled microplankton twice in coastal French waters. PCB in the two samples (1800 and 4500 µg/kg, dry weight) were relatively high and probably reflect coastal inputs. The only other generally available data for chlorinated hydrocarbons in Mediterranean euphasids appear to be those of Elder and Fowler (1977) for *Meganctiphanes norvegica* samples. The concentrations (38 to 620 µg/kg d.w.) were of the same order of magnitude as those measured in the species inhabiting the Tyrrhenian and Ionian Seas. Burns *et al.* (1985), show that there has been a reduction in the concentrations of PCB in planktonic organisms (about 6.5 times) and in plankton faeces (about 14 times) in samples collected from the same area over a 5-year period. The levels of organochlorine hydrocarbons, PCB, DDT and lindane found in *Cystoseires* collected at 7 stations in Cortiou (Marseille) area were reported by Arnoux *et al.* (1981d). The dry weight concentrations of PCB ranged from 2 to 34 ng/g; lindane from 0.4 to 3.0 ng/g and DDT total from 0.4 to 9.7 ng/g. These concentrations were significantly higher than those found by Chabert and Vicente (1981) in Phanerogames collected from the lagoon of the Brusca (Var-France). Concentrations of PCB, HCHs and DDT total residues in seaweeds of the east coast of Sicily were investigated during 1977/78 by Amico *et al.* (1979a). The highest concentrations found were in samples from an area (Priolo) intensively polluted by nearby industrial activity.

DDE, PCB, HCB, dieldrin and heptachlor-epoxide were found in the eggs of Audouin's Gull, Herring gull, and Black Vulture collected during 1978 from Chafarina islands, and Balearic Islands (Bijleveld *et al.*, 1979). On average, levels were lowest for dieldrin, heptachlorepoide, and hexachlorobenzene. The difference between the mean levels of DDE, PCB in Audouin's Gulls in the northern and southern parts of the western Mediterranean, is striking. DDE levels averaged from 1.94 ppm (F.W.) in the south to 3.67 ppm in the north. The average levels of pollutants found in the southern part of the western Mediterranean region still seem to fall within the range where normal reproduction can be expected. Average levels of PCB also appear to be much higher in the northern than in the southern part of the western Mediterranean, being 16.75 ppm and 3.82 ppm, respectively. Analysis of contents of unhatched eggs of the Black Vulture from the Balearic Islands revealed extremely low levels of all organochlorine compounds. The extreme differences found between levels of this terrestrial species and the two marine species, all of them placed at the end of food-chains, well illustrate the contamination of the marine environment. The level of PCB, DDT and metabolites were analyzed in the tissue of 22 dolphins (*Stenella coeruleoalba* stranded on the Mediterranean coast of France (Alzieu and Duguay, 1979). The immature animals, and particularly one new born, were more contaminated than adults. Analysis of blubber tissue from a common dolphin (*Delphinus delphis*) stranded on the French Mediterranean coast, showed very high concentrations of organochlorines (in µg/kg dry

weight); pp'DDT = 324,000; p,p' DDE=75,000; p,p' DDD = 2,700; lindane = 4,000 and PCB 700,000. Analysis of chlorinated pesticides and PCB of various tissues of a stranded leather turtle (*Dermochelys coriacea*) (Vicente and Chabert, 1982) showed that pesticide residues were present but at lower levels than were found in Mediterranean mammals. In 1977 Mendola *et al.* (1977) studying the eggs of six species of birds (only two of which were shorebirds) in the Camargue area, found that the levels of organochlorine compounds were, in general, relatively low compared with those recorded in the same (or similar) species from northern Europe and North America. Residues of lindane, dieldrin, p,p' DDD and PCB found in birds captured in the Po River delta during 1972 were reported by Viviani *et al.* (1974). The sea-gull (*Larus ridibundus*) showed the highest levels of DDT and its metabolites (4 ppm in the muscle and liver) whereas the common tern (*Sterna hirundo*) had the highest level of PCB (7.9 ppm in the breast muscle and 8.6 in the liver). By comparison with the data in literature the authors considered birds in the Po delta were not particularly contaminated by the organochlorine compounds investigated.

Eggs of the following species were analyzed over the period 1980/81: little egret, night heron, stilt, coot, avocet, black-headed gull, herring gull, slender billed gull, gull-billed tern, common tern and little tern from three areas along the Italian shore (Renzoni *et al.*, 1982). They found low levels of most of the analyzed chlorinated hydrocarbons compared with other marine areas of the world. However, the concentrations of PCB in the eggs of all species but avocet, stilt and coot, were quite high in all sampling areas suggesting widespread polychlorinated biphenyls contamination.

#### 3.3.2.4 Levels in seafood

(a) Mussels (*Mytilus galloprovincialis* and *Mytilus edulis*), crustaceans (various species), and other organisms

The concentrations of DDT total, BHC total, PCB and dieldrin found by various authors in mussels collected from various sites in the Mediterranean sea are summarized in Table 3.3.2.6 and for crustaceans in Table 3.3.2.7.

De Lappe *et al.* (1973) used the mussel *Mytilus edulis* as an indicator species to express PCB contamination in French coastal waters of the Western Mediterranean. High concentrations in mussels from Marseille and l'Estaque presumably reflect local input and the higher values at Grau-de-la-dent, to the west of the mouth of the Rhône, suggest also that the Rhône is a significant source. Low concentrations were however found in mussels from Valras Plage and Cannes.

A seasonal survey was carried out to measure existing concentrations of PCB, DDT and its metabolites in mussels (*Mytilus galloprovincialis*) which inhabit the northwestern Mediterranean coast of France and Italy. (Marchand *et al.*, 1976). The highest residue concentrations observed were in samples from enclosed locations, Thau pool at Sète, Marseille and Toulon.

Marchand *et al.* (1976) compared PCB concentrations (Table 3.3.2.8) taken at stations which correspond to those studied earlier by De Lappe *et al.* (1973).

Table 3.3.2.6

Chlorinated hydrocarbons in mussels (*Mytilus galloprovincialis*)  
(µg/kg fresh weight)

Area	Pollutant	Mean	Minimum	Maximum	References
II	DDT <sub>total</sub>	54.0	1.5	900	Arnoux <i>et al.</i> (1981b); Ballester <i>et al.</i> (1982); Bolognari <i>et al.</i> (1979); Contardi <i>et al.</i> (1979); Contardi <i>et al.</i> (1981); Ferro <i>et al.</i> (1979); De Lappe <i>et al.</i> (1973); Marchand <i>et al.</i> (1976); Marchand <i>et al.</i> (1985); Monod <i>et al.</i> (1979); Risebrough <i>et al.</i> (1976); Risebrough <i>et al.</i> (1983); Francoe Soler (1973)
	HCH <sub>total</sub>	8.5	0.5	67	
	PCB	177	9.1	2072	
IV	DDT <sub>total</sub>	34.7	9	57.3	Bolognari <i>et al.</i> (1979); Focardi <i>et al.</i> (1984)
	HCH <sub>total</sub>	3.2	2.3	4.3	
	PCB	96.4	20	172	
V	DDT <sub>total</sub>	34363	-	-	Stirn <i>et al.</i> (1974)
	HCH <sub>total</sub>	6160	-	-	
	DDT <sub>total</sub>	38.8	ND	301	Bolognari <i>et al.</i> (1979); Dujmov <i>et al.</i> (1979); Fossato and Craboledda (1981) Nasci & Fossato (1979); Nazansky <i>et al.</i> (1979); Picer, M. <i>et al.</i> (1981); Picer, M. & Picer, N. (1982); Picer, M. & Picer, N. (1985, unpublished results); Picer, M. <i>et al.</i> (1978a)
	HCH <sub>total</sub>	2.1	0.4	10.2	
	PCB	118	ND	1586	
	Dieldrin	0.6	ND	3.2	
VI	DDT <sub>total</sub>	33.1	9	35.6	Amico <i>et al.</i> (1979b); Bolognari <i>et al.</i> (1979)
	HCH <sub>total</sub>	1.8	0.3	3.3	
	PCB	78	42	101	
	Dieldrin	1.7	1.4	4.4	
VIII	DDT <sub>total</sub>	23.9	-	-	Kilikidis <i>et al.</i> (1981)
	HCH <sub>total</sub>	1.7	-	-	
	PCB	383	-	-	
	Dieldrin	1.6	-	-	

- = No available data

ND = Not detected (below detection limit)

Table 3.3.2.7  
Chlorinated hydrocarbons in crustaceans from the Mediterranean Sea  
(µg/kg wet weight)

Area	Organisms	Pollutant	Mean	Minimum	Maximum	References
II	Two species	DDT <sub>total</sub>	6.5	1.2	13	Bolognari <i>et al.</i> (1979); Contardi <i>et al.</i> (1979); Contardi <i>et al.</i> (1981); Ferro <i>et al.</i> (1979); Monod & Arnoux (1979)
		HCH <sub>total</sub>	0.8	0.01	5.3	
		PCB	7.1	21	203	
IV	<i>Nephrops norvegicus</i>	DDT <sub>total</sub>	3.3	0.2	16	Amico <i>et al.</i> (1979a); Bolognari <i>et al.</i> (1979); Focardi <i>et al.</i> (1984)
		HCH <sub>total</sub>	1.1	0.3	2.8	
		PCB	9.0	2.9	23.3	
		Dieldrin	0.3	0.2	0.5	
		Hexachlorobenzene	0.3	0.1	0.6	
V	6 species	DDT <sub>total</sub>	8.8	ND	30.2	Bolognari <i>et al.</i> (1979); Dujmov <i>et al.</i> (1979); Fossato (1983); Fossato & Craboledda (1981) Vilicic <i>et al.</i> (1979)
		HCH <sub>total</sub>	0.6	-	-	
		PCB	110	ND	796	
		Dieldrin	1.7	ND	5.6	
		Hexachlorobenzene	4.4	-	-	
VI	<i>Nephrops norvegicus</i>	DDT <sub>total</sub>	1.2	1.2	1.2	Amico <i>et al.</i> (1979a)
		HCH <sub>total</sub>	0.5	0.3	0.7	
		PCB	4.9	4.4	5.4	
IX	<i>Parapenaeus kerathurus</i>	DDT <sub>total</sub>	78.9	8.9	161	Bastürk <i>et al.</i> (1980)
		PCB	ND	ND	ND	

ND = Not detected (below detection limit);

- = No available data

The fact that organic residues, like PCB and DDT are lipophilic suggest a possible correlation between chlorinated hydrocarbons and lipid within mussels. Studies on *Mytilus* from the northwestern Mediterranean indicate that lipid reserves generally reach a maximum in mid-summer and then begin to diminish in early fall during the reproductive stage when the mussels release lipid rich gametes (Bourcart *et al.*, 1964). Although the data show only a limited correlation they do suggest that variation in the mussels lipid cycle might be responsible for some of the variation in chlorinated hydrocarbons concentrations observed in the survey of North Western Mediterranean mussels.

The concentrations of PCB in molluscs collected from the North West Mediterranean from 1976 to 1982 (Marchand *et al.*, 1985) appear to have increased slightly from 1976 to 1982 while DDT total concentrations showed a tendency for decrease.

The concentrations of HCHs, DDTs and PCB have been determined in samples of mussels collected in different stations of the Ligurian Sea. (Contardi *et al.*, 1979). The concentrations of PCB and DDTs found in mussels from the Genoa area are presented in Table 3.3.2.9. This table shows the range and mean concentrations for all the samples taken by Marchand in the period June 1973 to December 1974 and of those taken by Contardi *et al.* (1979) in the period December 1977 to July 1978. The latter values are appreciably smaller.

Lower levels of all chlorinated hydrocarbons were found in crustaceans (*Nephrops norvegicus*) in comparison with mussels (DDT total from 1.7 to 10.2 µg/kg F.W.; HCH total from 0.22 to 2.35 µg/kg F.W. and for PCB from 21 to 157 µg/kg F.W.). (Contardi *et al.*, 1979).

Concentrations of DDT, DDD, DDE and PCB were determined in samples of *Mytilus galloprovincialis* and *Nephrops norvegicus* taken in the Northern Tyrrhenian sea between spring 1978 and winter 1981. (Focardi *et al.*, 1984). The data did not show significant variations either with time or age and sex of the animals. In mussels, the levels of DDT and its metabolites were generally low (about 10 µg/kg F.W. or less), with the exception of samples collected near the mouth of the Arno river. An analogous pattern could be seen for PCB, although the concentration of these contaminants was higher, than DDTs. The low concentrations of chlorinated hydrocarbons in the Norwegian lobster may be due to the off-shore location of the sampling site.

Concentrations of chlorinated hydrocarbons (DDT and metabolites, PCB, aldrin, dieldrin, HCB and HCHs) were determined in the tissues of *Mytilus galloprovincialis* and *Nephrops norvegicus* sampled in some areas of the central Mediterranean from November 1976 to November 1977. (Amico *et al.*, 1979b). The results suggest that the major contaminants were DDTs and PCB, and that the ratio DDT total/PCB is generally less than 1. DDT concentrations were usually higher than those of DDE and DDD, a fact perhaps indicative of direct exposure to DDT inputs. Contamination by these substances was widespread through the area investigated and residue levels were more or less similar in all the sampling sites, the higher values being more frequent in the Tyrrhenian basin.

Table 3.3.2.8

Temporal comparison of PCB concentrations (ng/g) in mussels from four northwestern Mediterranean stations

Stations	Marchand <i>et al.</i> (1976) Collected July 1973-Dec.1974				De Lappe <i>et al.</i> (1973)
	Dry weight	Wet weight (calculated)	+ 1	Range	wet weight
Grau du Roi	2492	299	+ 91	208- 390	520
Marseille	7686	922	+432	490-1354	1920
St. Tropez	801	96	+ 32	64 - 128	120
Cannes	1978	237	+ 59	178- 296	450

Note: From the table there also appears to have been a general decrease in PCB content in mussels during the two year period

*Mytilus galloprovincialis*, *Carcinus mediterraneus* and *Nephrops norvegicus* were collected seasonally from the Italian coast of the northern Adriatic Sea over a four year period (1976-1979) and were analysed for their chlorinated hydrocarbon content (Fossato and Craboleda, 1981). The overall data on chlorinated hydrocarbons show that PCB residues predominate in all species at all stations regardless of season. Of the three fractions of DDT total, DDD was usually the smallest, while DDE made up the major percentage in crustaceans. DDT and DDE were present in approximately equal amounts in mussels. Measurable amounts of alpha and gamma isomers of HCH were found in all samples. Dieldrin and aldrin concentrations varied from 0.2-2.8 and 0.1-1.8 µg/kg for mussel and crab respectively, but aldrin was only rarely detected with certainty.

Table 3.3.2.9

PCB and DDT in mussels for Genoa area

Sampling period	DDT total (ng/g d.w.)		PCB (ng/g d.w.)	
	mean	range	mean	range
(1) June 1973 to December 1974	407	150 - 778	2179	480 - 5050
(2) December 1977 to July 1978	37	31 - 43	-	180 - 181

(1) Marchand *et al.* (1976);

(2) Contardi *et al.* (1979)

During 1976, a bimonthly survey was carried out to measure existing concentrations of some chlorinated hydrocarbons in mussels of the Laguna Veneta (Fossato and Craboledda, 1979). The distribution of chlorinated pesticides was quite uniform, significant differences in the distribution of PCB were observed for samples collected inside the Laguna, indicating the presence of local inputs.

Concentrations of chlorinated pesticides and polychlorinated biphenyls were determined in mussels (*Mytilus galloprovincialis*) collected from four areas in the eastern coastal waters of the middle and north Adriatic Sea (Picer M. *et al.*, 1978a). Most samples were collected in early spring and late summer of 1974 and 1975.

Although several major Northern Italian rivers discharge into the North Adriatic, samples from Istrian coastal waters did not have significantly higher concentrations of these pollutants than did other waters. Chlorinated hydrocarbon levels often differ dramatically in samples collected at stations which are close together, possibly because the first station waters had been contaminated with waste waters and the second station had not. Evidently urban waste waters even from relatively small settlements contribute significantly to the local contamination of Adriatic waters.

Concentrations of PCB were significantly higher than those of the DDT group in the samples of mussels collected in the vicinity of the industrial pollution sources of the Rijeka Bay (Picer M. *et al.*, 1981). In the samples collected away from industrial sources of pollution, concentrations of DDTs were higher than PCB concentrations. The level of contamination in mussels throughout the coastal zone of Rijeka Bay by persistent chlorinated pesticides appears to be the same. A possible explanation could be a recent higher usage of DDT and its analogues for pest control in agriculture and forestry, because the coastal zone is a typical karstic region, consequently once applied, pesticides are likely to drain into Rijeka Bay very quickly.

Kilikidis *et al.* (1981) measured organochlorine residues in samples of mussels from the Northern Aegean Sea. *M. galloprovincialis* samples show substantial significant differences in chlorinated hydrocarbon levels during the period of investigation. The concentration of PCB doubled between 1975-76 and 1978.

Relevante and Gilmartin (1975) investigated the distribution of chlorinated hydrocarbons in several samples of *Sepia officinalis* and *Loligo vulgaris*. Concentrations of DDT total ranged from 1 to 58 ppb wet weight but PCB were found in lower concentrations.

(b) Fish

Data on concentrations of DDT total, HCH total and PCB found by various authors in fish collected from the Mediterranean Sea are summarized in Table 3.3.2.10.

Franco Soler (1973) investigated the distribution of HCH, heptachlor, aldrin, dieldrin DDTs and PCB in sardines collected from Spanish coastal waters. The highest concentrations observed were of PCB (from 90 to 1800 µg/kg F.W.).

The concentrations of DDTs in anchovies were moderate, but concentrations of PCB were higher, particularly at the two sites located north of Elba off the Ligurian and Northern Tuscany coasts, which are heavily urbanized and industrialized (Focardi *et al.*, 1984). Concentrations in striped mullet were similar to those found in anchovies.

Regardless of the site of sampling of marine fish from the central Mediterranean (Amico *et al.*, 1979a), the concentration of organochlorine compounds in anchovies ranged between 10 and 80 ppb (F.W.), 9 and 176 ppb and 0.1 to 0.8 ppb for DDT, PCB and dieldrin respectively. For striped mullet the corresponding ranges were 4-85, 17-373 and 0.1-1.6 ppb, while in tuna the concentration ranges were 6-51, 9-44 and 0.1-0.4 respectively. These variations of residue levels among different species are probably to a large extent, related to their mean fat content.

Viviani *et al.* (1973) investigated the presence of residues of DDT, its metabolites and PCB in muscle and Crisetig *et al.* (1973) in ripe female gonads of the North Adriatic *Sardina pilchardus*, *Engraulis encrasicolus* and *Clupea sprattus*. The values of the residues found in the gonads during corresponding periods of "gonadic activity" were rather low, even if considered altogether (0.558 ppm in sardine, 0.184 in anchovies and 0.278 in the sprats, and were well below the levels found to cause deleterious effects on reproduction in trout (4-74 ppm).

Residues of lindane, dieldrin, DDT and its metabolites and PCB found in fish captured in the Po delta during 1972 were reported by Viviani *et al.* (1974). In *Gobius paganellus* chlorinated hydrocarbons were always less than 1 ppm (F.W.) whereas higher levels (up to 4 ppm) of DDT and its metabolites, and 12 ppm of PCB were found in the liver. The authors claimed that no particular accumulation of the chlorinated hydrocarbons investigated occurs in fish in the Po delta.

The distribution of chlorinated hydrocarbons in fish from the Italian coast of the northern Adriatic Sea were investigated by Fossato and Craboleda (1981). The data in Table 3.3.2.11 show that chlorinated hydrocarbon levels found in anchovy samples during the period November 1976 to June 1979 was significantly lower than those observed in the same species between 1968 and 1972.

Cantardi *et al.* (1979) determined the concentrations of HCH, DDT and PCB in samples of *Mullus barbatus*, *Engraulis encrasicolus*, *Euthynnus alletteratus* and *Sarda sarda*, collected from different stations of the Ligurian Sea during 1977-78. The concentrations of HCH isomers were very low in all species, (range 0.22 to 3.20 µg/kg F.W.), with the sole exception of a value of 8.10 for *Sarda sarda*. Much higher concentrations of DDTs were found (up to 2500 ppb) with even higher concentrations being found for the PCB (up to 14020 ppb).

The concentrations of chlorinated hydrocarbons were determined in several fish species (*Gobius* sp., *Mullus barbatus*, *Diplodus annularis*, *Oblada melanura*, *Merluccius merluccius*) collected from three areas in the eastern coastal waters of the middle and north Adriatic Sea (Picer M. *et al.*, 1978a). Average wet-weight concentrations of DDT total and PCB in fish sampled from the three areas were: Istrian coast, 124 and 144 ppb; Rijeka Bay 37 and 82 ppb; Losinj Island, 166 and 157 ppb. Dieldrin concentrations were in the low ppb range. Statistical analysis of the data showed that the only concentrations that differed significantly by areas were those of DDT total in samples from Rijeka Bay versus those from the Losinj area and in samples from the Istrian coast versus those from the Rijeka area. The differences in PCB concentrations were not significant.

Table 3.3.2.10

Chlorinated hydrocarbons in the Mediterranean fish  
(µg/kg fresh weight)

Area	Fish species	DDT TOTAL		HCH TOTAL		PCB		REFERENCES
		Mean	Range	Mean	Range	Mean	Range	
II	<i>Mullus barbatus</i>	68.6	3.0-133.2	0.75	0.03-2.75	556.7	70.3-1618.2	Bolognari et al. (1979); Contardi et al. (1979); Contardi et al. (1981); Monod & Arnoux (1979)
"	<i>Engraulis encrasicolus</i>	27.4	11.0-48.2	0.74	0.03-2.60	167.1	22.5-330.0	Bolognari et al. (1979); Contardi et al. (1981); Contardi et al. (1979); Ferro et al. (1979)
"	5 various species	234	1-2048	4	0.1-50	1756	39-11356	Franco Soler (1973); Monod & Arnoux (1979); Arnoux et al. (1981b); Ferro et al. (1979); Contardi et al. (1979); Contardi et al. (1981)
IV	<i>Mullus barbatus</i>	53.1	12.0-86.1	1.5	0.1-3.3	144.2	15.5-373.1	Amico et al. (1979a); Bolognari et al. (1979); Focardi et al. (1984)
"	<i>Engraulis encrasicolus</i>	37.3	11.1-73.4	3.1	0.6-5.8	1325.6	19.8-232.3	Amico et al. (1979a); Bolognari et al. (1979); Focardi et al. (1984)
"	<i>Thunnus thynnus</i>	37.0	22.5-51.3	0.4	0.2-0.6	40.0	35.5-44.5	Amico et al. (1979a)
V	<i>Mullus barbatus</i>	31.2	ND-164.2	3.5		89.1	ND-188.4	Bolognari et al. (1979); Fossato & Craboledda (1981); Picer M. et al. (1978a); Dujmov et al. (1979); Picer M. & Picer N. (1985)
"	<i>Engraulis encrasicolus</i>	52.9	3.8-102.5	33.6	05.-70.0	155.6	10.1-240.7	Viviani et al. (1973); Crisetig et al. (1973); Viviani et al. (1974); Bolognari et al. (1979); Fossato & Craboledda (1981); Picer M. et al. (1980)

Area	Fish species	DDT TOTAL		HCH TOTAL		PCB		REFERENCES
		Mean	Range	Mean	Range	Mean	Range	
V	Various fish (27 species)	149	ND-569	138	0.4-880	209	ND-2650	Viviani et al. (1973); Crisetig et al. (1973); Viviani et al. (1974); Bolognari et al. (1979); Fossato & Craboledda (1981); Picer M. et al. (1981); Picer M. et al. (1978a); Picer M. & Picer N. (1985); Revelante & Gilmartin (1975); Picer M. et al. (1981); Ferro et al. (1979); Vilicic et al. (1979); Stirn et al. (1974)
VI	<i>Mullus barbatus</i>	19.0	4-38	1.6	0.1-5.0	27	22-224	Amico et al. (1979a); Bolognari et al. (1979)
"	<i>Engraulis encrasicolus</i>	36	11.3-82.8	1.7	0.2-3.4	59	9-177	"
"	<i>Thunnus thynnus</i>	37		0.4		40		Amico et al. (1979a)
VIII	<i>Mullus barbatus</i>	76	4-400	4	0.4-10	432	14-1613	Satsmadjis and Gabrielides (1979); Voutsinou-Taliadouri and Satsmadjis (1982); Kilikidis et al. (1981)
"	<i>Thunnus thynnus</i>	1239		37		2613		Kilikidis et al. (1981)
"	<i>Merluccius merluccius</i>	43		0.4		510		Kilikidis et al. (1981)
IX	<i>Mullus barbatus</i>	175	11-379	2		1.4	ND-2	Balkas et al. (1979); Bastürk et al. (1980)
"	<i>Upeneus moluccensis</i>	74	27-84			2		Balkas et al. (1979); Bastürk et al. (1980)
X	<i>Mullus barbatus</i>	29	3-83	15	ND-572	60	ND-284	Ravid et al. (1985)
X	Various fish (3 species)	25	ND-106	15	ND-183	120	ND-800	Ravid et al. (1985)

PCB, DDT total and other chlorinated hydrocarbons in striped mullet from Saronikos Gulf were determined by Satsmadjis and Gabrielides (1979). The fish were collected from four areas at varying distances from the Greater Athens area. The residue levels seemed to increase with both the length of fish and the lipid content. Statistical analysis of their data showed the strong influence of the main sewage outfall of Athens on the level of chlorinated hydrocarbon concentrations in striped mullet collected from the Saronikos Gulf (Voutsinou-Taliadouri and Satsmadjis, 1982). The concentrations of major chlorinated hydrocarbons (PCB, DDE, DDT, DDD) increased dramatically in areas close to the outfall in comparison with areas distant from the outfall outlet.

Table 3.3.2.11

Temporal comparison of chlorinated hydrocarbon levels (means  $\pm$  SD,  $\mu\text{g}/\text{kg}$  wet weight) in *Engraulis encrasicolus* sampled off Porto Garibaldi and Cesenatico

Sampling period	Samples No	HCH total	DDT total	PCB	References
Nov.1967 - Sept. 1968		6		257 $\pm$ 102	Viviani <i>et al.</i> , 1969
Jan.1970 - Nov. 1970	6		280 $\pm$ 116	547 $\pm$ 280	Viviani <i>et al.</i> , 1973
Nov. 1972	1	40	80	370	Viviani <i>et al.</i> , 1974
Nov.1976 - June 1979	16	4.0 $\pm$ 2.4	65 $\pm$ 37	155 $\pm$ 43	Fossato & Craboledda, 1981

Further recent data

Organohalogens, especially PCB and DDTs have been determined in the Mediterranean marine environment since the initiation of the MED POL programme. Table 3.3.2.12 summarizes the data in marine biota by Mediterranean region. The concentrations of various halogenated hydrocarbons i.e. PCB, PCCs (Toxaphene), Mirex, DDT isomers, hexachlorobenzene (HCB) and hexachloro-cyclohexane (HCH) isomers, were analysed by Kanitz *et al.* (1990) in *Mullus barbatus*, *Xiphias gladius* and *Mytilus galloprovincialis* in various areas of the Ligurian sea. With the exception of delta HCH and Mirex, all the pollutants were consistently found in the samples analysed. Results are given in Table 3.3.2.13.

Within the framework of the same pilot project, a number of marine organisms from the Ebro delta and the coast of Barcelona were analysed for PCB (individual congeners) (Table 3.3.2.14) and organochlorine pesticides (Table 3.3.2.15). A total of 18 individual PCB congeners were determined in tissues of *Mytilus galloprovincialis* and *Mullus barbatus*. The total PCB values found in *Mytilus* and *Mullus* species were lower than those quoted in reports published during the last decade and, assuming the inter-comparability of analytical procedures, this could afford an indication of reductions in the emission of these compounds into the coastal areas in question.

A total of 20 organochlorine pesticides were systematically determined. The results show (Table 3.3.2.15) that in most cases a generally cosmopolitan distribution was found, reflecting a widespread scale of pollution, though in the case of some DDT isomers, HCHs and HCB, concentrations were lower than those reported in earlier literature.

Table 3.3.2.12  
Chlorinated hydrocarbons (µg/kg) in Mediterranean marine organisms  
(UNEP/FAO/WHO/IAEA, 1990)

Region	Chlorinated Hydrocarbon	Species	No. of samples	Mean concentration	Standard Deviation	Range
II	PCB	<i>Mytilus galloprovincialis</i>	17	307	266	22 - 1200
IV	"	"	13	95	114	5 - 420
V	"	"	159	84	221	5 - 2622
VIII	"	"	12	62	12	40 - 80
II	"	<i>Mullus barbatus</i>	33	813	1496	30 - 8000
IV	"	"	33	417	770	50 - 3950
V	"	"	86	234	473	1 - 3117
VIII	"	"	51	113	204	0 - 1110
IX	"	"	6	9.3	19	0.4 - 52
X	"	"	42	69	75	0 - 284
VIII	"	<i>Parapenaeus longirostris</i>	30	12.3	12.2	0 - 51
IX	"	"	3	1.5	-	0 - 2.5
X	"	"	11	31	57	0 - 157
II	"	<i>Carcinus mediterraneus</i>	10	12.3	12.2	0 - 51
V	"	"	3	1.5	-	0 - 2.5
X	"	"	11	31	57	0 - 157
IV	"	<i>Mullus surmuletus</i>	6	87	17	60 - 110
V	"	"	9	101	130	5 - 441
IV	"	<i>Nephtrops norvegicus</i>	28	25	17	8 - 90
II	pp DDT	<i>Mullus barbatus</i>	27	28	35	8 - 170
IV	"	"	33	23	17	6 - 89
V	"	"	102	17	26	0.2 - 205
VIII	"	"	51	23	25	4 - 110
IX	"	"	17	38	29	0.5 - 92
X	"	"	44	8	9	0 - 3

Table 3.3.2.12 (Continued)  
Chlorinated hydrocarbons (µg/kg) in Mediterranean marine organisms  
(UNEP/FAO/WHO/IAEA, 1990)

Region	Chlorinated Hydrocarbon	Species	No. of samples	Mean concentration	Standard Deviation	Range
II	pp DDT	<i>Mytilus galloprovincialis</i>	113	22	23	3 - 150
IV	"	"	12	7	5	1.2 - 17
VIII	"	"	180	15	77	0 - 1014
II	"	<i>Thunnus thynnus thynnus</i>	21	343	362	25 - 1401
IV	"	<i>Mullus surmuletus</i>	6	6	3	4 - 13
V	"	"	11	9	11	0.5 - 40
V	"	<i>Carcinus mediterraneus</i>	31	1.7	1.4	0.2 - 5
IX	"	"	6	1.6	0.7	0.4 - 2.6
VIII	"	<i>Parapenaeus longirostris</i>	29	0.9	1.4	0 - 6
II	"	"	4	4.2	3.5	0.3 - 9
X	"	"	10	0.1	0.2	0 - 0.8
II	Dieldrin	<i>Mullus barbatus</i>	11	6.2	5.3	0.5 - 19
IV	"	"	9	6	3.6	0.5 - 12
V	"	"	67	1.7	4.1	0.1 - 17
X	"	"	35	0.4	1.1	0 - 35
II	"	<i>Mytilus galloprovincialis</i>	2	3.5	-	1 - 6
IV	"	"	6	2.8	2.6	0.5 - 6
V	"	"	145	0.8	4.4	0.1 - 56
V	"	<i>Mullus surmuletus</i>	8	0.4	0.2	0 - 0.7
IV	"	<i>Nephrops norvegicus</i>	7	0.9	0.5	0.5 - 1.8
V	"	<i>Carcinus mediterraneus</i>	31	0.5	0.6	0 - 2.4
X	"	"	4	3.1	4.5	0.4 - 10

Table 3.3.2.12 (Continued)  
Chlorinated hydrocarbons (µg/kg) in Mediterranean marine organisms  
(UNEP/FAO/WHO/IAEA, 1990)

Region	Chlorinated Hydrocarbon	Species	No. of samples	Mean concentration	Standard Deviation	Range
II	Aldrin	<i>Mullus barbatus</i>	9	0.5	-	0.5 -
IV	"	" "	9	1.5	1.9	0.5 -
V	"	" "	5	0.5	0.4	0 -
X	"	" "	44	1.5	4.7	0 -
IV	"	<i>Mytilus galloprovincialis</i>	6	2	2.1	0.5 -
IV	"	<i>Nephtrops norvegicus</i>	7	0.6	0.2	0.5 -
X	"	<i>Carcinus mediterraneus</i>	5	1.6	2.8	0 -
IX	"	<i>Parapenaeus longirostris</i>	4	1.4	1	0 -
X	"	" "	11	0.2	0.6	0 -
II	Hexachloro-cyclohexane	<i>Mullus barbatus</i>	63	2.65	2.8	0.2 -
VIII	"	" "	4	3.9	8	0.8 -
IX	"	" "	5		3.9	1 -
V	"	<i>Mytilus galloprovincialis</i>	43	1.1	1	0 -
VIII	"	" "	55	1.9	1.5	0.4 -
V	"	<i>Mullus surmuletus</i>	4	1.2	1.7	0 -
V	"	<i>Carcinus mediterraneus</i>	27	0.9	-	0 -
IX	"	" "	6	20	-	12 -
VIII	"	<i>Parapenaeus longirostris</i>	7	0.7	0.3	0.2 -
II	Lindane	<i>Mullus barbatus</i>	17	19	14	2 -
IV	"	" "	9	1.5	1.4	0.5 -
V	"	" "	62	0.7	0.9	0 -

Table 3.3.2.12 (Continued)  
Chlorinated hydrocarbons (µg/kg) in Mediterranean marine organisms  
(UNEP/FAO/WHO/IAEA, 1990)

Region	Chlorinated Hydrocarbon	Species	No. of samples	Mean concentration	Standard Deviation	Range
II	Lindane	<i>Mytilus galloprovincialis</i>	7	4.8	6	0.5 - 20
IV	"	"	6	1.7	0.9	0.5 - 3
V	"	"	36	0.4	0.4	0 - 2
II	"	<i>Carcinus mediterraneus</i>	4	19	14	2 - 36
V	"	"	27	0.2	-	- -
IV	"	<i>Nephtys norvegicus</i>	7	0.5	-	- -
II	pp'DDD	<i>Mullus barbatus</i>	12	38	52	0 - 180
V	"	"	5	28	40	2.2 - 107
VIII	"	"	78	14	25	0 - 140
IX	"	"	17	18	14	0 - 44
X	"	"	44	1.6	3.8	0 - 21
II	"	<i>Mytilus galloprovincialis</i>	108	15	13	5 - 125
V	"	"	11	49	124	0 - 440
VIII	"	"	90	7	7	0 - 45
II	"	<i>Thunnus thynnus thynnus</i>	21	107	98	5 - 117
VIII	"	"	4	323	422	26 - 1052
V	"	<i>Mullus surmuletus</i>	3	7	6	2 - 15
II	"	<i>Carcinus mediterraneus</i>	10	10	9	1.2 - 26
IX	"	"	6	4.2	3.7	0 - 10
VIII	"	<i>Parapenaeus longirostris</i>	29	0.8	1.4	0 - 7
IX	"	"	4	2.2	1.3	0.5 - 4.2
X	"	"	11	0.4	0.8	0 - 2.7

Table 3.3.2.12 (Continued)  
Chlorinated hydrocarbons (µg/kg) in Mediterranean marine organisms  
(UNEP/FAO/WHO/IAEA, 1990)

Region	Chlorinated Hydrocarbon	Species	No. of samples	Mean concentration	Standard Deviation	Range
II	pp'DDE	<i>Mullus barbatus</i>	34	29	14	11 - 70
IV	"	"	33	33	18	7 - 93
V	"	"	43	8	12	0.1 - 75
VIII	"	"	88	33	39	1 - 255
IX	"	"	16	53	42	0.9 - 117
X	"	"	44	15	12	2 - 67
II	"	<i>Mytilus galloprovincialis</i>	114	13	9	2.2 - 42
IV	"	"	13	6	4	2 - 17
V	"	"	145	5	13	0.1 - 110
VIII	"	"	99	10	12	1 - 75
II	"	<i>Thunnus thynnus thynnus</i>	21	352	415	23 - 1582
VIII	"	"	4	601	659	161 - 1737
IV	"	<i>Mullus surmuletus</i>	6	11	3	6 - 15
V	"	"	10	12	12	0.1 - 33
II	"	<i>Carcinus mediterraneus</i>	10	36	24	14 - 72
V	"	"	4	2.5	30	0.1 - 6.2
VIII	"	"	3	23	3	20 - 26
IX	"	"	7	22	15	0.3 - 45
X	"	"	4	3.1	3.5	0.7 - 8
IV	"	<i>Nephrops norvegicus</i>	28	3.8	1.8	1.1 - 8
VIII	"	<i>Parapenaeus longirostris</i>	31	1.6	5	0 - 25
IX	"	"	4	3.1	1.6	1 - 5.4
X	"	"	11	1.5	2.6	0 - 9

Table 3.3.2.13

Levels of chlorinated hydrocarbons in fish and mussels from three areas in the Ligurian Sea, 1989. Data expressed as ng/g dry weight  
 M = May, N = November, ND = below detectable limits  
 (Kanitz *et al.*, 1990)

		<i>Mullus barbatus</i>			<i>Xiphias gladius</i>	<i>Mytilus galloprovincialis</i>		
		East	Central	West	West	East	Central	West
Toxaphene	M	30.10	18.78	34.75	26.92	168.29	89.97	109.31
	N	10.33	54.76	29.58	-	155.61	87.74	173.55
Aroclor 1260	M	153.85	705.27	576.28	619.85	221.83	117.39	52.57
	N	162.77	1,273.15	2,519.03	-	85.19	70.49	53.82
Aroclor 1254	M	244.34	698.62	261.93	983.70	341.06	313.05	203.36
	N	110.51	718.22	2,915.61	-	1,060.52	677.06	399.18
Total PCB	M	398.18	1,403.89	848.77	1,603.55	562.89	430.44	255.94
	N	273.29	1,991.37	5,434.64	-	1,145.70	747.55	452.99
Alpha-HCH	M	1.14	0.86	0.08	0.22	2.45	2.22	2.55
	N	0.82	0.99	1.81	-	0.68	1.73	1.60
Beta-HCH	M	2.09	1.49	0.08	0.13	3.98	3.71	1.50
	N	1.47	1.78	3.72	-	1.62	4.14	2.79
Gamma-HCH	M	0.99	0.97	0.15	0.32	1.69	1.87	1.91
	N	1.47	1.65	3.58	-	0.49	2.30	1.81
Delta-HCH	M	0.49	0.22	ND	0.13	0.77	ND	ND
	N	ND	ND	ND	-	0.23	ND	ND
Total HCH	M	5.86	3.53	0.31	0.80	8.89	7.80	5.96
	N	3.75	4.43	9.11	-	3.02	8.17	6.20
HCB	M	0.08	12.13	0.27	1.08	0.77	0.90	0.71
	N	1.04	1.12	1.54	-	2.38	3.28	3.00
Mirex	M	ND	ND	102.52	ND	ND	ND	ND
	N	ND	ND	ND	-	54.18	ND	ND
p,p'-DDE	M	35.62	40.32	9.75	250.57	32.94	24.38	15.79
	N	58.35	54.29	172.52	-	67.37	23.86	29.83
o,p'-DDD	M	3.43	0.33	0.81	4.27	3.06	2.85	2.89
	N	0.52	0.53	0.34	-	4.72	4.60	4.24
o,p'-DDT	M	1.94	0.97	0.27	21.28	0.36	0.23	0.30
	N	0.23	0.59	0.84	-	0.27	0.46	0.47
p,p'-DDD	M	6.97	5.47	3.79	19.81	11.15	12.28	7.88
	N	2.97	13.23	4.19	-	14.81	8.63	2.27
p,p'-DDT	M	0.34	12.87	3.02	88.55	9.92	3.28	1.57
	N	5.67	13.23	9.14	-	1.62	2.07	0.77
Total DDT	M	48.31	59.97	17.65	384.49	57.37	43.02	28.42
	N	67.74	81.87	186.73	-	88.79	39.62	37.59

Table 3.3.2.14

Distribution of individual PCB congeners in biota (ng/g, dry wt.)  
from 2 Mediterranean areas, 1989-1990  
(Albaiges and Bayona, 1991)

IUPAC No.	COASTAL BARCELONA						EBRO DELTA				
	<i>Mytilus sp.</i>			<i>Mullus sp.</i>			<i>Mytilus sp.</i>		<i>Ardea sp. eggs</i>		
	Max	Min	Mean*	Max	Min	Mean*	Max	Min	Max	Min	Mean*
28+31	3.5	0.08	3.0	8.7	0.1	3.0	1.6	0.6	120	0.4	80.7
52	3.0	0.04	4.4	17.3	0.2	6.1	0.8	ND	41.5	0.3	18.7
44	4.5	ND	-	NQ			1.6	ND	21.3	ND	-
101	11.5	0.4	8.5	37.6	0.5	13.1	1.4	0.3	46	ND	-
118	4.5	0.98	8.6	60.6	2.3	22.7	ND		174	ND	-
153	16.9	2.4	9.1	96.6	1.7	35.4	8.7	4.5	11.1	7.1	8.5
138+163	21.7	3.1	14.7	145	5.0	56.8	6.7	2.2	14.3	ND	-
187	14.6	6.1	7.8	NQ			7.2	ND	6.4	ND	-
128	7.3	0.7	3.4	NQ			1.1	0.4	60	ND	-
156	ND		-	NQ		ND	NQ		-		0.8
180	0.4	0.8	3.4	44.3	0.9	2.5	1.2	ND	0.3	ND	-
170	ND		-	ND		NQ	NQ		-		2.5
ΣPCB <sub>cong</sub>	80	15	62.9	411	11	140	30	8	495	7.8	-
ΣPCB <sub>1254</sub>			201			445	74	27	739	26	

\* Mean of three samples  
**ND** Not detected  
**NQ** Not quantified

Table 3.3.2.15

Distribution of organochlorinated pesticides in biota (ng/g, dry wt.)  
from 2 Mediterranean areas, 1989-1990  
(Albaiges and Bayona, 1991)

	COASTAL BARCELONA			EBRO DELTA			
	<i>Mytilus sp.</i>			<i>Mytilus sp.</i>		<i>Ardea sp.</i> eggs	
	Max	Min	Mean*	Max	Min	Max	Min
Methoxychlor	63.9	ND	-	ND		ND	
Dieldrin	ND			ND		181	7.9
Heptachlor	20	ND		2.8	2.1	ND	
Endosulfan	23.9	5.3	15.5	6.1	ND	ND	
I+II	1.3	0.5	0.8	1.6	0.8	15.1	10.4
HCB	2.9	0.2	1.2	1.0	0.3	11	ND
α-HCH	2.7	1.6	2.3	1.5	ND	11.3	
γ-HCH	29.3	ND	-	10.7	ND	115	8.9
o,p'-DDT	27.1	3.4	11.8	5.4	ND	84	ND
p,p'-DDT	11.5	ND	-	12.1	3.2	64	6.1
p,p'-DDD	17.1	ND	-	3.9	2.5	0.14	ND
o,p'-DDE	151	51	96	42	31	152	4.2
p,p'-DDE							

\* Mean of three samples  
ND Not detected

### 3.3.3 Organophosphorus compounds

The FAO/UNEP/IAEA/WHO *ad-hoc* meeting on organophosphorus compounds (18-20 November, 1987) decided on the basis of the then available information on the quantities currently produced and/or used in the Mediterranean countries and taking into account their toxicity, persistence and bioaccumulation, that six organophosphorus compounds should be treated as "case-examples" for the purpose of the assessment and the pilot survey. Four of the six compounds are pesticides (ethyl-parathion, methyl-parathion, fenitrothion and malathion) while the other two are non-pesticide organophosphorus compounds [tributyl phosphate (TBP) and tris(2-chloroethyl) phosphate (TCEP)].

#### 3.3.3.1 Sources and inputs

The types of marine areas at risk from contamination by organophosphorus compounds are:

- river mouths and estuaries
- lagoons
- shallow waters
- marshes.

Agricultural run-off, directly or indirectly through rivers and streams, is by far the largest input of organophosphorus compounds in the marine environment. Industrial effluents containing organophosphorus residues may, however, also be discharged directly into shallow waters through pipelines from on-shore plants.

A third source of pollution is aerial transportation of both non-pesticide and pesticide organophosphorus compounds. Common organophosphorus pesticides are appreciably volatile and considerable losses from treated crops may take place into the atmosphere. Volatilization following application and subsequent wet and dry deposition probably does constitute a major route of entry of these pesticides in the marine environment.

#### 3.3.3.2 Environmental levels

Information on point sources of the organophosphorus compounds into the Mediterranean is scarce. Most of the information available is related to surface waters. In the Tiber river maximum concentrations of malathion of 0.5 - 0.6 µg/L have been detected during the years 1970-73 (Leoni and Puccetti, 1971, 1978). Values have also been published for different pesticides in surface waters of the Ferrara Province during the period 1975-84 (Baldi *et al.*, 1986). For malathion, the concentrations were usually below 0.4 µg/L, although, in 1977 and 1982, 2.6 and 4.2 µg/L respectively were noted. Parathion-methyl concentrations were usually lower than 1 µg/L; a maximum level of 11.1 µg/L was found in 1981. Parathion-methyl values were essentially below 0.1 µg/L, except in 1976 where a 4.4 µg/L concentration was recorded. No fenitrothion has been detected in any water sample in this Italian Province. In France, 2 to 4 µg/L parathion-ethyl and malathion have been reported in the river Saône in 1968 (Mestres *et al.*, 1969), as compared to values below 8 µg/L in the drainage waters of the Camargue in 1978 (Podjelski and Dervieux 1978). In the latter drainage waters, the concentration of the pesticide decreased from 5 µg/L to 0.2 µg/L three days after application.

In Spain, values have been reported for fenitrothion in lake Albufera at Valencia (Carrasco *et al.*, 1987). For the period 1983-85, concentrations varied from 0.1 to 2.0 µg/L; these values decreased each time to non detectable levels (below 0.05 µg/L) within two weeks. For the non-pesticide TBP, data were published in 1987 for the Besos river mouth in Spain, (Gomez-Belinchon *et al.*, 1988); the organophosphorus levels ranged from 0.02 to 1 µg/L, with some peaks of 14 µg/L. In the Llobregat estuary TBP and TCEP were found at concentrations of up to 0.3 and 0.4 µg/L respectively (Barceló *et al.*, 1990). In Italy, TBP has been monitored in surface and drinking waters in Northern Italy in 1987. TBP levels in the river Po varied from 0.02-0.03 µg/L in Ferrara, to 0.04-0.13 µg/L in Turin (Galassi *et al.*, 1986).

In Greece, organophosphorus pesticides (diazinon, azinphos, methyl and parathion-methyl) have been detected in the Ioannina lake (appr. 33.5, 21 and 18 ng/L maximum annual values) and in the Kalamas river (appr. 32, 12.5 and 8 ng/L maximum annual values) during the period 1984-1985 (Albanis *et al.*, 1986).

A pilot survey organized in the framework of the Long-term Programme for Pollution Monitoring and Research in the Mediterranean (FAO/UNEP/IAEA/WHO, 1989) found lower values in two Mediterranean estuaries (Ebro and Llobregat in Spain) and in the Northern Adriatic coast (Lido delle Nazioni and Marina di Ravenna in Italy) than those reported for surface waters. The summary of the findings is as follows:

- (a) Fenitrothion and malathion were not detected in any of the sampling sites. Parathion-methyl was present only in the Llobregat estuary, where concentrations ranged from 1 to 30 ng/L. Parathion was detected at the two Adriatic sites where concentrations ranged from <1.0 to 3 ng/L. Phorate was not detected while diazinon was detected at every site with the exception of Ebro estuary. Concentrations were low in the Adriatic (<1.0 to 2 ng/L) but in the Llobregat estuary they ranged from <1.0 to 30 ng/L.
- (b) Industrial organophosphorus compounds usually gave higher concentrations than pesticides. The concentration of tributyl phosphate was 1-300, <1.0 to 20, 8 to 34 and 3 to 1000 ng/L at the Llobregat estuary, Ebro estuary, Lido Nazioni and Marina di Ravenna respectively. The corresponding concentrations were for tris-2-chloroethyl phosphate: <1.0 to 400, <1.0, <1.0 to 100 and <1.0 to 300; for tris-isobutyl phosphate: <1.0 to 900, <1.0, 40 to 200, 13-64. Trischloro-isopropyl phosphate was estimated only at the two Adriatic sites, where concentrations ranged from non detectable to 31 in Lido Nazioni and from non detectable to 9 ng/L in Marina di Ravenna.
- (c) The pilot study included two other areas which were the Haifa Bay and the Nile delta. At these sites no organophosphorus pollution could be detected but the detection limits (500 and 700 ng/L) were high and therefore the negative results only exclude the possibility of toxic contamination.

### 3.3.3.3 Levels in seafood

The pilot survey organized in the framework of the Long-Term Programme for Pollution Monitoring and Research in the Mediterranean (FAO/UNEP/IAEA/WHO, 1989) included estimations in biota.

(a) Mussels

In the Adriatic sites all the organophosphorus compounds were below the detection limit in mussels.

(b) Fish

In the Ebro estuary organophosphorus pesticides were detected in *Mullus barbatus* the maximum values of which were: diazinon, 12 ng/g; fenitrothion, 16 ng/g; paraoxon, 16 ng/g; parathion-methyl 2.2 ng/g. Industrial organophosphorus compounds could not be detected in biota.

### 3.3.4 Polycyclic aromatic hydrocarbons

The monitoring WHO/UNEP/FAO survey which was undertaken during 1989 and 1990 in the northern Mediterranean Coast of Spain, the Ligurian sea, the Ebro delta and the eastern Adriatic coast included analysis of PAH in mussels and sediments.

Concentrations of a number of Polycyclic aromatic hydrocarbons (PAH) in mussels were analysed from 13 sites along the Ligurian coast between 1989 and 1991 (Piccardo and Valerio, 1991). PAH analysed were Anthracene, Pyrene, Fluoranthene, Benzo(a)anthracene, Benzo(b)fluoranthene and Dibenzo(a,h)anthracene. The concentration of each PAH showed wide variations between the different sites. Results are given in Table 3.3.4.1.

A variety of parent compounds ranging from 3 to 6 aromatic rings and their alkylated derivatives were identified in *Mytilus galloprovincialis* and in sediments. Environmental levels were generally comparable with others previously reported from the Mediterranean region. Results are given in Table 3.3.4.2, where the ratio between parent and monoalkalated phenanthrenes reflects the contribution of pyrolytic versus fossil sources of pollution. The latter were more predominant in samples from areas under river influence. Conversely a significantly high predominance of pyrolytic sources was evident in the rest of the sampling sites.

Table 3.3.4.1

Concentrations of PAH (ng/g) in mussels collected along the Ligurian coast between 1989 and 1991. (Piccardo and Valerio, 1991)

SITE	An	Py	Flu	BaA	BbF	BaP	BkF	BP-DBA
1	3.33	48.95	80.24	39.26	28.86	8.27	9.95	6.20
2	1.72	15.07	26.69	10.24	13.84	6.90	4.27	3.67
2	0	18.65	32.01	26.22	14.90	4.88	0.51	3.76
3	0.88	8.66	8.48	4.60	7.50	3.95	4.73	1.16
4	1.93	13.37	11.10	6.02	7.80	3.47	2.77	1.48
5	0	2.73	1.80	1.39	1.68	0.57	0.16	1.1
6	0.95	3.07	2.31	1.46	3.07	1.47	0.66	0.72
6	0.58	4.29	6.29	0	0.25	0.17	0.28	1.08
7	0.87	2.72	0.80	0	0.65	0.31	0.08	0.29
8	0.55	3.39	0.62	0	2.12	0.62	0.02	0.89
9	0	10.27	3.20	6.19	6.50	2.85	4.45	4.29
10	0	1.23	0.32	0	0.49	0.13	0.34	1.39
11	0.75	3.21	5.24	0	1.27	0.21	0.55	1.76
12	0	2.94	4.96	0	0.75	0.20	0.59	0.97
13	0.70	2.46	2.02	0	1.57	0.63	0	0.44

Sites 2 and 6 sampled twice  
Site 13 - "control" site

An = Anthracene  
 Py = Pyrene  
 Flu = Fluoranthene  
 BaA = Benzo(a)anthracene  
 BbF = Benzo(b)fluoranthene  
 BaP = Benzo(a)pyrene  
 BkF = Benzo(k)fluoranthene  
 BP-DBA = Benzo(g,h,i)fluoranthene, Dibenzo(a,h)anthracene

Table 3.3.4.2

Distribution of PAH in sediments (ng µg/g, dry wt.) and biota (ng/g, dry wt.)  
from 3 Mediterranean areas, 1989-1990  
(Albaiges and Bayona, 1991)

COMPOUND	COASTAL BARCELONA			EBRO DELTA			LIGURIAN SEA
	Sediments (depth, m)			Sediments (depth, m)			
	A	B	C	D	E		
	10	40	43	30	520		<i>Mytilus sp.</i>
Phenanthrene (1)	30	405	57	9.2	16	32	38
Anthracene	10	150	16	0.6	1.3	ND	14
C <sub>1</sub> -Phenanthrenes	107	271	71	14.1	17.1	195	89
Fluoranthene (2)	97	757	373	17.8	30.7	8	322
Pyrene (3)	42	715	314	12.6	25.4	7	571
Benz[a]anthracene (4)	68	274	270	6.1	15.2	3	372
Chrysene + Triphenylene (5)	45	451	338	13.9	36.5	8	448
Benzo[b+j+k]fluoranthenes (6)	98	749	797	2.6	69	ND	310
Benzo[a]fluoranthene (7)	ND	129	58	0.5	24	ND	51
Benzo[e]pyrene (8)	29	364	369	3	30	ND	158
Benzo[a]pyrene (9)	33	525	452	0.2	15.2	ND	18
Perylene (10)	9	166	155	40	3	NQ	NQ
Indeno[1,2,3-cd]pyrene (11)	31	240	361	8.7	40	NQ	NQ
Benzo[ghi]perylene (12)	82	749	474	9.4	28	ND	NQ
ΣPAH	681	5945	4105	139	351	253	2391
Ph/ΣC <sub>1</sub> Ph	0.28	1.49	0.8	0.66	0.93	0.16	0.42
Fl/Py	2.3	1.06	1.19	1.41	1.21	1.18	0.56