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ASSESSMENT OF THE STATE OF POLLUTION OF THE MEDITERRANEAN SEA BY ORGANOHALOGEN COMPOUNDS

In co-operation with:

FAO WHO IAEA

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BACKGROUND

One of the primary aims of the Coordinated Mediterranean Pollution Monitoring and Research Programme (MED POL Phase I) launched in 1975 as the scientific/technical component of the Mediterranean Action Plan, was to compile information on the quality of the Mediterranean marine environment which could be used for the implementation of the Barcelona Convention and its related protocols.

Organohalogen compounds were among those substances which received high priority and a pilot project on baseline studies and monitoring of DDT, PCBs and other chlorinated hydrocarbons in marine organisms (MED III) was initiated and jointly coordinated by FAO and UNEP.

The results of this pilot project are published in MAP Technical Reports no. 3 and 9. Halogenated hydrocarbons are among the mandatory parameters for monitoring in the framework of MED POL Phase II.

The Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based sources (LBS protocol) was adopted in 1980 and entered into force in 1983.

Article 5 of this Protocol stipulates that:

a) The Parties undertake to eliminate pollution of the Protocol Area from land-based sources by substances listed in annex I to this Protocol.

b) To this end they shall elaborate and implement, jointly or individually, as appropriate, the necessary programmes and measures.

c) These programmes and measures shall include, in particular, common emission standards and standards for use.

d) The standards and the time-tables for the implementation of the programmes and measures aimed at eliminating pollution from land-based sources shall be fixed by the Parties and periodically reviewed, if necessary every two years, for each of the substances listed in annex I, in accordance with the provisions of article 15 of this Protocol.

Annex I includes organohalogen compounds and substances which may form such compounds in the marine environment with the exception of those which are biologically harmless or which are rapidly converted into biologically harmless substances.

The meeting on the technical implementation of the LBS protocol (December, 1985) recommended that an assessment document on the state of the pollution in the Mediterranean Sea should be prepared for each of the substances listed in Annex I and II of the LBS protocol.

The assessments should be used as a basis for proposing specific measures to the Contracting Parties.

The Contracting Parties which approved the recommendations of the meeting added that these assessments should include inter alia chapters on:

- sources, point of entries and amounts of pollution for industrial, municipal and other discharges to the Mediterranean Sea
- levels of pollution
- effects of pollution
- present legal, administrative and technical measures at national and international level.

The present document on the assessment of the state of pollution of the Mediterranean Sea by organohalogen compounds and proposed measures has been prepared in conformity with the above decisions. The document does not deal with all organohalogen compounds but only with some of those specified by the Working Group for Scientific and Technical Co-operation for MED POL (6-10 April 1987) which are the following pp and op DDT, ppDDE, ppDDD, aldrin/dieldrin, hexachlorobenzene, heptachlor/heptachlor epoxide, -HCH and all other isomers of HCH and PCBs. Little or no data could be found for endrin, chlordane, toxaphene or endosulfan and the document therefore makes no further mention of them.

1. INTRODUCTION

The Mediterranean Sea is an almost completely land-locked body of water which is contaminated by extensive discharges from the industrialized hinterland, by the dumping of sewage sludge and by various other sources of pollution. This has stimulated interest in the assessment of existing levels of potentially harmful chemicals in the Mediterranean Sea environment.

In recent years, considerable concern has been expressed over the worldwide distribution, the fate and ecotoxicological effects of various organic, persistent chemicals, especially the so-called chlorinated pesticides such as DDT, HCH, aldrin, dieldrin, heptachlor, mirex and chlorinated hydrocarbons such as polychlorinated biphenyls, terphenyls, and paraffins used in industry.

The present document presents a picture of the state of pollution in the Mediterranean by certain specific organohalogen compounds, outlines the scientific rationale for establishing controls and measures and recommends measures to be adopted by the Contracting Parties.

Part I, which comprises the bulk of the document, gives details of the compounds covered and their uses and provides information on sources and inputs and reviews the available data on levels in the various compartments of the marine environment (seawater, sediments, biota, etc).

Part II includes information on existing national and international controls and measures for the prevention of pollution by certain organohalogen compounds. It also outlines the scientific rationale for the establishment of environmental quality criteria and control measures.

2. GENERAL FACTS ON ORGANOHALOGEN COMPOUNDS

Organohalogens is a group of organic compounds which are substituted with halogens ie. chlorine, bromine, fluorine or iodine. The list of organohalgen compounds which is believed to be of economical or pollutional importance consists of more than one thousand substances. 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 (PCBs).

2.1 DDT and its metabolites

DDT is the abbreviation for dichloro-diphenyl trichloroethane but is correct chemical name for the p,p' isomer is 2,2-bis (p-chlorophenyl)-1,1,1-trichloroethane. The technical product usually contains up to 30% of the o,p' isomer and the material is used against a wide variety of agricultural and forest pests and against insect pests including disease vectors such as mosquito and tse-tse fly.

In the environment can be degraded by solar radiation or metabolised in organisms. Dehydrochlorination gives the metalolite DDE and dechlorination the metabolite DDD. (See Fig. 1 for the structural formulas).

2.2 Hexachlorocyclohexane (HCH)

This fully chlorinated alicyclic compound (Fig. 1), was also known (incorrectly but commonly) as benzene hexachloride (BHC). HCH can exist in seven stereo-isomers but the technical product contains only 5 of these, the most common being alpha, beta, gamma and delta. The gamma-isomer known as lindane is the one normally used as an agricultural pesticide.

HCH is a reasonably stable compound and only under alkaline conditions decomposes to yield trichlorobenzene. It is considered as one of the less persistent organochlorine pesticides.

2.3 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 (Fig. 1).

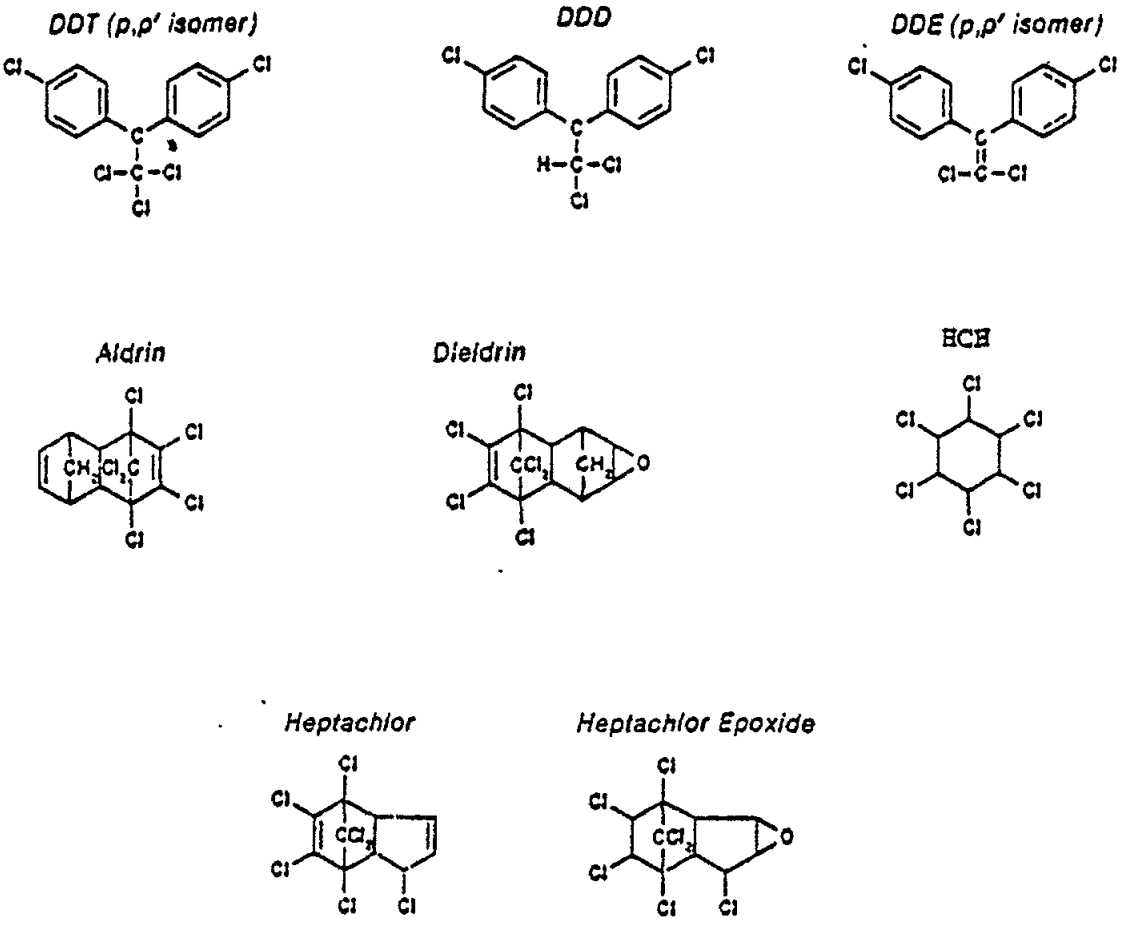


Fig.1 Structural formula of some chlorinated pesticides and PCBs

Further degradation of the epoxide dieldrin does take place but much more slowly. Endrin is a stereoisomer of dieldrin and is one of the most toxic of the chlorinated pesticides.

2.4 Hexachlorobenzene (HCB)

Hexachlorobenzene is a fully chlorinated compound formed when all the hydrogen atoms in benzene are substituted by chlorine atoms. It is generally accepted to be stable and persistent. It is used as a general fumigant and especially as a fungicide in grain storage. It occurs in many products as an impurity and thus may reach the environment by a variety of routes.

2.5 Heptachlor/Heptachlor epoxide

Heptachlor is the common name for 1,4,5,6,7,8,8- heptachloro-3a,4,7,7a-tetrahydro-4,7-methan-1H-indane and has the structural formula shown in Fig. 1. In the environment it is degraded or metabolised and is more commonly found as its epoxide. It is used as an insecticide and it also occurs in technical chlordane.

2.6 Polychlorinated biphenyls (PCBs)

PCBs are a group of aromatic organochlorine industrial products similar in structure to chlorinated hydrocarbon insecticides such as DDT. PCBs are produced commercially by the chlorination of biphenyl with anhydrous chlorine. The mixture obtained is purified and, during this process, hydroxylated biphenyls and chlorinated dibenzofurans can be formed. Commercially produced PCBs are mixtures of chlorinated biphenyl isomers and homologues. Impurities found in commercial PCBs can include polychlorinated naphthalenes (PCNs) and polychlorinated dibenzofurans (PCDFs). The structure, extent of chlorination, and theoretical number of derivatives of chlorinated biphenyls, chlorinated naphthalenes, and chlorinated dibenzofurans are given in Table I (Geyer et al., 1984).

3. SOURCES AND INPUTS OF HALOGENATED HYDROCARBONS INTO THE MEDITERRANEAN SEA

3.1 Production and use

3.1.1 Chlorinated pesticides

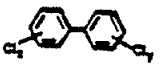
There are no sales or production statistics for the Mediterranean countries. In the implementation of MED POL X of MED POL Phase I consumption figures were collected for the 1973/1976 period which are shown in Table II. However, Cyprus, Egypt, Greece, Israel, Italy, Libya and Turkey reported to FAO that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

3.1.2 Polychlorinated biphenyls

PCBs have been produced industrially since 1929 and were or are manufactured in many industrial countries, including some Mediterranean countries. PCBs are nowadays used primarily in the electrical industry

Table I

Structures, extent of chlorination, and maximum number of chlorinated derivatives of chlorinated biphenyls, naphthalenes, and dibenzofurans.

Name	Structure	Number of chlorine	Number of chlorinated derivatives
Poly-chlorinated biphenyls (PCBs)		x + y = 1-10	209
Poly-chlorinated naphthalenes (PCNs)		x + y = 1-8	75
Poly-chlorinated dibenzofurans (PCDFs)		x + y = 1-8	135

- Extracted from Geyer et al. (1984)

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 III includes the trade name of PCBs manufactured in Mediterranean countries and production figures.

3.2 Inputs into the sea

3.2.1 Atmposphere inputs

Exchange of matter across the air/sea interface can occur in a variety of ways, illustrated by the simple outline below: (GESAMP, 1980).

Table II

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

Kind of Pesticide	Consumption (t active ingredient per year)												estimated area treated ($10^3 km^2$)
	Cyprus (1976)	Egypt (1975/76)	Greece (1973)	Israel (1974)	Italy[1] (1975)	Lebanon (1973)	Libya (1974)	Spain[2] (1976)	Syria[2] (1976)	Tunisia (1973/74)	Turkey (1976)	Total	
1. 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
1.1 DDT and related compounds	11.2	169.3	-	10.3	866.4	-	-	12.7	36.7	-	864.1	1970.7	29.1
1.2 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
1.3 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
1.4 Other organo-chlorine compounds	3.0	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 Umbrian regions
[2] Mediterranean watershed only

Table III

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

Country	Manufacturer	Trade name	Production (m.tons)
France	Prodelec	Phenoclor, Pyralene	6557 [a]
Italy	Caffaro	Fenoclor, Apirolio	1479
Spain	Cross, S.A.	Fenoclor	1241

[a] Includes T 60 which is 100% triphenyl

a) Downward transport

Gaseous
(i) Wet - incorporation in precipitation
(ii) Dry - direct transfer across air-sea interface

Particulate
Wet:
(iii) Rainout
(iv) Washout

Dry:
(v) Gravitational / Brownian deposition
(vi) Trapping by whitecap bubbles

b) Upward transport

Gaseous
(vii) Molecular evaporation from surface
(viii) Purging by bubbles

Particulate
(ix) Bursting bubbles and spray

The discovery of DDT and other chlorinated hydrocarbons in many parts of the world's oceans far from apparent direct inputs, shows that the mechanisms of global dispersion of some of these pollutants had to be by a more rapid mode than was possible by oceanic turbulence and current systems. The trans-Atlantic atmospheric transport of DDT by the Northeast Trade Wind System was first deduced from observations by Risebrough et al., (1968). The presence of chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface waters has been investigated more intensively by Bidleman and Olney (1974 and 1975).

Atmospheric polychrorinated biphenyls were monitored over a two-year period at a coastal sampling station in Monaco and from ships in the Mediterranean sea (Villeneuve, 1985). Concentrations of PCBs in the near ocean atmosphere at Monaco, temperature and wind direction are

presented in Table IV. Plotting PCB concentrations versus temperatures gives a correlation coefficient of 0.95 for wind blowing from the north and 0.79 for winds blowing from north/northwest. This can be explained by the fact that wind coming from the north passes over the Alps where there are no industries, whereas winds coming from north/northwest are loaded with industrial discharges from the Rhône Valley. An increase in PCB concentrations of one order of magnitude was also noted with an increase of temperature of 20 K. Table V shows PCB concentrations in samples taken during various cruises aboard research ships in the Mediterranean sea. Results from Table V gave an average of 0.23 ng m^{-3} for 1975 cruises and 0.07 ng m^{-3} for 1977 cruises. The wide spatial coverage and relatively small number of analyses reported in the paper for atmospheric samples mean that the decrease in atmospheric levels recorded over the two year period is of doubtful significance. Concentrations of PCBs reported in the atmosphere of the Mediterranean sea were similar to values reported for the Central Pacific (0.19-0.32 ng m^{-3}) the Antarctic ocean (0.11-0.25 ng m^{-3}) the South Pacific (0.012 ng m^{-3}) the North Pacific (0.049 ng m^{-3}) and for Bermuda samples (0.21-0.65 ng m^{-3}) collected during 1974.

Although Ljubljana (Yugoslavia) is more than 50 km inland, it is interesting to note the results of the investigation of chlorinated hydrocarbons in the atmosphere carried out by Jan et al. (1978). Airborne particulate matter was continuously sampled from the atmosphere of the residential town area of Ljubljana and trapped on a filter. The PCB concentration in the particulate matter in the atmosphere was 1.3 ng m^{-3} and the concentration levels of the total DDT, dieldrin, alpha, gamma, delta HCH and heptachlor epoxide were 0.86, 0.03, 0.08, 0.05, 0.03 and 0.01 ng m^{-3} respectively. Since gaseous forms of chlorinated hydrocarbons were not efficiently trapped, true atmospheric levels could be considerably higher than those actually reported here (Jan et al., 1978).

Table VI summarises data on the concentration of PCBs and chlorinated pesticides in some samples of rain water collected during 1979/80 in Rijeka, Yugoslavia (Picer and Picer, 1985) and in the south of France, Menton (Villeneuve and Cattini, 1986). The concentrations reported in this study are in line with those reported in the word literature for other areas (Table VII). No other published data on the concentrations of chlorinated hydrocarbons in rainwater could be found for either the open or coastal waters of the Mediterranean Sea.

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 (Table VIII).

3.2.2 Other 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 and was based on a number of

Table IV

PCB concentrations in the near ocean atmosphere
(Musée Océanographique Monaco).

Date	Temperature °C	Volume of Sample m^{-3}	wind direction	PCB (Ar. 1254) ng m^{-3}
75-08-05	25.6	190	N/NW	0.5
-08-25	21.5	200	N/NW	0.5
-10-03	20.1	370	N/NW	1.0
-10-06	18.9	400	N/NW	0.4
-10-07	14.5	320	E	0.5
-10-28	16.6	400	N/NW	0.2
-12-01	11.9	410	N	0.3
-12-08	11.3	410	N	0.4
-12-09	11.2	410	N/NW	0.4
-12-10	11.5	430	E	0.3
76-01-14	10.4	360	N	0.3
-01-26	6.4	380	SW	0.1
-01-27	4.5	280	N/NW	0.04
-01-28	4.8	400	N	0.04
-01-29	6.1	390	N	0.05
-02-02	8.2	390	NW	0.08
-02-03	10.2	390	N/NW	0.07
-02-04	9.3	390	N/NW	0.07
-02-05	10.7	380	E/NE	0.04
-02-06	13	380	NE	0.03
-02-09	6.1	410	E	0.07
-02-10	8.2	410	N/NW	0.05
-02-11	9.1	410	N/NW	0.08
-02-12	9.3	410	NW	0.05
-11-09	12	340	N/NW	0.96
-11-15	11.5	320	N/NW	0.5
77-01-25	10.5	430	SW	0.47
-01-31	9.5	410	N/NW	0.48
-02-03	8	410	N/NW	0.47
-02-07	10	380	E/NE	0.91
-02-10	12	510	W/SW	0.66
-02-14	10	430	S/SW	0.38
-02-23	11	380	E/NE	0.63
-02-25	13	510	W/SW	0.45
-03-02	10	470	N/NW	0.41

- Extracted from Villeneuve (1985)

assumptions as to use patterns, with the end result being expressed as a percentage of the field used pesticides entering the sea. The results are summarised in Figure 2 and Table IX 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 V

Over ocean air concentration of PCBs in the Mediterranean sea (Aroclor 1254 equivalents).

	Sampling station		(PCB) ng m^{-3}
Western Basin			
September 1975	Cavalaire Harbour	OC	0.3
	42°30'N 6°30'N	OC/1	0.3
	40°30'N 6°30'E	OC/3	0.2
	37°30'N 6°30'E	OC/6	0.2
July 1977	41°12'N 8°41'E	CS 41	0.08
	40°00'N 7°30'E	CS 44	0.05
Tyrrhenian Sea			
September 1975	40°00'N 11°40'E	OC/9	0.1
Ligurian Sea			
September 1975	42°17'N 9°45'E	OC/13	0.3
Adriatic Sea			
November 1977	Off Split	CAL	0.1
	Off Mljet	CAL	0.04
	40°20'N 18°54'E	CAL 1	0.08

- Extracted from Villeneuve (1985)

Surveys of chlorinated hydrocarbons in marine environments along the French coast (Elder, 1976) have shown that high concentrations occur near the mouth of the Rhône river. Similar results were obtained by Burns and Villeneuve (1982) working off the Var river estuary near Nice. Contamination of the waters and sediments of the Tiber estuary with polychlorinated biphenyls and hexachlorobenzene was studied in 1976 and 1977 (Puccetti and Leoni, 1980). PCBs were detected in all samples analysed at mean levels of 0.297 $\mu g\ l^{-1}$ (1976) and 0.135 $\mu g\ l^{-1}$ (1977). The amounts of PCBs are expressed as decachlorobiphenyl. It is interesting that where contamination was found it increased with increasing distance from the shore. Possibly, Tiber waters act as a microbiological decontaminating agent, as, in fact, waters of the estuary are strongly polluted by microorganisms. Hexachlorobenzene was

Table VI

Organohalogens in rainwater over Rijeka (Yugoslavia) and Menton (southern France). Concentrations in ng l^{-1}.

Compound	Rijeka (19/9/80) Mean	Menton (1985) Dissolved	Menton (1985) Mean total
pp DDT	0.95	1.54	3.44
pp DDE	0.30	0.06	1.47
pp DDD	0.12	-	-
Dieldrin	0.05	-	-
alpha HCH	-	4.7	5.74
Lindane	-	30	31.25
HCB	-	0.64	0.65
Toxaphen	-	7.2	32.4
PCBs	4.53	1.3	25.1

References: Picer and Picer (1985); Villeneuve and Cattini (1986)

Table VII

Chlorinated hydrocarbons in rain water (ng l^{-1}) (Marchand et al. (1983) modified).

Area	Year	DDT	total average	HCH total range	PCB
1. New Brunswick, Canada	1967-1968	10-1330			
2. Ohio, USA	1965	187(70-370)	25	6-50	
3. Florida, USA	1970	1000			
4. Hawai, USA	1970-1971	3(1-13)	5	1-19	
5. California, USA	1972				10
6. New, York, USA	1974	n.d.-2			
7. Tokyo, Japan	1968-1969		322	74-1228	
8. Great Britain	1964-1965	2-3(pp DDT)	75	12-164	
9. Great Britain	1966-1967	79(30-115)	83	37-156	
10. Great Britain	1970				50-100
11. Germany	1970-1972	1-100			
12. Great Britain	1975-1976	7.8(0.3-44)	10.4	5.7-17	14.9(1.8-74)
13. Great Lakes, Canada	1976	3.3±4.6	17.0		21±30
14. Brest, France	1977-1978	1.7±0.6	29.2		8.3±3.7

n.d.- under sensitivity limit
± - standard deviation

identified in only 16% of the water samples analysed and was not detected in sediment samples. Although hexachlorobenzene was always detectable at the fresh water surface (Leoni and D'Arca, 1976), its only occasional presence and the low values which were found at sea suggest that this compound is not stable in the marine environment or is diluted there (Puccetti and Leoni, 1980).

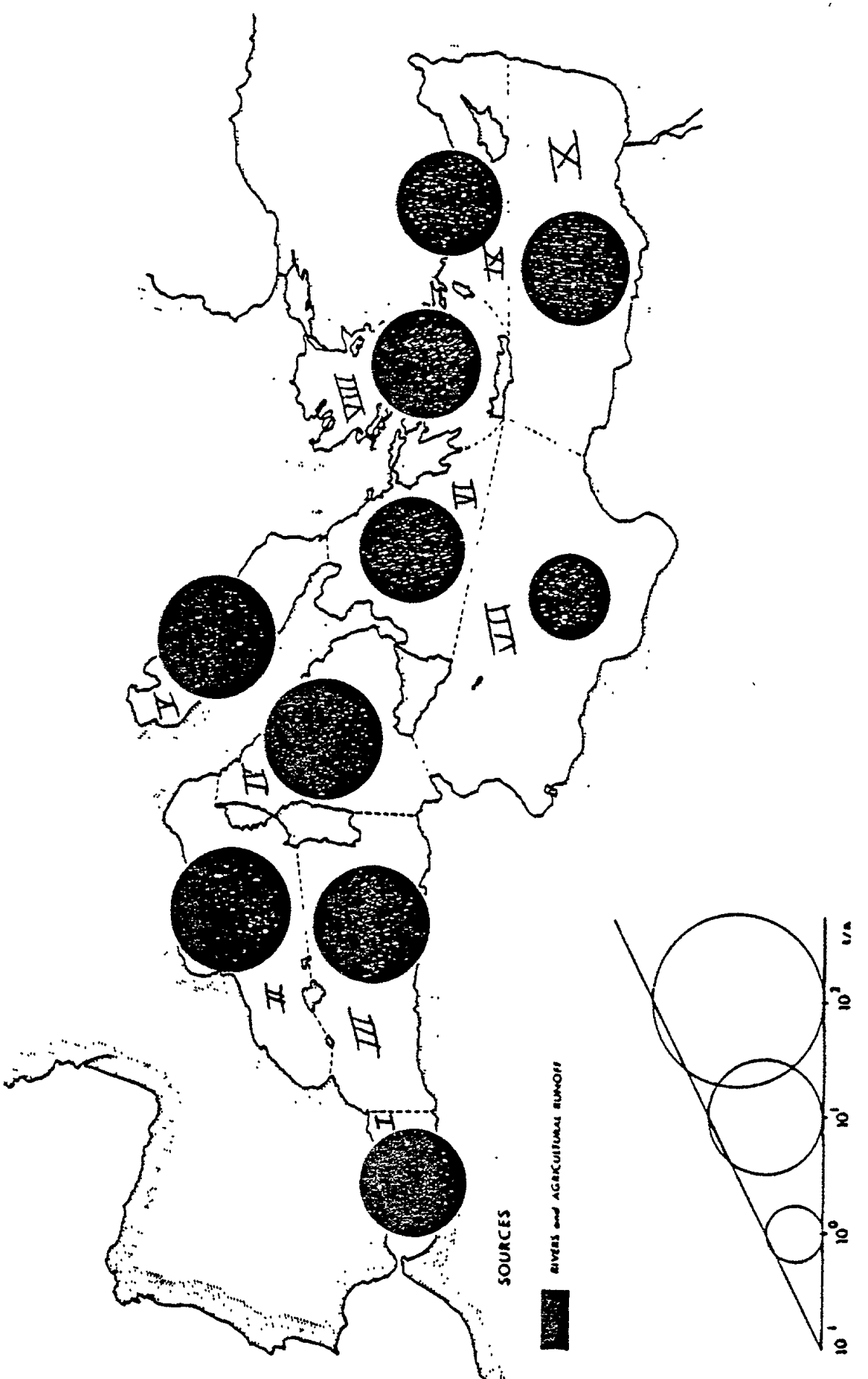


Fig. 2 Regional contributions of organochlorine pesticides

Table VIII

Comparison of Atmospheric and Riverine Input Rates of Organochlorine Compounds to the World Oceans ($\mu g\ m^{-2}\ yr^{-1}$).

Compound	Atmospheric	Estimated Riverine	% Atmospheric
ΣHCH	14.3	0.1-0.2	99
ΣPCB	0.72	0.1-0.2	78
ΣDDT	0.49	0.01	98
Chlordane	0.066	0.01	87
Dieldrin	0.13	0.01	93
HCB	0.23	0.01	96

Table IX

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

Mediterranean Region	Pollution load tons/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

- Table extracted from UNEP (1984)

The process of dispersion and the diminution of concentrations of chlorinated hydrocarbons (PCB, DDT and Lindane) in sediment of Rhône estuary is very well shown in Fig. 3 (Marchand et al., 1985). Stations where sediment samples were collected are presented in Fig. 4.

Fig. 5 shows the amounts (in mg sec^{-1}) of chlorinated pesticides which were carried by the river Po in January, April and July 1973 (Anonymous, 1977).

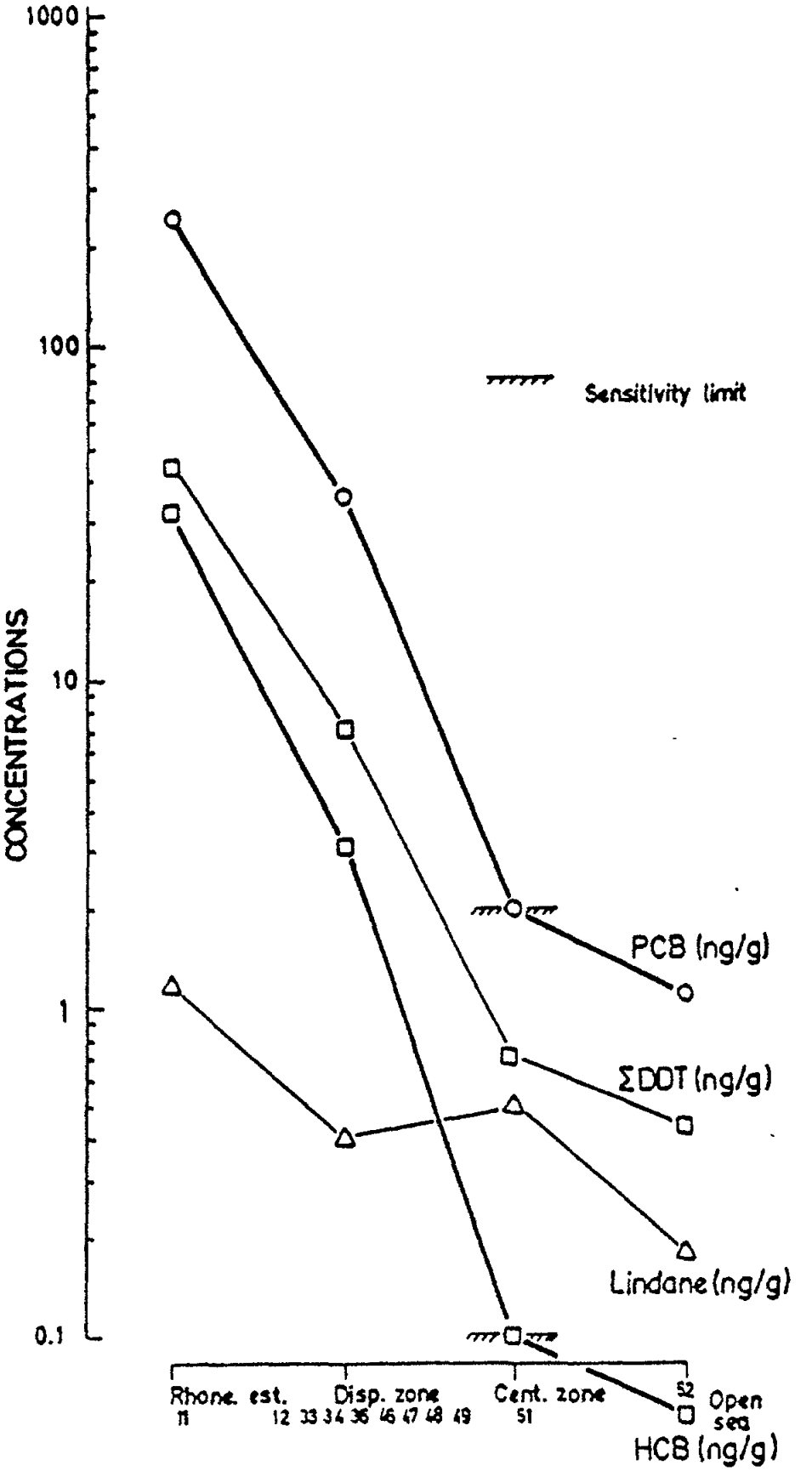


Fig. 3 Dispersion of chlorinated hydrocarbons in the Rhône estuary and the Golfe du Lion (Marchand et al., 1985)

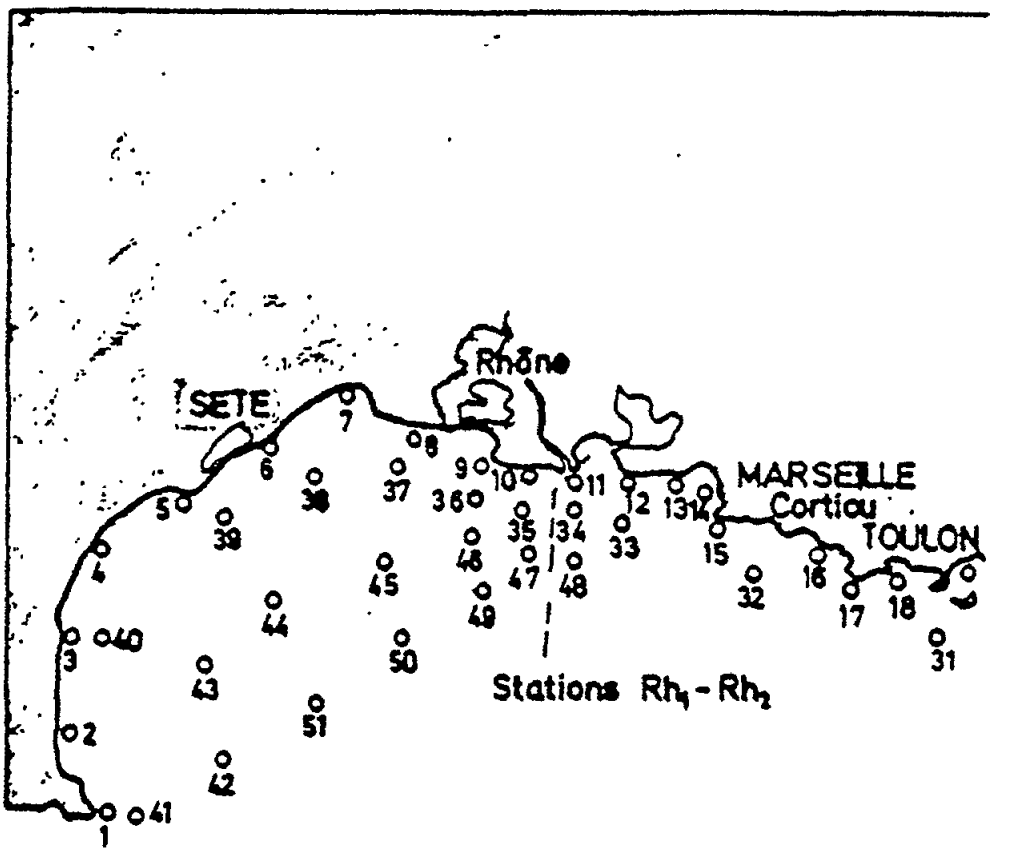


Fig. 4 Sediment sampling stations in the Rhône estuary

Polychlorinated biphenyls can be used as tracers of long-term integrated flow of contaminants in the sea. Dexter and Pavlou (1973) used PCBs to map the distribution of effluents from sewage outfalls on the southern Greek coast. For both DDT and PCB distributions, the trends are similar and indicate that the observed gradients result mainly from diffusive transport of contaminated material discharged at the sewage outfall. The PCB distribution also shows relatively high concentrations in the western Keratsini Bay and south of Cape Kinosoura. The latter suggests either the existence of a significant local input, or the highly industrialized eastern Elefsis Gulf, as a major PCB source.

The influence of metropolitan waste on the concentration of chlorinated hydrocarbons in striped mullet sampled in the Saronikos Gulf (Greece) was studied by Voutsinou-Taliadouri and Satsmadjis (1982). They demonstrated the powerful influence of the main sewage outfall. As can be seen in Table X from the ratios A/E, B/E etc., the concentrations of the major chlorinated hydrocarbons fall dramatically from one area to the next in the sequence A,B,C,D, and E (Fig. 6), and especially from A to B. This shows that Mullus barbatus readily takes in the compounds, either through the gills or from food at the bottom of the sea. The rate of decrease depends on the constituent.

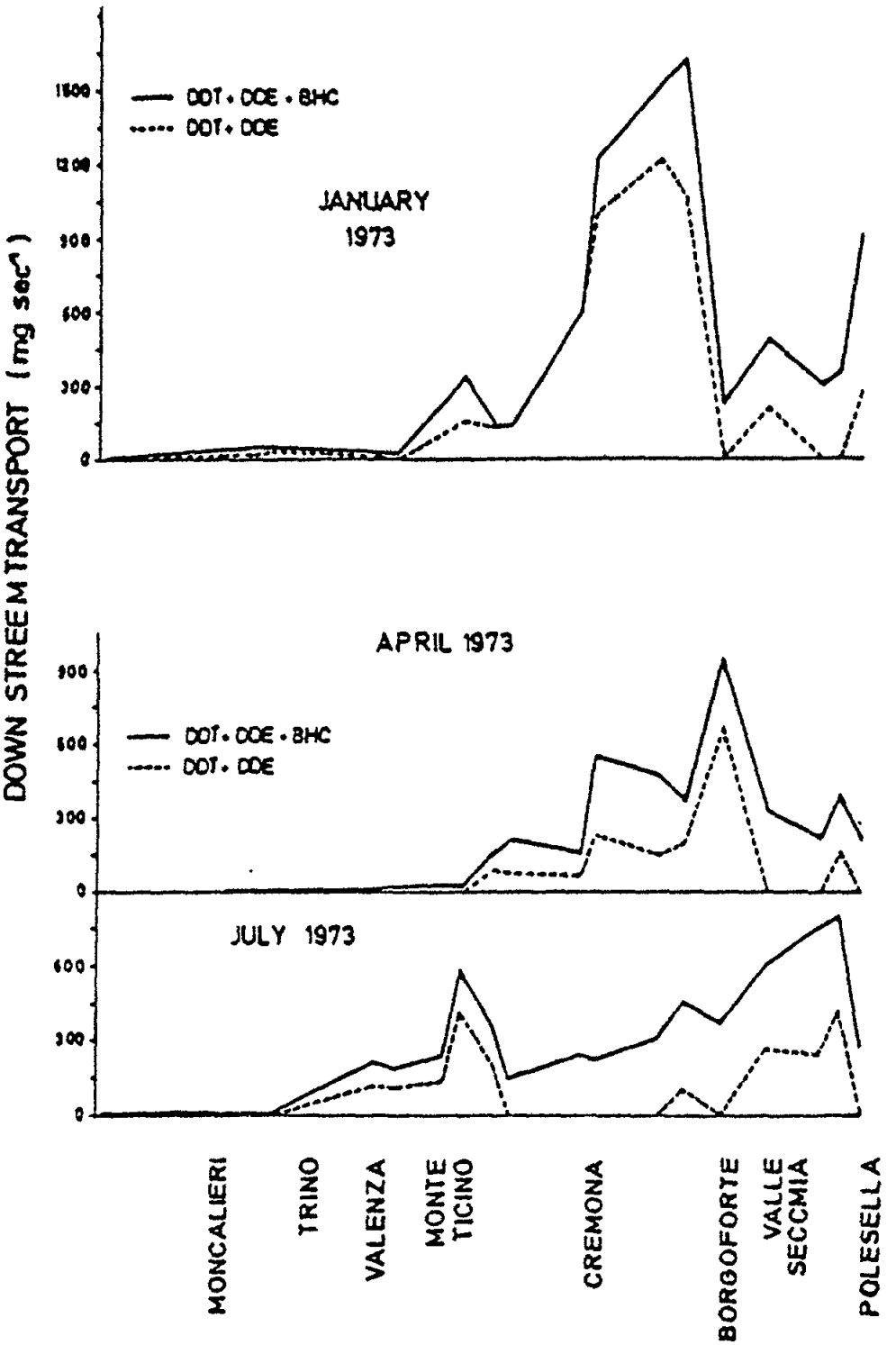


Fig. 5 Downstream transport of chlorinated hydrocarbons in the river Po. (Anonymous, 1977)

Table X

Influence of metropolitan waste on the concentration of chlorinated hydrocarbons in striped mullet from the Saronikos Gulf.

Area (No. sampl)	Para-meter	Length (mm)	Weight (g)	Extract (%)	PCBs (ppb)	DDE (ppb)	DDT (ppb)	DDD (ppb)	DDTs (ppb)	BHCs (ppb)	Hept. epox. (ppb)	Dieldrin (ppb)	Endrin (ppb)
A	Mean	135	44	4.24	460	72	78	66	216	5.6	0.3	17	2.3
(13)	High	145	58	7.40	1200	151	118	145	400	8.2	0.5	50	3.5
	Low	125	35	2.80	170	39	48	26	125	3.8	0.2	0.4	0.9
		7	8	1.70	380	35	24	52	105	1.4	0.2	17	1.5
	A/E	1.07	1.29	2.42	17.56	8.89	15.6	27.5	13.94	3.73	1.5	34	11.5
B	Mean	147	58	2.92	176	29.7	20.3	12.4	62.4	5.6	0.3	2.4	1.5
(14)	High	205	139	5.30	340	48	41	20	102	10	0.6	4.7	2
	Low	124	29	1.16	63	8.6	5.3	5	20.1	1	0.1	0.1	0.5
		34	62	1.84	87	12	10	8	24	3.5	0.2	2.2	0.8
	B/E	1.17	1.71	1.67	6.72	3.67	4.06	5.17	4.03	3.73	1.5	4.8	7.5
C	Mean	137	44	3.59	36.5	14.2	9.7	4.3	28.2	4.6	0.3	1.1	0.9
(17)	High	155	68	6.20	90	35	18	7.7	58	9.9	0.7	3.1	2.2
	Low	129	33	1.33	3.8	4	3.5	0.6	8.4	0.4	0.0	0.0	0.3
		9	16	1.65	36	14	8	3.3	23	4.8	0.1	1.4	0.9
	D/E	1.09	1.29	2.05	1.39	1.75	1.94	1.79	1.82	3.07	1.5	2.2	4.5
D	Mean	137	44	3.59	36.5	14.2	9.7	4.3	28.2	4.6	0.3	1.1	0.9
(17)	High	155	68	6.20	90	35	18	7.7	58	9.9	0.7	3.1	2.2
	Low	129	33	1.33	3.8	4	3.5	0.6	8.4	0.4	0.0	0.0	0.3
		9	16	1.65	36	14	8	3.3	23	4.8	0.1	1.4	0.9
	D/E	1.09	1.29	2.05	1.39	1.75	1.94	1.79	1.82	3.07	1.5	2.2	4.5
E	Mean	126	34	1.75	26.2	8.1	5	2.4	15.5	1.5	0.2	0.5	0.2
(12)	High	145	56	3.79	53	20.5	12	5.2	37.7	2.5	0.5	0.9	0.6
	Low	107	21	0.79	13.9	2.3	1	0.3	3.6	0.3	0.1	0.1	0.0
		11	11	1.05	13.1	5.9	3.5	1.9	10.8	0.8	0.2	0.3	0.2

- Extracted from Voutsinou-Taliadouri and Satsmadjis (1982)

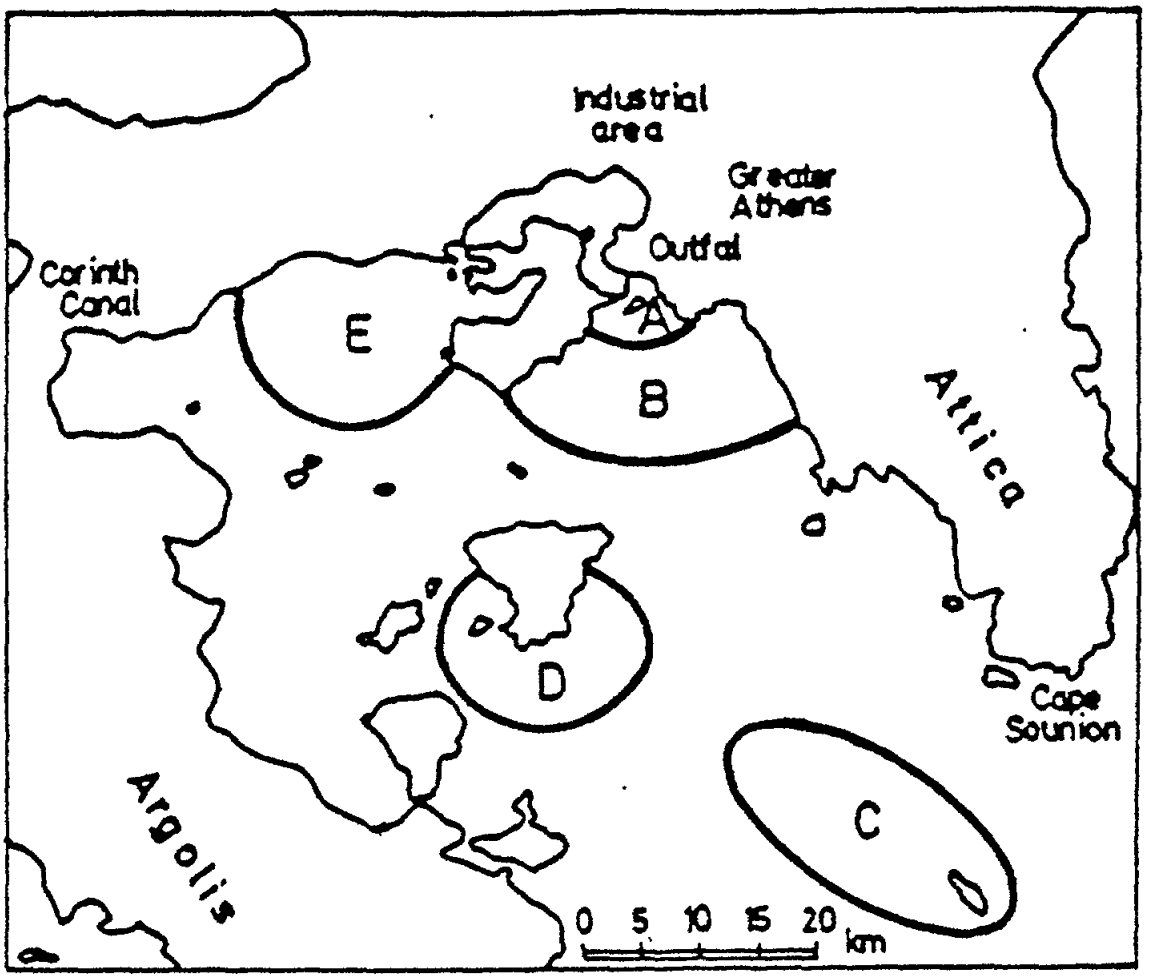


Fig. 6 Study area in the Saronikos Gulf

The potential effects of pesticidal pollutants carried by the river Nile and its associated canals and drainage systems were investigated by El-Sebae and El-Amayem (1979). The results (Table XI) indicated the presence of some chlorinated hydrocarbon pesticides in concentrations ranging from 0.34 to 0.95 $\mu g\ l^{-1}$ in Mahmoudieh canal water and from 0.19 to 0.95 $\mu g\ l^{-1}$ in slaughter waste water.

In order to evaluate the effects of municipal waste-waters on communities, one of two experimental basins in the lagoon of Strunjan (North Adriatic -Piran) was treated with 300 1 of primary settled sewage daily, while the other was kept clean as control (Salihoglu et al., 1980). The resulting accumulation of organochlorine compounds in mussels, sediments, crabs and holothuria was determined. The concentrations of chlorinated hydrocarbons in sediments of the polluted

basin were found to be higher than in the clean one. The sum of the DDT and DDT derivatives was approximately three times higher in the polluted basin than the values obtained in the clean basin. The same applied to PCBs. Similar trends were also found in mussels and holothuria, but this was not the case for the crabs which are both predators and scavengers.

Table XI

Chlorinated pesticides in Alexandria city municipal waters.

Pesticide	Canal raw water	($\mu g\ l^{-1}$) Slaughter-house waste water
BHC	0.39	0.19
Lindane	0.34	0.63
Heptaclor	0.70	0.19
p,p' DDE	0.65	0.95
o,p' DDT	0.95	0.25

- Extracted from El-Sebae and El-Amayem (1979)

4. FATE OF CHLORINATED HYDROCARBONS IN THE MEDITERRANEAN SEA

Despite the difficulties associated with the analysis of organochlorane compounds, especially at the low concentrations normally found in marine samples, there is now little doubt that the chlorinated hydrocarbons such as DDT, dieldrin and PCBs, are major long-term contaminants of the total environment and small traces can be found in almost all compartments of the world's ecosystem (Edwards, 1975). An attempt to summarize the cycling of pesticides through the environment is made in Fig. 7 which illustrates the movements of residues through the various compartments of the environment. Care must however be exercised in applying data from different studies to the compartmentalised conception of the environment, because of the analytical problems referred to earlier.

4.1 Pollutant-particle association and dynamics in coastal marine environment

A wide variety of substances, including chlorinated hydrocarbons, become associated with "particles" in coastal marine environment. This association may result from:

(i) precipitation or hydrophobic interactions with the particle surface,
(ii) co-precipitation with hydrous oxides of iron and manganese either as coatings, or as flocs of the precipitate,
(iii) incorporation into mineral lattices, organisms or faecal material or
(iv) flocculation of colloidal organic and inorganic matter during river and sewage mixing. (Olsen et al., 1982).

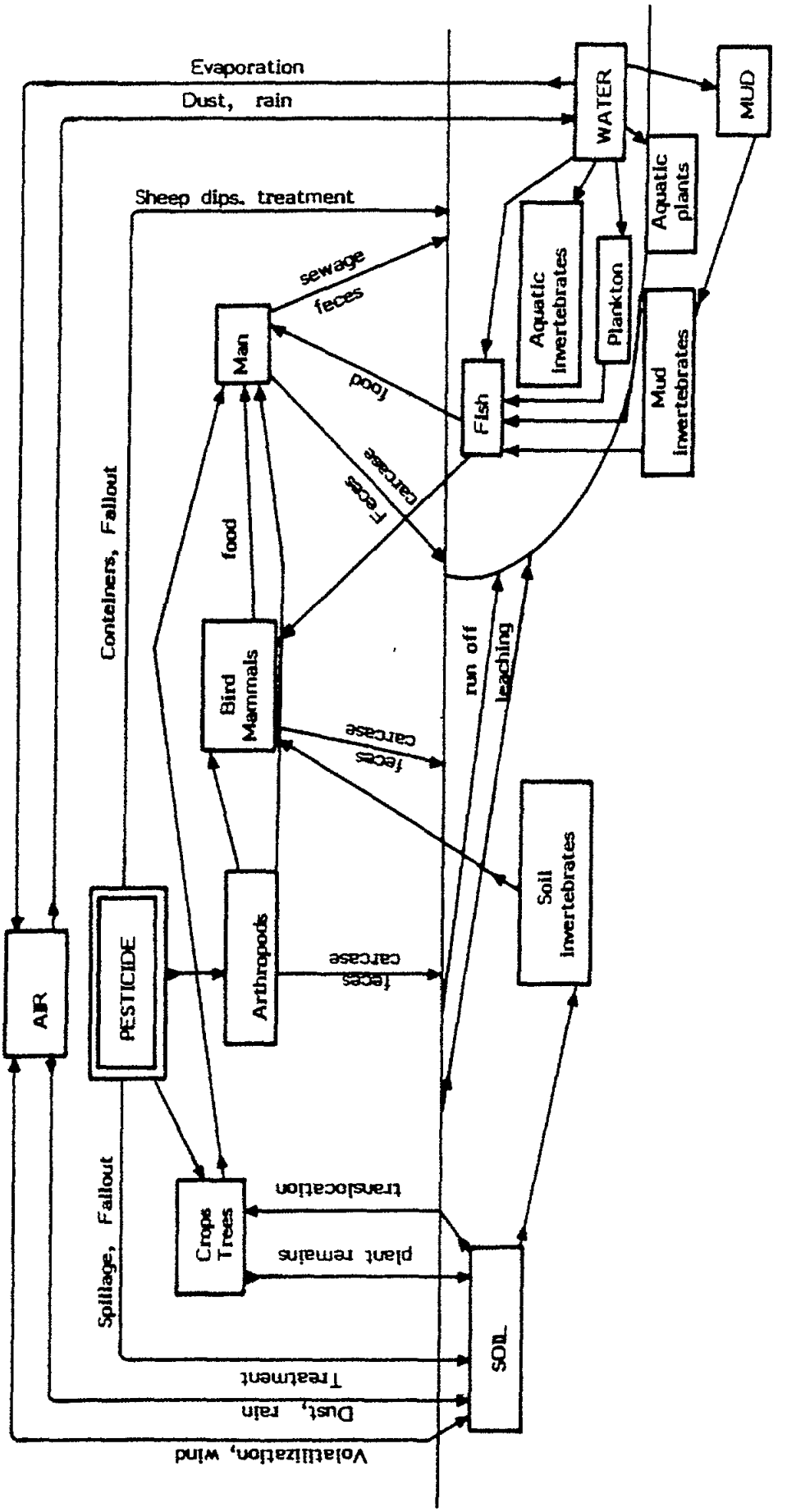


Fig. 7 Movement of a pesticide between environmental compartments

One of the most basic geochemical tools for assigning a quantitative value to this association is the distribution coefficient which is here defined as $K_d=C_p/C_w$ where C_p is the concentration of a specific pollutant associated with a given weight of particles and C_w is the concentration of the pollutant in an equal weight of water. Distribution coefficients for highly reactive pollutants such as chlorinated insecticides and PCBs are generally of the order of 10^5. Consequently, in an aqueous system having a suspended matter concentration of 10 mg l^{-1} (which is typical in near-shore coastal areas) approximately 50% of the mass of such pollutants will be absorbed into suspended particles and another 50% will be "dissolved" in the water. In shelf and slope waters, where suspended particle concentrations are on the order of 1 mg l^{-1} or less, much of the pollutant mass is transported with the water phase, but particulate phases play an important role in the removal of these pollutants from the water column, and the bottom sediments are their major sink.

4.1.1 Hydrophobic association with surfaces

The distribution coefficient for a specific pollutant may vary depending on the chemical form and concentration of that pollutant. Bopp (1979) showed that the lower-chlorinated biphenyls (di and tri-chlorobiphenyls) have a lower distribution coefficient ($<10^4$) relative to the higher-chlorinated biphenyls (penta- and hexa-chlorobiphenyls), which have a K_d value of the order of 10^5.

If the substance is non-polar, i.e. uncharged and unable to engage in electrochemical interactions, it will probably have a very low solubility and a strong affinity for phase boundaries such as air-sea interface or the surface of particles. This tendency of non-polar substances to adhere to one another or to phase boundaries in aqueous environments has been called hydrophobic bonding. Many of the organic molecules of chlorinated hydrocarbon pollutants are non-polar or have non-polar functional groups. In natural waters, these surface active compounds are readily adsorbed, via their hydrophobic functional groups, out of the aqueous phase.

Another important chemical property of non-polar organic pollutants is their affinity for other less-soluble organic phases. For example, the solubility of DDT in water is less than 10^{-4} g l^{-1}, whereas its solubility in vegetable oils, kerosene, and gasoline is 10^2 g l^{-1}, and its solubility in benzene is 10^3 g l^{-1}. Consequently, there is a strong tendency for organic pollutants to become associated and accumulate with other organic phases, whether that be lipid or adipose tissue in organisms (Clayton et al., 1977), oils in sea surface films (Duce et al., 1972), dissolved or particulate humic substance in seawater (Pierce et al., 1974), or organic detritus in sediments (Bopp, 1979).

The equilibrated distribution of DDT between its liquid and solid phases in the Adriatic seawater medium was investigated by means of the radiotracer seawater technique (Picer, M. et al., 1977; Picer, N. et al., 1977). These various investigations examined the influence of DDT concentration on its adsorption on several model solid phases and natural sediments from the Adriatic, the North-West Mediterranean and the Pacific. Desorption experiments indicated that the adsorption process is reversible. Desorption was greatest from quartz than from

limestone, and was significantly lower from marine sediments. Examination of the equilibrium distribution of DDT between sea water and the examined surfaces suggested that DDT in the investigated systems existed as a colloidal dispersion.

Investigations of the fate of DDT and its metabolited DDE and TDE as well as dieldrin and Aroclor 1254 (PCB) in laboratory-grown phytoplankton cultures have been described by Picer et al. (1979a; 1979b), and tended to confirm this suggestion. Ranges of recovered investigated pollutants and their distribution within the experimental system are shown in Table XII. The ranges presented suggest that the distribution of the pollutants under the investigated circumstances varies considerably, especially from Millipore filter and Erlenmeyer flask walls. The explanation for such a great variability of results was that the DDT and other pollutants in the experiments described did not exist as a sea-water solution but as a kind of colloidal aggregate. It is obvious that the fate of DDT and other investigated low-solubility organic pollutants added to laboratory grown phytoplankton systems in concentrations which are higher than their solubility, is born very complex and unpredictable.

4.1.2 Biological incorporation, aggregation and cycling

Pollutant incorporation into biogenic particles, coupled with subsequent organism migration, food chain transfer, or faecal pellet deposition, provides a rapid and ecologically important transport system in the marine environment. Pollutant associations with organisms are a result of direct uptake from ingestion of sediment particles, organic-pollutant complexes or contaminated food or passive sorption as water passes over gills, mucous layers, tests, or other exposed surfaces. Bio-assimilation varies depending on the chemistry of the incorporated pollutants. For example, hydrophobic chlorinated hydrocarbons (DDT and PCBs etc.,) are fat soluble and readily become associated with lipid tissue (Olsen et al., 1982).

Salihoglu et al. (1980) investigating the influence of pollution on marine organisms and sediments in experimentally polluted ecosystems with waste water, he also looked into the particle size of sediment samples (Table XIII). The pesticide and PCB content of the smaller sized sediment samples was higher than in the larger ones. This was not unexpected, since total surface areas increase with decreasing size which consequently causes an increase in the adsorption of chlorinated hydrocarbons. Villeneuve and Burns (1983) discussed transport of lindane in the Mediterranean Sea in connection with its adsorption properties. They considered the lindane concentration seen in sediments too high to be accounted for just by water mixing and subsequent partitioning into sediments. By using an equilibrium partition model they calculated that in the Mediterranean sediment samples there were three orders of magnitude greater concentrations of lindane than would be expected by partitioning from water. Even assuming complete mixing and equilibration with surface waters this would not account for the sediment concentrations observed.

The rate of vertical mixing in the ocean is too slow to account for the quantities of polychlorinated biphenyls found in Mediterranean abyssal sediments (Elder et al., 1976) if one assumes that they penetrate into the deep ocean only in the dissolved state. An

Table XII

Ranges of recovered investigated pollutants and their distribution within the experimental system.

		DDT	DDE	TDE	Dieldrin	Aroclor
Total recovery(%)	from	3	9	3	4	2
	to	29	32	41	42	18
Recovery distribution of pollutants by system component (%)						
Millipore filter	from	0	13	0	0	28
	to	99	90	100	93	93
Filtrate	from	0	0	0	0	0
	to	5	03	01	66	9
Erlenmeyer flask walls	from	0	3	0	0	7
	to	86	75	72	59	36
Vacuum flask walls	from	0	0	0	0	0
	to	15	15	27	26	10
Aluminium cap	from	0	0	0	0	0
	to	26	15	4	4	20

alternative explanation is that PCBs are carried to the sediments by rapidly sinking particles. Elder and Fowler (1977) found that freshly released euphausid faecal pellets collected from natural populations contained relatively high concentrations of PCBs and they proposed that such biogenic particles make a significant contribution to the vertical transport of PCBs in the ocean. Concentrations of PCBs in euphausid bodies, molts and faecal pellets as well as in the microplankton upon which they feed are given in Table XIV.

It is conceivable that PCBs could be transported to sediments by way of faecal pellets, molts, eggs, and carcasses released from an overlying euphasiid population. Defaecation would be far more effective in removing PCBs from surface waters than other described processes (Elder and Fowler, 1977). For the three sampling periods shown in Table XIV values for faecal-released PCBs ranging from 5.2 x 10^{-5} to 15 x 10^{-5} $\mu g\ m^{-3}\ day^{-1}$ were calculated. By integrating over for the entire photic zone, the authors obtained delivery rates of PCBs to sediments of 1.4 to 4.1 $\mu g\ m^{-2}\ year^{-1}$, i.e. between one and two orders of magnitude lower than estimates based on deposition by all routes. However, measurements of zooplankton biomass in the same region indicated that M. norvegica comprises only 1 to 5 percent of the total zooplankton mass. The close similarity between PCB flux rates

Table XIII

Chlorinated hydrocarbon content of sediments
(ng g^{-1} dry weight).

Sampling Point	Particle Size	Lindane (b)	Aldrin	DDT	PCB	DDT / PCB
1 (Polluted)	Coarse (c)	18	55	104	97	1
1 (Polluted)	Fine (d)	37	83	228	50	4.6
2 (Clean)	Coarse	10	0.5	0.4	1	-
2 (Clean)	Fine	28	5	24	44	0.6
3	Coarse	78	18	7	1	-
3	Fine	90	33	33	8	4
4	Coarse	27	6	17	-	-
4	Fine	42	14	25	-	-
5	Fine	18	20	57	67	0.9
6	Fine	5	11	50	96	0.5
7(e)	Fine	14	57	110	201	0.6
8	Fine	32	85	52	37	1.5
9	Fine	23	78	48	39	1.3
10(f)	Fine	21	40	29	55	0.5
11	Fine	-	30	27	43	0.7

(b) The given values are the sum of the alpha-, beta-, gamma-, and delta- isomers
(c) Particle size between 0.4 and 0.1 mm
(d) Particle size equal or less than 0.1 mm
(e) More than 90% of the sediment has a size less than 0.1 mm
(f) Shell fish waste content of the sediments obtained from sampling points 8, 10 and 11 was approximately 30%
-Extracted from Salihoglu et al. (1980).

derived from faecal pellet data and those based on sediment values suggests that sinking zooplankton faecal pellets do contribute significantly to the downward vertical transport of surface-introduced PCB compounds.

Measured faecal pellet sinking rates suggest that copepod pellets have the potential to reach the bottom in areas of shallow depth such as most coastal regions (Fowler et al., 1979). However, in deeper waters it is probable that only the rapidly sinking, large pellets from bigger forms (e.g. large copepods and euphasiids) can act as particulate conveyors of pollutants to depth. In these areas, smaller pellets would play an important role in the cycling of these compounds in the upper water layers.

Settling particles collected in semi-permanent particle interceptor devices (PITS) at 100 m depth in a water column of 250 m, 2 km off the Monaco coast in the north western Mediterranean were analysed for petroleum and chlorinated hydrocarbons (Burns et al., 1985). The fluxes of organic contaminants were complicated by irregular inputs but also displayed rapid vertical transport during seasons of high productivity and slow fluxes during seasons of low productivity. PCB fluxes calculated from sediment and settling particles averaged 2 to 4 ng cm^{-2} $year^{-1}$ with good agreement between

Table XIV

Polychlorinated biphenyls in euphasiids (Meganyctiphanes norvegica), their particulate products, and microplankton which serve as the euphausids' food.[x]

Sample	Ratio of wet weight to dry weight and Date	PCB (DP-5 equivalent $\mu g\ kg^{-1}$ dry weight
Whole animal	November 1974	620
Molts	4.7	1400
Faecal pellets	4.6	16400
Microplankton [a]	10.7	4500
	January 1975	
Whole animal [b]		260; 290
Molts		170
Faecal pellets		4800
	March 1975	
Whole animal		38
Molts		Not detectable
Faecal pellets [b]		11000 ; 38000
Microplankton [a]		1800

[x] Water sampled during the November 1974 colection contained 2.5 ng PCB per liter.
[a] Principally copepods, phytoplankton, and detritus.
[b] Two separate samples.
- Extracted from Elder and Fowler (1977)

different data sets. Fluxes of PCBs, DDE and lindane predicted from biomass estimates and observed concentrations of chlorinated hydrocarbons in animal faeces are presented in Table XV. Since only two analyses of faeces for DDE and lindane were available it is not possible to speculate on the importance of faeces in the transport of these residues from these data.

Lindane is a relatively soluble residue and probably leached from the PIT material during the trap deployment time. However, the fluxes of the semi-soluble pesticides into sediments clearly demonstrate that both soluble and particulate organic contaminants can be rapidly transported from surface to depth in the ocean by means of sinking zooplankton faeces.

Burns et al. (1985) estimated residence times based on their measurements of PIT material at 100 m and on fluxes calculated from sediment data (Table XVI). There were large discrepancies in the residence times calculated for suspended particles and the particles that actually settle. Thus calculations based on suspended particles may give erroneous values and careful consideration of the underlying assumptions and data must be made before drawing conclusions on the actual residence times of hydrocarbons in surface waters. The authors believe that their estimates for PCB fluxes based on settling particles are fairly accurate since they are supported by agreement with fluxes into sediments. Thus, the residence time of PCBs in the upper water column should lie in the range of 2 to 4 years. Table XVI shows the

Table XV

A. Fluxes of selected hydrocarbons predicted from biomass estimates and observed concentrations of hydrocarbons in animal faeces.
B. Average flux of hydrocarbons through the water column based on analysis of sediment trap material
C. Average flux of hydrocarbons into the sediment based on surface sediment concentrations and calculated sedimentation rate.

	PCB	DDE	Lindane
A. Estimated flux on faeces	2.2 ± 1.7 (10) ng $cm^{-12}yr^{-1}$	0.03 ± 0.002 (2) ng $cm^{-2}yr^{-1}$	0.002 ± 0.001 (2) ng $cm^{-2}yr^{-1}$
B. Measured flux at 100 m	4.2 ± 3.4 (30) ng $cm^{-2}yr^{-1}$	0.14 ± 0.10 (14) ng $cm^{-1}yr^{-1}$	0.05 ± 0.03 (13) ng $cm^{-1}yr^{-1}$
C. Flux into sediments	2.8 ± 2.6 (3) ng $cm^{-1}yr^{-1}$	0.08 ± 0.06 (3) ng $cm^{-2}yr^{-1}$	4.8 ± 0.5 ng $cm^{-1}yr^{-1}$
D. Log (mg l^{-1})	-1	-1	+1

*Calculations are based on the following:

1. Average zooplankton biomass in the top 100 m in this region of the N.W. Mediterranean was estimated at approximately 0.01 g dry wt m^{-3}
2. An average faecal pellet production rate for zooplankton is about 0.05 g dry faeces per g dry zooplankton per day
3. Mean concentrations of residues in plankton faecal pellets were 1,222 ± 953 (10) ng g^{-1} PCB; 0.85 ± 0.36 ng g^{-1} Lindane; 14.2 ± 8.4 (2) ng g^{-1} DDE

-Extracted from Burns et al. (1985)

very large discrepancy in calculating residence times for lindane. Lindane is apparently leached from/or degraded in PIT material during trap deployment, making it impossible to accurately estimate fluxes from these settling particles. Thus the residence time for lindane in surface waters is much shorter than that predicted on the basis of the observed partitioning between dissolved and particulate phases in surface waters and is probably of the order of 1 year.

4.2 Bioaccumulation and biomagnification processes

For several years data have been accruing on the distribution of chlorinated hydrocarbon pollutants in marine ecosystems. An overall picture of ambient levels in biota, water and sediments is now emerging. However, despite the vast amount of data collected, questions still arise as to whether chlorinated hydrocarbons are indeed biomagnified through the marine food web. Evidence both for and against trophic concentration of PCB and DDT compounds has been cited (Robinson et al., 1967; Baird et al., 1975; Schaefer et al., 1976; Addison, 1976). The answer remains unclear due to lack of adequate knowledge about the relative importance of food and water in the uptake

Table XVI

Estimated residence times, R, of chlorinated hydrocarbon residues in the top 100 m of the Mediterranean water column.

Data Base	PCB	Lindane
Surface particles and sea water concentrations [a]	0.5 yrs	5.8 yrs
Sediment trap material [b]	2.3 yrs	100 yrs
Seawater and sediment concentrations [c]	4.0 yrs	0.9 yrs

[a] calculated using the assumptions of Tanabe and Tatsukawa (1983)

$$\text{and } R = \frac{N\ 100}{3.86\ CHss\ C\ prod}$$; where N 100 is the amount of hydrocarbons present in the water column 1 m^2 by 100 m depth, CHss is the average concentration of chlorinated hydrocarbons on suspended matter in the surface waters and C prod is the rate of primary production of carbon at the surface.

[b] calculated from sediment trap data;

$$R = \frac{N\ 100}{\text{flux at 100 m}}$$

[c] calculated from sediment data given in the Burns and Villeneuve (1983) and water concentrations integrated over 100 m of the water column;

$$R = \frac{N\ 100}{\text{flux into sediments}}$$

of these compounds as well as the fact that conclusions are often confounded by comparing pollutant concentrations in successive links in the food chain sampled at different geographical locations and/or at different points in time. Fowler and Elder (1978) have tried to eliminate some of these problems by examining PCB and DDT residue concentrations in species belonging to a relatively well-defined pelagic food chain sampled at one point in space and time. Food chain inter-relationships among examined pelagic organisms have been relatively well defined. Concentrations of PCBs as DP-5 and p,p'- DDE in these organisms are given in Table XVII (Fowler and Elder, 1978).

Table XVII

Chlorinated hydrocarbons in pelagic organisms collected in November 1974 off Villefranche-sur-Mer.

Organism	Wt. ratio wet/dry	p,p'-DDE µg kg^{-1}	PCB dry weight	PCB[a] C.F.
Microplankton[b]	10.4	N.D.[c]	4500	170,000
Meganyctiphanes norvegica	5.0	26	620	50,000
Sergestes arcticus	4.0	15	470	47,000
Pasiphaea sivado	4.2	5	210	20,000
Myctophus glaciale	3.2	1	50	6,000
(Surface water)		N.D.		2.5ng l^{-1}

[a] Concentration factor defined as ppb wet PCB in organism/ppb PCB in water
[b] Principally copepods, small crustaceans, chaetognaths, phytoplankton and detritus
[c] N.D. = not detectable = 0.5 µg kg^{-1}

- Extracted from Fowler and Elder (1978)

Considered on a whole organism, dry weight basis, data show that PCB and p,p'DDE concentrations are not biomagnified in this particular food chain. In fact, an approximate 100-fold reduction in PCB concentrations is noted between microplankton and myctophid fish. It must be remembered, however, that accumulation through the food chain is probably only one of several factors affecting the concentration of these compounds in pelagic organisms. Nevertheless, if food intake is the predominant route, it is evident that only by sampling organisms at the same time and from the same water mass will it be possible to acquire a clearer picture of the actual trends in trophic level concentrations of chlorinated hydrocarbons (Fowler and Elder, 1978).

Polikarpov et al. (1979) investigated sediments, water and food chains as sources of chlorinated hydrocarbons for benthic organisms in the Mediterranean Sea. The sediment dwelling polychaete worm, Nereis diversicolor, is able to accumulate PCBs from both sediments and seawater. Despite a significantly higher concentration factor for PCBs from water (800) than from sediment (3.5), it was concluded that sediments are the major source of PCBs for worms under existing concentrations of PCBs in the Mediterranean Sea water and sediments. Depuration of PCBs from worms living in an uncontaminated environment follows an exponential function. Experiments with Mytilus galloprovincialis showed that PCBs accumulated over a period of 97 days are readily lost when the mussels are transferred to clean water. The loss of PCBs from the soft tissue of these molluscs amounted to 50%

after one day, 91.3% after one month and 99.6% after three months. The benthic shrimp, Lysmata seticaudata, rapidly accumulated PCBs from both food and water. The experimental results clearly indicate that PCBs in the marine environment are readily cycled through the benthic biota.

Contardi et al. (1983) reported three years data on the distribution of DDTs and PCBs in some organs of Mullus barbatus, Euthynnus alletteratus and Sarda sarda the from Ligurian Sea. Examination of the results clearly showed DDT accumulation in the liver relative to other organs. This accumulation was more evident in Sarda sarda and Euthynnus alletteratus than in Mullus barbatus and it is even more apparent referring to a wet weight basis. Since in general DDE concentrations do not show marked increase in the liver, it seems likely that there is a preferential DDT--DDD metabolism in this organ. With regard to polychlorinated biphenyls, the liver tends to contain more components high in chlorine content, similar to Fenclor 64. This seemed to apply to all the samples examined some of which (e.g. Sarda sarda) varied greatly in length.

The concentrations of chlorinated pesticide residues and polychlorinated biphenyls in ripe female gonads of Clupeiforms of the Adriatic Sea (Sardina pilchardus (Walb.), Engraulis encrasicolus L., and Clupea sprattus L.) were investigated by Crisetig et al. (1973). The values of the residues in the gonads during the corresponding periods of "gonadic activity" are rather low, even if considered altogether (0.558 mg kg^{-1} in the sardine, 0.184 in the anchovy and 0.278 in the sprat). These concentrations are well below the lowest levels (4.74 mg kg^{-1}) observed as being capable of causing deleterious effects to reproduction in trout.

5. LEVELS AND TRENDS OF CHLORINATED HYDROCARBONS IN THE MEDITERRANEAN SEA

5.1 Methodology and intercalibration exercises

For the quantification of chlorinated pesticides and olychlorinated biphenyls electron capture gas chromatography is most commonly used. However, it is first necessary to employ a suitable and often elaborate cleanup procedure. In the case of polychlorinated biphenyls the normal comparison with a standard compound is not possible because these substances consist of many compounds. Mostly for these compounds, analysis has in the past been performed by matching an arbitrary number of peaks in the sample chromatogram with those of the nearest commercially available PCB formulation and measuring the height or area of the peaks. In most cases PCBs were determined by comparison with Aroclor 1254 and/or 1260, Phenoclor DP-5 or DP-6, or Clophen A 60 as the reference standard.

In some cases quantitative PCB determination was effected after perchlorination to decachlorobiphenyl (DCB) with antimony pentachloride followed by quantification by gas chromatography. It has to be stressed that this method usually yields higher PCB concentrations than those estimated by comparing the chromatograms of commercial mixtures.

It has to be stressed that analysis for chlorinated hydrocarbons in marine samples is difficult and only data from the same laboratory or from investigators who have participated in an interlaboratory comparison exercise should be compared. Otherwise differences in occurrence might just be due to a different analytical efficiency of the reported laboratory work.

In order to overcome these problems and to assist the Mediterranean research centres with their projects on chlorinated hydrocarbons monitoring in marine organisms intercalibration exercises are organized by the International Laboratory of Marine Radioactivity, IAEA, Monaco within the framework of the MED POL programme. The results reported from the world-wide as well as the Mediterranean region laboratories in the 1976-78 period were compiled and treated statistically. The evaluation of the reported results on the oyster sample (MA-M-1/oc) are given on Table XVIII, (Fukai et al., 1979). The "probable concentrations" were estimated on the basis of the results obtained by about 7 experienced laboratories. The standard deviation of the Mediterranean measurements was around ± 30%. In general, ± 20% is considered to be a "state-of-the-art" reproducibility for PCBs environmental samples measurements.

Table XVIII

Evaluation of the intercalibration results for chlorinated hydrocarbon measurements on the oyster homogenate (MAM-1) reported by the Mediterranean research centres.

Compound	Mediterranean			Worldwide		
	No.of results received	No.of "accep-table" results	No.of "good" results	No.of results received	No.of "accep-table" results	No.of "good" results
AR 1254	11	10 (91%)	7 (64%)	26	22 (85%)	15 (58%)
DDT	12	12 (100%)	11 (92%)	34	32 (94%)	20 (59%)
DDD	11	6 (54%)	3 (27%)	30	20 (67%)	7 (23%)
DDE	12	10 (83%)	7 (38%)	36	31 (86%)	24 (67%)
Dieldrin	5	4 (80%)	4 (80%)	22	20 (91%)	8 (82%)
HCH alpha	3	3 (100%)	2 (67%)	14	8 (57%)	7 (50%)
HCH gamma	4	4 (100%)	3 (75%)	25	14 (56%)	9 (36%)

- Extracted from Fukai et al. (1979)

As of May 1984, seven laboratories from the Mediterranean had returned results of testing Reference method 14 for the determination of chlorinated hydrocarbons in organisms (ILMR, 1984). These data suggest there is less variation due to differences in methods applied by the same laboratory than the same method applied by different laboratories.

Although some Mediterranean laboratories do report the results of their performance in chlorinated hydrocarbons intercalibration exercises, most do not apply the observed differences to correct the results of their analyses of actual samples (Bastürk et al., 1980; Salihoglu et al., 1981; Marchand, 1983). The group for organic pollutants analysis at the Center for Marine Research, Zagreb, Yugoslavia has been involved in 5 international intercalibration exercises and after summing up all results, has decided to use correction factors (from 1.4 to 2.1) for all their results of measuring chlorinated hydrocarbons in marine samples (Picer, M. et al., 1976).

5.2 Levels and trends

5.2.1 Water

The concentrations of DDT total, HCH total, PCBs and incertain 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 XIX.

Elder (1976), found the highest concentrations of PCBS 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^{-1}), was found at the mouth of the Rhône suggesting that the Rhône is an important source of PCBs for northwestern Mediterranean coastal waters.

During various cruises conducted during 1977-79, 76 surface and subsurface seawater samples were collected and analysed for PCBs (Villeneuve et al., 1981). Although attempts were made to determine other organochlorine compounds, due to the low levels of other organochlorine compounds in open Mediterranean waters only PCBs could be quantitatively determined. The results show that, although higher PCB concentrations at the surface are encountered at some stations, no systematic vertical variation is generally observed (Table XX). The levels of PCBs in near surface waters were not very much different from those in deep layers beyond 2 km. Thus, it is reasonable to estimate the mean concentration of PCBs in open Mediterranean seawater by averaging all the values available. The data reported by Villeneuve et al. (1981) span a range of 0.1 to 2.5 ng l^{-1}, with an average of 0.7 ng l^{-1}. This compares to an average of 2.0 ng l^{-1} (range: 0.2 - 8.6 ng l^{-1}) obtained for 80 seawater samples from a similar area in 1975 (Elder and Villeneuve, 1977). Villeneuve et al. (1981) suggest that since these two mean values are significantly different the concentration of PCBs in open Mediterranean seawater appears to have decreased from 1975 to 1977-79. However, it is worth remembering that as early as 1974 Gordon et al. stressed that improvements in analytical methodology and reduction in associated sample contamination may have been responsible for some or all of the observed decrease in concentrations of oceanic contaminants in Atlantic Ocean samples (Gordon et al., 1974).

Table XIX

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^{-1}).

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

Table XIX (continued)

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

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

Table XX

Concentration of PCBs in the open Mediterranean seawater (ng l^{-1}).

Station No.	AT-02	AT-03	AT-04	AT-05	AT-06	AT-07
Date of coll.	77-04-21	77-04-21	77-04-22	77-04-23	77-04-24	77-04-25
Position	33°00'N 32°00'E	33°50'N 30°00'E	34°00'N 29°00'E	33°20'N 24°00'E	34°50'N 21°00'E	36°00'N 18°00'E
Depth (m)						
Surface	0.6	0.3	0.3	0.8	0.9	1.2
50	1.0	-	0.8	-	0.7	0.4
100	0.5	-	0.7	-	1.4	1.2
225	0.6	-	0.9	1.1	-	-
300	-	-	-	0.6	-	1.1
400	-	-	-	-	-	1.1
500	1.2	-	0.7	-	-	1.9
750	0.8	-	0.4	-	-	1.1
1000	0.8	-	0.4	-	-	1.0
1500	1.5	-	0.7	-	-	1.1
2000	-	-	0.5	-	-	-
2500	-	-	-	-	-	0.7
2900	-	-	0.6	-	-	-
3800	-	-	-	-	-	1.3

Station No.	HY-08	HY-16	HY-23	HY-25	HY-39	SH-01
Date of coll.	77-06-15	77-06-17	77-06-18	77-06-19	77-06-22	77-07-08
Position	36°34'N 21°04'E	39°33'N 19°21'E	38°36'N 15°25'E	39°54'N 14°36'E	40°34'N 10°53'E	33°02'N 33°14'E
Depth (m)						
Surface	1.9	1.7	2.5	0.2	1.1	0.1
500	-	0.7	0.6	0.1	1.0	0.2
1100	-	0.7	1.0	-	-	-
1200	-	-	-	1.1	-	-
2300	-	-	-	-	1.5	-
4500	0.9	-	-	-	-	-

Station No.	AT-02	AT-03	AT-04	AT-05	AT-06	AT-07
Date of coll.	77-07-09	77-07-10	77-07-11	77-07-19	77-07-19	77-07-19
Position	33°10'N 32°24'E	33°21'N 32°35'E	33°42'N 28°06'E	41°30'N 10°12'E	41°12'N 08°41'E	41°00'N 07°30'E
Depth (m)						
Surface	0.1	0.1	0.1	0.3	0.3	0.6
500	0.3	0.2	0.2	-	-	-

- Extracted from Villeneuve et al. (1981)

Table XX (continued)

Station No.	CS-44	CS-46	CS-49	CS-50	CS-51
Date of coll.	77-07-20	77-07-20	77-07-21	77-07-21	77-07-21
Position	40°00'N 07°30'E	40°00'N 06°10'E	39°35'N 03°40'E	39°25'N 03°25'E	39°10'N 03°15'E
Depth (m)					
Surface	0.2	0.3	0.2	0.2	0.2

Station No.	RS-01	RS-02	RS-03	RS-04
Date of coll.	79-06-18	79-06-19	79-06-21	79-06-21
Position	31°59'N 29°58'E	31°59'N 28°00'E	34°01'N 25°01'E	35°00'N 23°30'E
Depth (m)				
Surface	0.5	0.4	0.3	0.2
500	-	0.3	0.2	-
1000	-	0.2	0.1	-
1500	-	0.1	0.1	-

Designation of the cruises for the station No.: AT, Atlantis II: HY, Hayes: SH, Shikmona: CS, Cornide de Saavedra: RS, Researcher.

- Extracted from Villeneuve et al. (1981)

Risebrough et al. (1976) reported significantly lower concentrations of PCBs in French coastal waters than Elder (1976). They concluded, on the basis of mass balance calculations that PCB values in seawater in excess of 1 ng l^{-1} in both the Atlantic and the Pacific appear to be too high since pentachlorobiphenyls, the dominant PCB present in seawater extracts, had not been manufactured in sufficient amounts to account for estimated burdens in seawater.

Persistent chlorinated hydrocarbons were analysed over a two-year period (1977-78) in about 50 water samples collected from North Adriatic coastal waters (1977-78). Most of the results lie below the analytical sensitivity of the method used (for DDT 0.05 ng l^{-1} and for PCBs 0.1 ng l^{-1} (Picer N. and Picer M., 1979). Only a few samples show traces of chlorinated hydrocarbons.

Villeneuve and Burns (1983) have reported data for the concentrations of lindane in seawater from both coastal and open Mediterranean Sea areas (1976-1979). Their results showed levels of this chlorinated hydrocarbon insecticide to be highest at stations close to terrestrial run-off and river inputs from agricultural areas. Levels in surface seawater at off-shore areas of the eastern basin ranged from 61 to 120 pg l^{-1}. Two deep profiles showed that deep waters had concentrations of lindane 3 to 100 times lower than surface waters. As expected on the basis of relative solubility, most lindane occurred in the dissolved state even in the estuaries where particle loading was highest.

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). PCBs were found to be present in 85 samples out of 86 at a mean value of 0.297 $\mu g\ l^{-1}$ in 1976, and of 0.135 $\mu g\ l^{-1}$ in 1977. In contrast, HCB was identified in only 16% of the analysed samples.

On the basis of the data on the concentrations of chlorinated hydrocarbons in seawater and particulate matter in water samples from the North Adriatic it seems that an important fraction of chlorinated hydrocarbons is associated with the suspended matter. Moreover, this amount increases (gamma HCH<DDT<PCB) when their solubility in water decreases (gamma HCH>DDT>PCB). Thus, the distribution of chlorinated hydrocarbons in waters of the northern Adriatic Sea may be influenced by the concentration and, perhaps, by the composition of the suspended matter. The levels of chlorinated hydrocarbons in waters from the open north Adriatic are relatively low when compared with published results from other areas of the Mediterranean and the world.

In the period from 1971 to 1975 investigations were carried out concerning the level and extext of contamination of South Adriatic coastal waters by DDT and HCH (Elezovic et al., 1980). 240 water samples were collected and analysed from Kotor, Budva, Bar and Ulcinj.

Table XXI summarises the levels of PCBs in Mediterranean samples analysed by similar methods over the years and often by the same analyst (Burns et al., 1985). The data show there has been a reduction in all components analysed and this may reflect reduced PCB inputs after the implementation of restrictions on industrial discharges by many countries. Nevertheless, PCBs remain an important class of pollutants in the spectrum of halogenated contaminants in Mediterranean samples. Burns et al. (1985) also noted the increasing importance of other chlorinated hydrocarbon contaminants such as lindane and hexachlorobenzene.

5.2.2 Sediments

The concentrations of DDT total, HCH total, PCBs and in one case dieldrin found by various authors in sediment samples collected from various sites in the Mediterranean Sea are summarized in Table XXII.

Arnoux et al. (1981a,b,c) investigated the contamination of sea sediments during 1976 and 1978 between Toulon and Ajaccio, Fos gulf and Marseille area. Several years after this investigation, Marchand (1983) analysed chlorinated hydrocarbons in sediments collected from the same areas. The average concentrations were only significantly different apart from the Marseille area.

Burns and Villeneuve (1984) measured the concentrations of PCBs in flocculent particles and compacted sediments in a core from the Monaco coastal waters (Table XXIII).

Table XXI

Concentrations of PCB (quantified as Aroclor 1254 or Phenoclor DP-5 equivalents) in the Mediterranean ecosystem and factors of change in approximately 5 years time.

	1974-78	N	1978-82	N	factors of change in approximately 5 years
Seawater	3.2 + 2.2 ($ng\ l^{-1}$)	9[a]	1.0 + 0.4 (ng l-1)	6[b]	-3.3 X
Plankton	1.5 + 1.8x10^3 ($ng\ g^{-1}$)	6[c]	2.3 + 1.5(10^2) ($ng\ g^{-1}$)	14[b]	-6.5 X
Plankton (faeces)	1.7 + 1.4(x10^4) ($ng\ g^{-1}$)	4[c]	1.2 +0.9(x10^3) ($ng\ g^{-1}$)	10[b]	14 X
Sediment trap material	4.6 +2.5(x10^2) ($ng\ g^{-1}$)	4[d]	1.3+1.7(x10^2) ($ng\ g^{-1}$)	30[b]	-3.5 X

N = Number of samples
[a] Elder and Villeneuve (1977); [b] Burns & Villeneuve (1982)
[c] Elder and Fowler (1977); Fowler and Elder (1978)
[d] Fowler et al. (1979)
- Extracted from Burns et al. (1985)

Since the core slices analysed were 5 cm thick, the most recently delivered particles containing PCBs would be diluted by unpolluted older sediments in depth. This dilution effect gives about two orders-of-magnitude difference in the concentration between flocculent particles and compacted sediments.

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 PCBs, but HCB was not found in the sediment samples.

Levels of PCBs, DDTs and HCHs were measured in sediments taken from the central Mediterranean (area IV and VI). HCH was usually 1 ng g^{-1}; DDT total ranged from 1 ng g^{-1} to 27.5 ng g^{-1}; PCBs generally ranged from ca. 1 ng g^{-1} to 80 ng g^{-1} (Amico et al., 1982). The highest levels, particularly with PCBs, were found in the area of the straits of Messina and along the northern coast of Sicily. The exceedingly high levels of PCBs observed within the Augusta Harbor compare closely with those (360-470 ng g^{-1}) found for the Japanese Port of Taganoura, regarded as highly polluted (Rhead, 1975). Contrary to what is normally observed in living organisms, no significant correlation exists between the concentration of chlorinated hydrocarbons and the extractable organic matter from sediments.

Table XXII

Chlorinated hydrocarbons in sediments from the Mediterranean Sea
(μg kg^{-1} dry weight).

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

Table XXII (continued)

Area	Pollutant	Average	Minimum	Maximum	References
VII	DDT_{total}	0.2	0.1	0.4	Cousteau (1979); Villeneuve & Burns (1983)
	HCH_{total}	1.1	0.2	2.2	
	PCB	0.8	0.1	1.1	
VIII	DDT_{total}	128	0.3	1893	Cousteau (1979); Dexter & Pavlou (1973); Villeneuve et al. (1981); Villeneuve & Burns (1983)
	HCH_{total}	0.6	0.4	0.8	
	PCB	155	0.6	775	
IX	DDT_{total}	12.0	0.4	29.0	Balkas et al. (1979); Bastürk et al. (1980); Cousteau (1978); Villeneuve et al. (1981); Villeneuve & Burns (1983)
	HCH_{total}	0.2	0.2	0.3	
	PCB	1.5	ND	3.0	
X	DDT_{total}	2.7	ND	780	Cousteau (1979); Villeneuve & Burns (1983); Villeneuve et al. (1981)
	HCH_{total}	0.7	-	-	
	PCB	2.2	0.6	51.1	

Table XXIII

Concentrations per gram dry weight of polychlorinated biphenyls in flocculent particles compared to the compacted sediments of the core.

Flocculent particles		104.5	(ng g^{-1})
Sediments	0- 5 cm	0.5	
	5-10 cm	0.2	Flocculent-sediments = 10^2
	10-15 cm	0.3	
	15-20 cm	0.1	

- Extracted from Burns and Villeneuve (1984)

The contamination of the Bay of Naples and adjacent marine area sediments by chlorinated hydrocarbons was assessed using grab and corer sediment samples collected in July 1980 (Baldi et al., 1983). Inside the Bay of Naples, PCBs attain very high levels (3200 ng g^{-1} d.w.). Outside the Bay, levels of PCBs though lower, never fall below 10 ng g^{-1}. Concentrations of DDT total (mainly as DDE) are lower than 20 ng g^{-1} 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).

One hundred and fifty five surface sediment samples were collected in six zones of the Gulf of Venice and analysed for DDT total and PCBs (Donazzolo et al., 1982). Mathematical analysis of the data indicated a significant correlation between the chlorinated hydrocarbon content and the percentage of the 63 µm fraction of sediment; there was also a linear relationship between the logarithm of the concentration and the percentage of pelite in sediment. A closer examination of the mean values of each zone indicated that three zones are characterized by higher DDT total concentrations, probably because of solid materials transported by the rivers from highly cultivated areas of northern Italy (Donazzolo et al., 1982).

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 Picer M., 1979; Picer M. et al., 1981; Picer M. and Picer N., 1982; Picer N. et al., 1985; Picer M. and Picer N., 1985). Istrian coastal water sediment samples from the Pula area show a significantly higher concentration of DDT total and especially PCBs 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.

Salihoglu et al. (1980) found much higher concentrations of DDT total and PCBs in sediments from an experimental basin polluted with waste water in comparison with unpolluted one. The high concentration of chlorinated hydrocarbons in the sediment of the polluted basin was attributed to a sewage discharge.

Dexter and Pavlou (1973) measured PCBs and pesticide residues in surface sediment samples collected through the Saronikos Gulf. For both DDT and PCB distribution, the trends were similar and indicated that the observed gradients result mainly from the diffusive transport of contaminated material discharged at the Keratsini sewage outfall. 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. However, the oligotrophic nature of the waters, together with the relatively low flushing rate, may increase the impact of pollutants on this marine ecosystem (Dexter and Pavlou, 1973).

The organochlorine residue content of sediments in the vicinity of Erdemli (Icel) Turkey were investigated by Balkas et al. (1979). As with biota samples, DDT and other pesticides residues in sediments were found at much higher concentrations than PCBs.

From July 15 to December 7, 1977, the research vessel Calypso gathered samples of sediments at 141 locations distributed in 12 Mediterranean countries (Cousteau, 1978). The results of the 457 analyses of sediment samples for polychlorinated biphenyls and DDTs were included in Table XXII. 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. Several of the cores from deep water showed a distinct subsurface maximum in lindane conentrations in the 1-2 cm slices.

Polychlorinated biphenyls were measured in 12 core sediment samples collected from the open Mediterranean Sea during 1977-79. PCBs were detectable in all subsamples analysed with considerably high concentrations in the top centimeter of some core samples. It was generally noted that a subsurface maximum of PCBs appears around 3 cm from the sediment surface, followed by a substantial decrease of PCBs from the first to the second centimeter. The penetration of PCBs below 5 cm depth was considered either to be related to the specific behaviour of PCBs within the sediment layers or, more probably, due to the results of bioturbation. (Elder et al., 1976).

5.2.3 Plankton and plants

The concentrations of DDT total, HCH total and PCBs found by various authors in plankton and plant samples collected from various sites in the Mediterranean Sea are summarized in Table XXIV.

Table XXIV

Chlorinated hydrocarbons in plankton and plants from the Mediterranean Sea (μg kg^{-1} fresh weight).

A. PLANKTON

Area	Pollutant	Average	Minimum	Maximum	References
II	DDT_{total}	1.3	ND	2.2	Burns & Villeneuve (1982); Elder & Fowler (1977);
	HCH_{total}	0.3	0.1	0.7	Fowler & Elder (1978)
	PCB	55	5.0	180	
	Hexachlorobenzene	0.8	0.1	2.2	
IV	DDT_{total}	6.3	0.8	13	Fowler & Elder (1980)
	PCB	16.7	2	66	
V	DDT_{total}	4.9	ND	59	Catani et al. (1980); Fossato (1983);
	HCH_{total}	2.9	0.1	12.8	Nazansky et al. (1979); Picer, M. et al. (1981);
	PCB	48.2	ND	453	Picer, M. & Picer, N. (1985) Dujmov et al. (1979);
	Dieldrin	0.6	ND	3.2	Vilicic et al. (1979)
VI	DDT_{total}	3.4	0.3	61.1	Fowler & Elder (1980)
	PCB	4.7	0.6	9.6	

ND = Non detected (under sensitivity limit)

Table XXIV (continued)

B. PLANTS

Area	Organisms	Pollutant	Average	Minimum	Maximum	References
II	Plants (4 species)	DDT_{total}	3.3	ND	25.6	Alzieu & Duguy (1979)
		HCH_{total}	0.2	0.05	0.5	
		PCB	20.8	ND	28.8	
V	Plants (2 species)	DDT_{total}	1.6	-	-	Fossato (1983)
		HCH_{total}	0.4	-	-	
		PCB	4.3	-	-	
		Hexachlo-benzene	6.5	-	-	
VI	Plants (12 species)	DDT_{total}	0.9	0.1	3.9	Amico et al. (1979a)
		HCH_{total}	0.3	0.1	0.5	
		PCB	11.7	2.7	39.4	

ND = Non detected (under sensitivity limit);
- = No available data

Elder and Fowler (1977) sampled microplankton twice in coastal French waters. PCBs in the two samples (1800 and 4500 μg kg^{-1}, dry weight) were relatively high and probably reflect coastal inputs. The same authors surveyed chlorinated hydrocarbons in pelagic plankton organisms from the central and eastern basins of the Mediterranean Sea (Fowler and Elder, 1980). Euphausids were the pelagic organisms most common to all stations. A student's t-test indicated that the average DDT total/PCB ratio was significantly higher in euphausids from the central region (Tyrrhenian and Ionian Seas) than in the eastern sector. This is due to a greater relative decrease in DDT total compared with PCB in going from the central region to the eastern region. The only other generally available data for chlorinated hydrocarbons in Mediterranean euphasids appear to be those of Elder and Fowler (1977) for Meganyctiphanes norvegica samples. The concentrations (38 to 620 μg kg^{-1} d.w.) were of the same order of magnitude as those measured in the species inhabiting the Tyrrhenian and Ionian Seas. The pelagic tunicate, Pyrosoma atlanticum, from the Ionian sea appears to contain far less PCB and DDT than similar sized individuals from the eastern Mediterranean. A vertically migrating fish, Myctophum glaciale was separated into three size classes. Although no trends were noted for the absolute amounts of PCB and DDT in the different sized fish, the DDT total/PCB and DDE/PCB ratios increased with the increasing size of fish. Since these individuals were from the same water mass and, presumably, the same population, the change in ratios may represent differential metabolism of the two compounds as the fish grow. Finally a good correlation is evident between PCBs and both DDE (r=0.63) and DDT total (r=0.63), (Fowler and Elder, 1980).

Burns et al. (1985), show (Table XXI) that there has been a reduction in the concentrations of PCBs in plankton organisms (about 6.5 times) and in plankton faeces (about 14 times) in samples collected from the same area over a 5-year period.

Cattani et al. (1981) reported levels of HCH total, DDT total and PCBs found in zooplankton samples collected from two stations in the Italian coastal waters of the Northern Adriatic. The levels of PCBs, which were consistently higher than pesticides, show seasonal variations which seem to be correlated with biomass of Cladocera which are more abundant during summer. The results suggest that levels of chlorinated compounds in zooplankton of the Northern Adriatic were generally lower than levels previously reported for this same area (Stirn et al., 1974). However, a comparison between the data of concentrations of pesticides in planktonic organisms is not straight forward since results can be affected by e.g. the determination, such as taxonomic composition of samples and the size of planktonic organisms.

Picer M. et al. (1981) found that concentrations of chlorinated hydrocarbons in plankton samples collected from the Rijeka Bay varied considerably. Frequently, concentrations at the same station differed by nearly one order of magnitude. In the light of these variations it is not suprising that, as with the sediment samples it was not possible to detect any influence of local pollution sources in the Rijeka Bay.

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 PCBs ranged from 2 to 34 ng g^{-1}; lindane from 0.4 to 3.0 ng g^{-1} and DDT total from 0.4 to 9.7 ng g^{-1}. These concentration samples were significatly higher than those found by Chabert and Vicente (1981) in Phanerogames collected from the lagoon of the Brusc (Var-France).

Concentrations of PCBs, HCHs and DDT total residues in seaweeds of the east coast of Sicily were investigated during 1977/78 by Amico et al. (1979a). The residues have been determined in thalli of 12 species of marine algae. Different seaweeds tend to retain variable amounts of water, so residue concentrations expresssed in terms of dry weight are very important. The highest concentrations found were in samples from an area (Priolo) intensively polluted by nearby industrial activity. The ratio DDT total/PCBs were consistently lower in algae than in animals from the same area, whereas the opposite applied to the ratio DDT total/DDE, and peak patterns of PCB obtained from seaweeds were not comparable in proportion with those from animals and were characterized by higher intensity peaks of shorter retention time. The observed differences are probably explained by assuming that the metabolic breakdown of DDT and PCB is a much slower process in seaweeds than in animals. However, it cannot be excluded that a differential intake of contaminants contributes to these differences. A comparison between the values observed in 1977 and those in 1978 suggests a tendency for a decline in DDT concentration (Amico et al., 1979a).

5.2.4 Mussels (Mytilus galloprovincialis and Mytilus edulis) and crustacea (various species)

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

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 PCBs, DDT and its metabolites in mussels (Mytilus galloprovincialis) which inhabit the northwestern Mediterranean coast of France and Italy. (Marchand et al., 1976). Fig. 8 shows that each station has a certain uniqueness compared with neighbouring stations, with respect to residue level, variation of concentrations with time and ratio of DDT total to PCB. The ratio of DDT total to PCB was generally less than 1. The most notable exceptions were at stations located in Italy; this is probably because DDT was still in use in Italy. The highest residue concentrations observed were in samples from enclosed locations, Thau pool at Sète, Marseille and Toulon.

Table XXV

Chlorinated hydrocarbons in mussels (µg kg^{-1} fresh weight).

A. Mediterranean Sea (Mytilus galloprovincialis)

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

- = No available data
ND = Non detected (under sensitivity limit)

Table XXVI

Chlorinated hydrocarbons in crustaceans from the Mediterranean Sea
(μg kg^{-1} wet weight).

Area	Organisms	Pollutant	Average	Minimum	Maximum	References
II	Two species	DDT_{total}	6.5	1.2	13	Bolognari et al. (1979); Contardi et al.
		HCH_{total}	0.8	0.01	5.3	(1979); Contardi et al. (1981); Ferro et al.
		PCB	71	21	203	(1979); Monod & Arnoux (1979)
IV	Nephrops	DDT_{total}	3.3	0.2	16	Amico et al. (1979a); Bolognari et al. (1979);
	Norvegicus	HCH_{total}	1.1	0.3	2.8	
		PCB	9.0	2.9	23.3	Focardi et al. (1984)
		Dieldrin	0.3	0.2	0.5	
		Hexachlorobenzene	0.3	0.1	0.6	
V	6 species	DDT_{total}	8.8	ND	30.2	Bolognari et al. (1979); Dujmov et al. (1979);
		HCH_{total}	0.6	-	-	Fossato (1983); Fossato & Craboledda (1981)
		PCB	110	ND	796	Vilicic et al. (1979)
		Dieldrin	1.7	ND	5.6	
		Hexachlorobenzene	4.4	-	-	
VI	Nephrops	DDT_{total}	1.2	1.2	1.2	
	Norvegicus	HCH_{total}	0.5	0.3	0.7	Amico et al. (1979a)
		PCB	4.9	4.4	5.4	
IX	Parapaneus	DDT_{total}	78.9	8.9	161	
	kerathurus	PCB	ND			Bastürk et al. (1980)

ND = Non detected (under sensitivity limit);
- = No available data

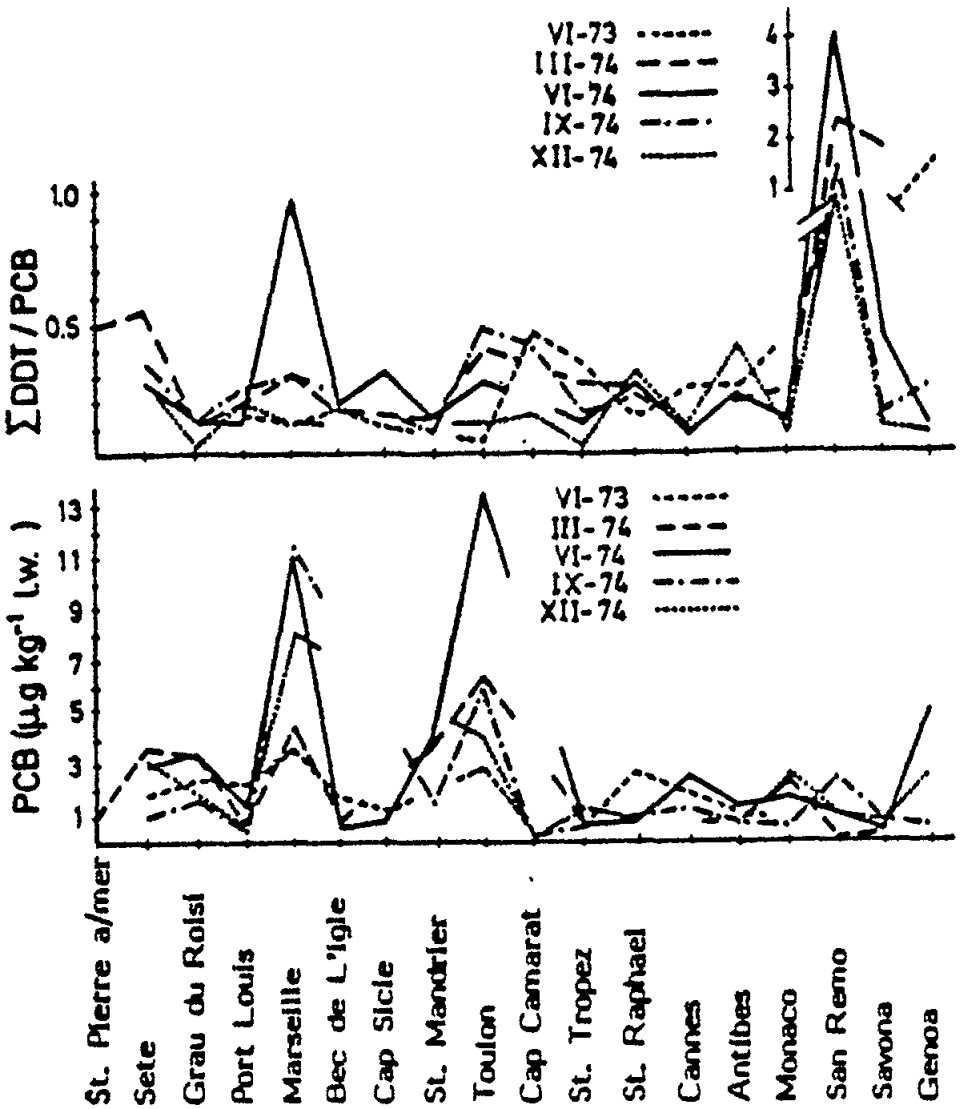


Fig. 8 Seasonal changes in PCB residue and ratio Σ DDT/PCB in the mussel Mytilus galloprovincialis Lmk. from the northwestern Mediterranean coast

Since the fluctuations in residue levels are not consistent at each station, it is difficult to determine the exact causes of the variations noted in this survey. The authors listed three important factors which may play a role in causing the observed fluctuations:

i. Change in the residual pollutant levels in ambient waters.

ii. Variations in environmental parameters in the surrounding waters.

iii. The seasonal reproduction cycle in mussels which can alter their metabolism to a marked degree.

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

The fact that organic residues, like PCBs and DDTs 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). In order to assess whether this seasonality in lipid content affected chlorinated hydrocarbon concentrations, samples were examined from eight different stations. Although the data (Fig. 9) 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.

Fig. 10 shows PCB and DDT total concentrations in molluscs collected from the North West Mediterranean from 1976 to 1982 (Marchand et al., 1985). The concentrations of PCBs appear to have increased slightly from 1976 to 1982 while DDT total concentrations showed a decrease tendency.

Ballester et al. (1982) studied the distribution of chlorinated hydrocarbons in mussels collected from a drilling platform situated in the Ebro river delta. The concentrations of pesticides found in mussels were lower than those living near shore. PCBs were present but in very low concentration levels.

The concentrations of HCHs, DDTs and PCBs have been determined in samples of mussels collected in different stations of the Ligurian Sea. (Contardi et al., 1979). The concentrations of PCBs and DDTs found in mussels from the Genoa area are presented in Table XXVIII. 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^{-1} F.W.; HCH total from 0.22 to 2.35 μg kg^{-1} F.W. and for PCBs from 21 to 157 μg kg^{-1} F.W.). (Contardi et al., 1979).

Concentrations of DDT, DDD, DDE and PCBs 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^{-1} F.W. or less), with the exception of samples collected near the mouth of the Arno river. An analogous pattern could be seen for PCBs, 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.

Table XXVII

Temporal comparison of PCB concentrations (ng g^{-1}) in mussels from four northwestern Mediterranean stations.

	Marchand et al. (1976) Collected July 1973-Dec.1974			De Lappe et al. (1973)
Stations	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

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

Concentrations of chlorinated hydrocarbons (DDT and metabolites, PCBs, 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 PCBs, and that the ratio DDT total/PCBs 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 frequently in the Tyrrhenian basin. Bioaccumulation of chlorinated compounds is a relatively slow process compared to variations of the lipid content in investigated organisms so, in terms of extractable material, chlorinated contaminants are "diluted" during lipid accumulation.

Mytilus galloprovincialis, Carcinus mediterranus 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 Craboledda, 1981). The overall data on chlorinated hydrocarbons show that PCB residues predominate in all species at all stations regardless of season. The PCB pattern varied from species to species: in mussels it closely matched that of Aroclor 1254, while in other species it was similar to that of mixtures of Aroclor 1254 and 1260. For instance the Aroclor 1254/Aroclor 1260 mean ratio for Mediterranean shore crabs and Norway lobster were 2.5 to 4.2. 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 $\mu g\ kg^{-1}$ for mussel and crab respectively, but aldrin was only rarely detected with certainty.

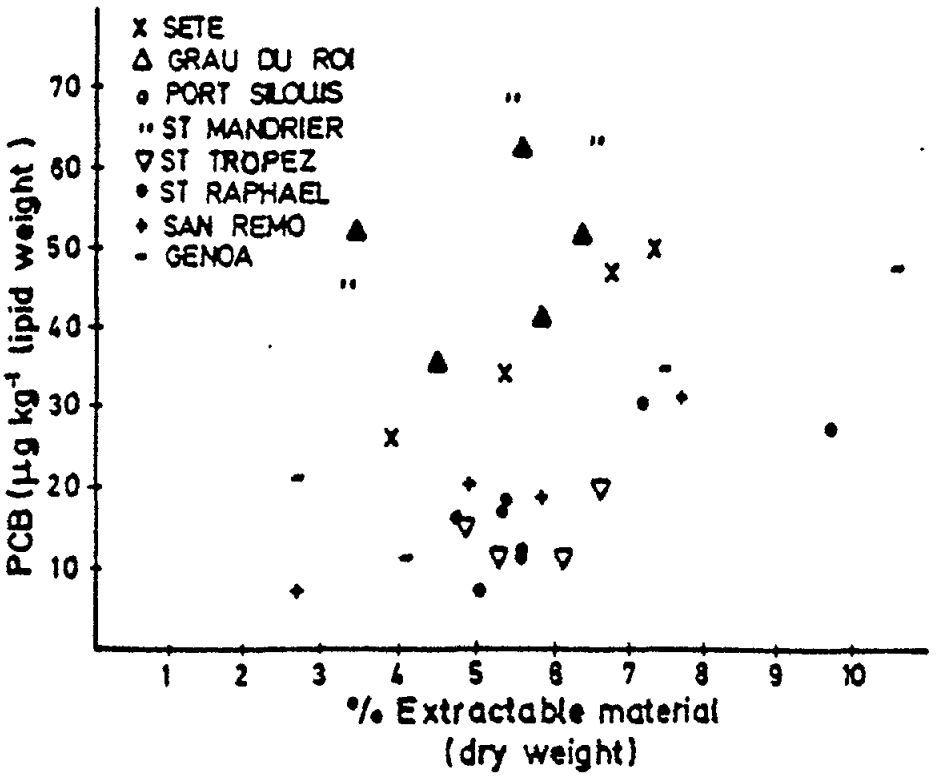


Fig. 9 PCB concentration as % hexane extractable material for certain sampling sites

Table XXVIII

PCBs and DDT in mussels for Genoa area.

Sampling period	DDT total (ng g^{-1} d.w.)			PCB (ng g^{-1} d.w.)			
	min.	aver.	max.	min.	aver.	max.	Ref.
(1) June 1973 to December 1974	150	407	778	480	2179	5050	1
(2) December 1977 to July 1978	31	37	43	180	-	181	2

(1) Marchand et al. (1976); (2) Contardi et al. (1979)

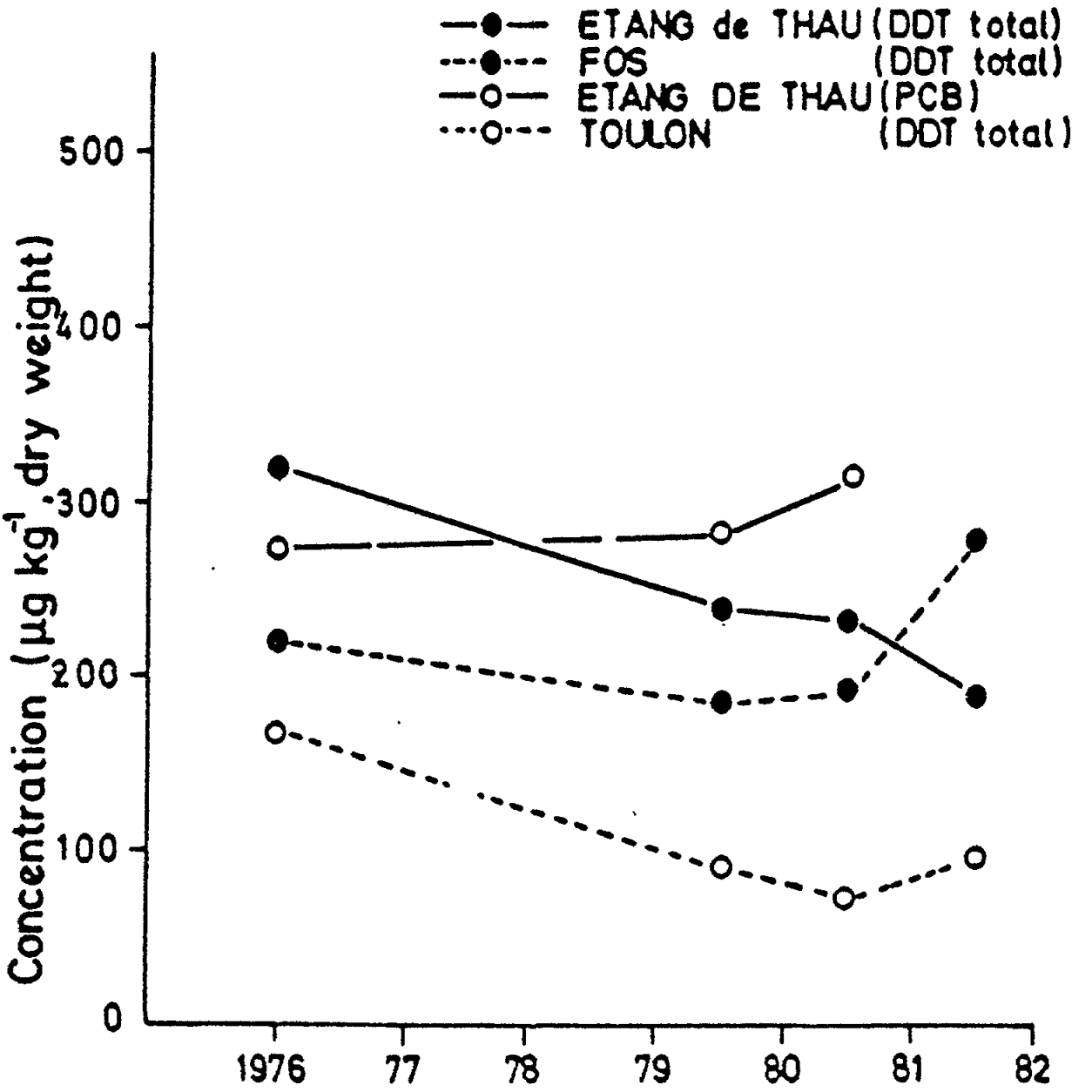


Fig. 10 Annual variation of chlorinated hydrocarbons in mussels from the North West Mediterranean

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 PCBs 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. Significant correlation between DDT total and PCB concentrations existed only in mussels from the Istrian coastal area. This suggests two possibilities: different sources of DDT and PCB residues in the areas investigated, or different uptake and loss pathways of total DDT and PCBs for investigated organisms. Although several major north 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 PCBs 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 PCBs concentrations. The level of contamination in mussels throughout the coastal zone of Rijeka Bay by persistent chlorinated pesticides appears to be the same. This was somewhat unexpected because it is well known that urban waste waters are relatively rich in persistent chlorinated insecticides (Picer M. et al., 1978b). 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.

Chlorinated hydrocarbons were analysed in certain mussels and crabs (Carcinus mediterraneus) in two experimental basins located in the lagoon of Strunjan (North Adriatic - Koper Bay) (Salihoglu et al., 1980). One of the basins regularly received sewage from the town of Piran, while the other basin served as an undisturbed control. The chlorinated hydrocarbon content in both basins in fast moving crabs was the same but the concentrations in sessile mussels from the polluted basin were significantly higher.

Pesticide concentrations were measured in Parapenaeus longirostris and Carcinus mediterraneus collected from the coast of Israel in the period from 1976 to 1979; in about 25% of the Parapenaeus specimens no pesticides were detected (Ravid et al., 1985). There was no correlation between the concentrations of DDT and body length of Parapenaeus longirostris, but there was a significant negative correlation between the concentrations of PCBs and body length.

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 (Fig. 11). Concentration of PCBs doubled between 1975-76 and 1978.

5.2.5 Fishes

Data on concentrations of DDT total, HCH total and PCBs found by various authors in fishes collected from the Mediterranean Sea are summarised in Table XXIX.

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 PCBs (from 90 to 1800 $\mu g\ kg^{-1}$ F.W.).

The concentrations of DDTs in anchovies were moderate, but concentrations of PCBs 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 fishes from the central Mediterranean (Amico et al., 1979a), the concentration of organochlorine compounds in the anchovies ranged between 10 and 80 ppb (F.W.), 9 and 176 ppb and 0.1 to 0.8 ppb for DDTs, PCBs 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 PCBs 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 PCBs 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.

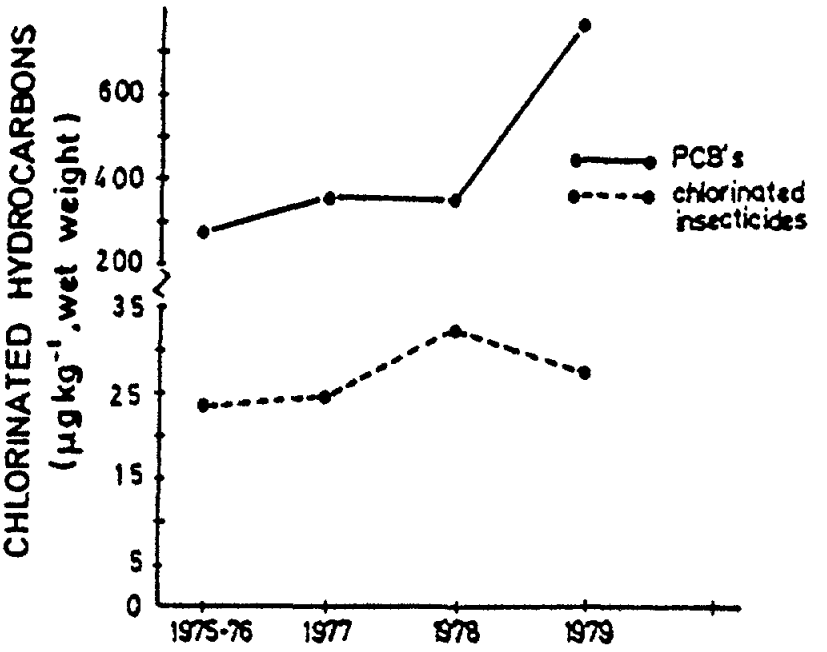


Fig. 11 Annual variation of chlorinated hydrocarbons in M. galloprovincialis from the Aegean Sea

The distribution of chlorinated hydrocarbons in fish from the Italian coast of the northern Adriatic Sea were investigated by Fossato and Craboledda (1981). The sequence of species according to tissue level of chlorinated hydrocarbons (Nephrops, Carcinus, Mytilus, Mullus, Engraulis, Thunnus) only partly reflects their lipid content. Levels in anchovies were comparable to those found in mullet, although the lipid contents of the two species were very different. Tuna, the biggest predatory fish of the Adriatic, contained the highest concentrations of DDT and PCB while having a lipid content comparable to or lower than mullet. Evidently, the food, the habitat and the physiology of various organisms strongly influence their accumulation capability. Clear evidence about the correlation between lipid concentrations and organochlorine residues concentrations in investigated species was not obtained. Of the several species studied, Engraulis encrasicolus is the only one for which comparison over a long period can be made for the area under consideration. The data in Table XXX 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.

Contardi et al. (1979) determined the concentrations of HCHs, DDTs and PCBs 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^{-1} F.W.), with the sole exception of a value of 8.10 for the Sarda sarda. Much higher concentrations of DDTs were found (up to 2500 ppb) with even higher concentrations being found for the PCBs (up to 14020 ppb).

Table XXIX

Chlorinated hydrocarbons in the Mediterranean fish
($\mu g\ kg^{-1}$ fresh weight).

AREA	FISH SPECIES	DDT TOTAL AVERAGE	DDT TOTAL RANGE	HCH TOTAL AVERAGE	HCH TOTAL RANGE	P C B AVERAGE	P C B RANGE	REFERENCES
II	Mullus barbatus	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)
"	Engraulis enrasicolus	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	Mullus barbatus	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)
"	Engraulis encrasicolus	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)
"	Thunnus thynnus	37.0	22.5-51.3	0.4	0.2-0.6	40.0	35.5-44.5	Amico et al. (1979a)
V	Mullus barbatus	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)

Table XXIX (continued)

AREA	FISH SPECIES	DDT TOTAL AVERAGE	DDT TOTAL RANGE	HCH TOTAL AVERAGE	HCH TOTAL RANGE	P C B AVERAGE	P C B RANGE	REFERENCES
"	Engraulis encrasicolus	52.9	3.8-102.5	33.6	0.5-70.0	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)
"	Various fishes (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. (1980); Picer M. et al. (1978a); Picer M. et Picer N. (1985); Revelante & Gilmartin (1975); Picer M. et al. (1981); Ferro et al. (1979); Vilicic et al. (1979); Stirn et al. (1974);
VI	Mullus barbatus	19.0	4-38	1.6	0.1-5.0	27	22-224	Amico et al. (1979a); Bolognari et al. (1979)
"	Engraulis encrasicolus	36	11.3-82.8	1.7	0.2-3.4	59	9-177	"
"	Thunnus thynnus	37		0.4		40		Amico et al. (1979a)
VIII	Mullus barbatus	76	4-400	4	0.4-10	432	14-1613	Satsmadjis and Gabrielides (1979); Voutsinou-Taliadouri and Satsmadjis (1982); Kilikidis et al. (1981)
"	Thunnus thynnus	1239		37		2613		Kilikidis et al. (1981)

Table XXIX (continued)

AREA	FISH SPECIES	DDT TOTAL AVERAGE	DDT TOTAL RANGE	HCH TOTAL AVERAGE	HCH TOTAL RANGE	P C B AVERAGE	P C B RANGE	REFERENCES
"	Merluccius merluccius	43		0.4		510		Kilikidis et al. (1981)
IX	Mullus barbatus	175	11-379	2		1.4	ND-2	Balkas et al. (1979); Bastürk et al. (1980)
"	Upeneus moluccensis	74	27-84			2		Balkas et al. (1979); Bastürk et al. (1980)
X	Mullus barbatus	29	3-83	15	ND-572	60	ND-284	Ravid et al. (1985)
"	Various fishes (3 species)	25	ND-106	15	ND-183	120	ND-800	Ravid et al. (1985)

Table XXX

Temporal comparison of chlorinated hydrocarbon levels (means ± SD, µg kg^{-1} wet weight) in Engraulis encrasicolus sampled off Porto Garibaldi and Cesenatico.

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

The highest levels of contamination were found in the Sarda sarda. Regardless of the species considered, no substantial differences were observed between samples coming from the two areas, even though they were characterized by coastal settlements of very different kinds. Fig. 12 shows the seasonal variations in the concentrations of chlorinated hydrocarbons in various organisms from the Genoa area (Contardi et al., 1981).

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 PCBs 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.

Revelante and Gilmartin (1975) studied the distribution of chlorinated pesticides and PCBs in muscle, digestive tract, liver and gonads of several pelagic (6 species) and benthic (11 species) fish from Northern Adriatic Sea. The distribution of some chlorinated pesticides and PCBs was also investigated Dujmov et al. (1979) in fishes of the Middle Adriatic and by Kljajic et al. (1976) and Vilicic et al. (1979) in fishes of the South Adriatic.

PCBs, 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 authors found a perfect relationship between lipids (% extractable organic matter) on the one hand and PCBs, DDE, DDD and DDT total on the other hand. For DDT the correlation coefficient was 0.88. 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 (PCBs, DDE, DDT, DDD) fall dramatically from areas close to the outfall in comparison with areas distant from the outfall outlet. This suggests that Mullus barbatus readily takes in the compounds, either through the gills or from food at the bottom of the sea. The lipids (hexane extract) seem to play a major part in the retention by Mullus barbatus of organochlorine residues.

Residues of DDE, DDT and PCBs were determined in Mugil auratus (Salihoglu et al., 1981) Mullus barbatus, Mullus surmuletus and Upeneus moluccensis (Bastürk et al., 1980) obtained from the eastern Mediterranean coast of Turkey. The DDT total concentrations in all

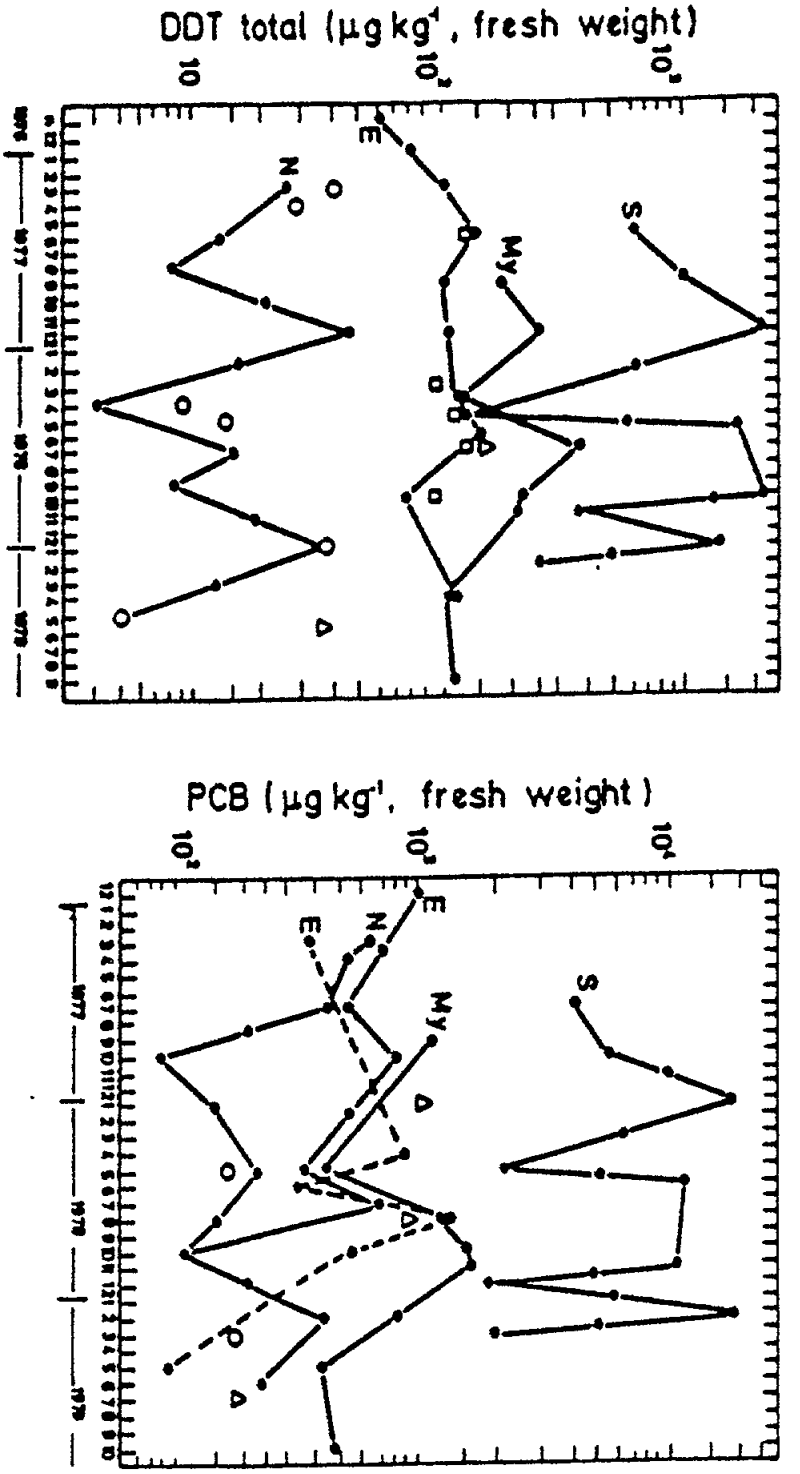


Fig. 12 Seasonal oscillations of the concentration the chlorinated hydrocarbons in various organisms from the Genoa area: S= Sarda sarda; My= Mytilus galloprov.; E= Engraulis encrasicolus; N= Nephrops norvegicus

biota samples analysed were EOM dependent. Using the "least square method" the mean DDT total values for 3 different fish species were plotted against % EOM, Fig. 13 shows that a straight line relationship was obtained (correlation coefficient of 0.83, standard error ± 1.1).

5.2.6 Birds, mammals and other organisms

DDE, PCBs, 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, heptachlorepoxide, and hexachlorobenzene. The difference between the mean levels of DDE, PCBs 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 PCBs 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. The levels found are relatively low in comparison with some of those found, for example, in North German Sea and in general there are no indications, as yet, that PCBs are involved in any reduction in the reproduction of birds. 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 levels of PCB, DDT and metabolites were analysed in the tissue of 22 dolphins Stenella coeruleoalba stranded on the Mediterranean coast of France (Alzieu and Duguy, 1979). The organochlorine content was higher in the blubber and liver than in the other organs. The immature animals, and particularly one new born, were more contaminated than adults. Certain observations suggest that the health of the dolphin may be endangered if PCB level in the liver exceeds 20 mg kg^{-1} of dry frozen tissue.

Analysis of blubber tissue from a common dolphin (Delphinus delphis) stranded on the French Mediterranean coast, show very high concentrations of organochlorines (in µg kg^{-1} dryweight): pp'DDT= 324,000; p,p' DDE 75,000; p,p' DDD = 2,700; lindane = 4,000 and PCB 700,000. These concentrations, and particularly the concentrations of PCB, are the highest so far observed by the authors, and were considered to be the probable cause of the death of the animal. (Vicente and Chabert, 1978).

Arnoux et al. (1981d) besides analysing chlorinated hydrocarbons in mussels and, fishes and algae, performed analyses of these compounds in some samples of Paracentrotus lividus and Octopus vulgaris. In Octopus vulgaris they detected only lindane but in Paracentrotus lividus they found PCBs and DDTs in relatively low concentrations.

Analysis of chlorinated pesticides and PCBs 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.

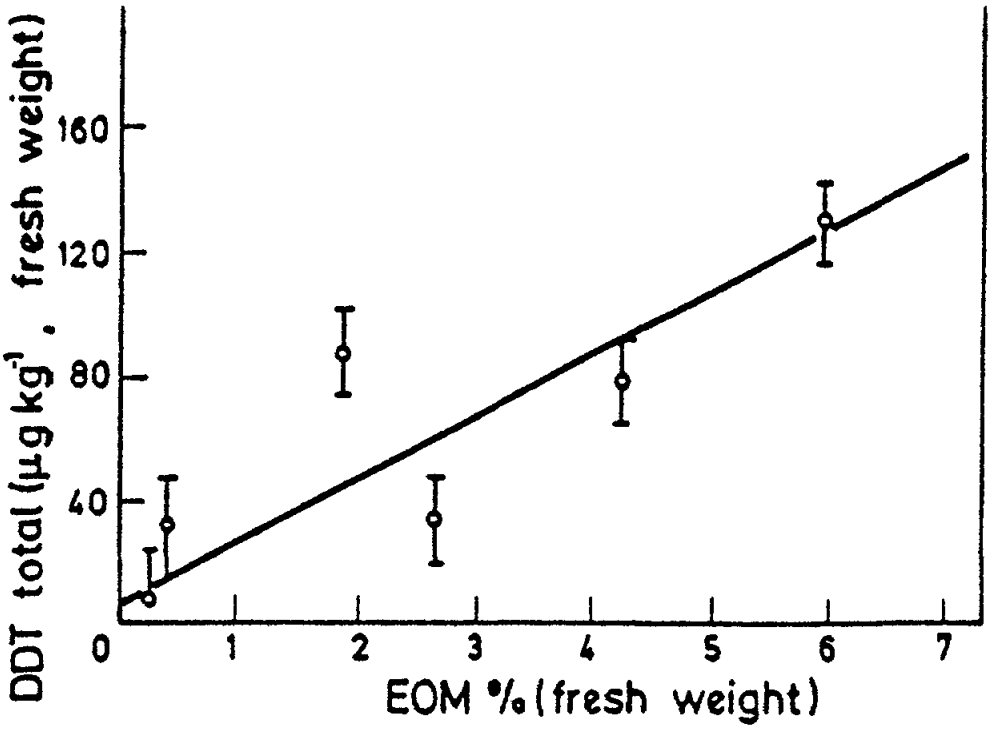


Fig. 13 t-DDT in living organisms as a function of % EOM. Curve fitting has been done by using "least -square method"

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.

Bourne and Bogan (1976; 1980) in commenting on their own results and those of previous authors, concluded that there seems to be no immediate cause for concern over the possible threat to Mediterranean sea-birds posed by organochlorine compounds.

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 analysed 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 analysed 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.

Revelante 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 PCBs were found in lower concentrations.

5.3 Concluding remarks concerning concentrations of organochlorine compounds in the Mediterranean

The analytical uncertainty of the measurements of chlorinated hydrocarbons in marine samples makes the evaluation of, and comparison between the data of different authors very difficult. Intercalibration exercises show a large dispersion of results.

The different areas of the Mediterranean have been surveyed very unevenly. Some data were obtained from only one or two sites (air, rain, waste waters) in the entire Mediterranean. Even for some biota samples (for instance mussels and Mullus barbatus) for which there are a lot of data, the scatter of sampling between regions in the Mediterranean Sea is very uneven. With the exception of Israel and Turkey, very few data are available from the Southern and eastern coast of the Mediterranean.

As a measure of the "quality" of all available data and also to see how representative these data are for the investigated area, Table XXXI gives the DDT total and PCB concentration ratios for water, sediment, mussels and striped mullet from the Mediterranean sea by region. Average concentrations were calculated using data for the period from 1970 to 1984 (but mainly from 1976/1979 period) obtained by all the various research groups which have published data. There are very large differences for many "concentration factors". For instance only 300 for DDT total between sediment/water in area IV but 142,000 for area VIII. Similarly, large differences are obtained by comparing concentration factors for mussel/water: 2800 for DDTs in region IV but 255,000 for region VIII, etc., etc. These differences are probably not only the consequence of analytical problems but also very large scatter in the levels of the investigated pollutants from region to region and, especially for sediments and mussels, also within a region. There are also differences between concentration ratios for fish/sediment and mussel/fish but they are not so large as for other compartments.

In order to obtain some measure of the quantitative relationship between investigated regions, a pollution order was calculated for the following matrices, water, sediment, mussels, Mullus barbatus also Engraulis encrasicolus and Thunnus thynnus. Because even for these relatively "popular" matrices there is considerable scatter among the data the number of "points" is divided by the number of regional data.

For instance DDT total in water was measured in three regions. As is seen from the presented results the highest value of averages is in region IV. Points are calculated 3 x 3/9 = 1. The second one is region V and it was obtained: 2 x 3/9 = 0.7 etc. For instance mussels were analysed in five regions and the highest averages were obtained for DDT in region II hence the mean points are 5 x 5/9 = 2.8. All the calculations were made in this way and the results are presented with "order" of pollution levels separately for DDTs and PCBs and together as summed in Table XXXII. It has to be stressed that for areas marked 1 to 5 the reliability is probably relatively good because similar numbers of data are available for each matrix.

Table XXXI

DDT_{total} and PCB concentrations ratios between various matrixes from the Mediterranean Sea.

Area	Sediment/water		mussels/water		fish/water		mussels/sediment		fish/sediment		fish/mussels	
	DDT_{total}	PCB	DDT_{total}	PCB	DDT_{total}	PCB	DDT_{total}	PCB	DDT_{total}	PCB	DDT_{total}	PCB
II	NA	17.8E3	NA	14.4E3	NA	1.6E3	6.6	2.1	12.2	7.9	1.9	3.8
III	NA	0.4E3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
IV	0.3E3	44.3E3	2.8E3	41.7E3	4.3E3	62.6E3	8.1	0.9	12.3	14.	1.5	1.5
V	1.3E3	21.7E3	7.6E3	28.8E3	6.1E3	21.7E3	4.9	4.6	3.7	0.8	0.7	
VI	NA	21.2E3	NA	43.3E3	NA	15.0E3	3.2	2.0	1.8	0.7	0.6	0.3
VII	NA	0.9E3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
VIII	142.2E3	10.3E3	26.7E3	255.3E3	84.4E3	28.8E3	0.2	2.5	0.6	2.8	3.2	1.1
IX	NA	NA	NA	NA	NA	NA	NA	NA	10.2	0.9	NA	NA
X	NA	5.5E3	NA	NA	NA	15.0E3	NA	NA	10.7	27.3	NA	NA

NA = Non applicable; E3 = x 10^3 Concentrations: Sediment - dry weight, mussels and fish (Mullus barbatus) - wet weight

Table XXXII

"Pollution order" of the Mediterranean Sea areas with DDT_{total} and PCB calculated on base of published average levels of these pollutants in water sediment, mussels and fishes (Mullus barbatus, Engraulis encrasicolus and Thunnus thynnus).

Order	DDT_{total} Area	Number of matrices	Points[x]	Order	PCB Area	Number of matrices	Points	Order	DDT_{total} + PCB Area	Number of matrices	Points
1.	VIII	5	14.8	1.	II	5	22.6	1.	II	9	35.5
2.	IX	2	13.4	2.	VIII	5	20.2	2.	VIII	10	35.0
3.	II	4	12.9	3.	IV	6	19.2	3.	IV	12	29.7
4.	V	5	11.0	4.	V	5	16.4	4.	V	10	27.4
5.	IV	6	10.5	5.	VI	6	12.6	5.	VI	11	21.5
6.	VI	5	8.9	6.	III	2	11.1	6.	III	3	18.1
7.	III	1	7.0	7.	X	3	6.2	7.	IX	4	16.2
8.	X	2	3.6	8.	VII	2	2.8	8.	X	5	9.8
9.	VII	1	1.0	9.	IX	2	2.8	9.	VII	3	3.8

[x] Calculation of "points" is described in text

6. EFFECTS ON MARINE ORGANISMS

6.1 DDT and its metabolites DDE and DDD

6.1.1 Marine flora

Tests conducted using concentrations as low as 1 μg l^{-1} have been reported to reduce photosynthesis with some marine phytoplankton (Wurster, 1968). Bousch and Matsumura (1975) indicated that above 100 μg l^{-1}, DDT (and its metabolites DDE and DDD) have no effect on the growth of Agmellenum quadruplicatum; also there was a little difference in the individual toxicity of the three substances. Mosser et al. (1972) demonstrated that of the two species they tested, the competitive success of Tetraselmis pseudomonas was reduced relative to Dunaliella tertiolecta, even at concentrations as low as 1 μg l^{-1}. This tended to confirm the conclusions reached by Menzel et al. (1970) in an investigation of Wurster's claim that DDT was unlikely to affect photosynthesis overall, but that it might have an effect on overall species dominance.

6.1.2 Marine fauna

Inverterbrates

Although ciliates are not very sensitive to either DDT or DDE (Kooley and Keltner, 1970; Persoone and Uyttersprot, 1975) the brackish water copepod Nitocra spinipes is apparently rather sensitive to DDE (Bengtsson, 1978). Bengtsson also pointed out that the difference between the 14 day LC50 and the concentration which caused a 50% reduction in reproduction over the same period was only a factor of 2, a difference which is probably barely significant.

The data on the toxicity of DDT and DDE to molluscs suggests that they are only killed by concentrations in excess of 1000 μg l^{-1} (Eisler, 1970a; Portmann and Wilson, 1971). Butler's (1963) data however, suggest that they are sensitive to concentrations of only about 10 μg l^{-1}(oyster shell regrowth was reduced). However, regardless of temperature or period of exposure, oysters are not sensitive to concentrations of DDT of 0.1 μg l^{-1} or less (Butler, 1971). Another sublethal effect which has been used in the assessment of the effect of DDT on molluscs is the effect on byssus thread formation in the common mussel (Mytilus edulis); no detectable effect could however, be found at 100 μg l^{-1} (Roberts, 1975). The settling response of barnacles was affected at concentrations of 60 μg l^{-1}, a concentration well below that which would be lethal (Meith-Avcin, 1974).

Crustacea appear to be seriously disturbed by concentrations of DDT of the same order or less as those which affect oyster shell regrowth. Andryuschenko (1972) using the Black Sea shrimp, found that the sensitivity of this species to DDT was markedly affected by both season and temperature. He reported that the most sensitive response was the effect of DDT on the respiration of shrimps; a response he could detect down to 0.01 μg l^{-1}. The only data available on the comparative toxicity of DDT and DDE to crustacea was reported by Butler (1963) for the brown shrimp; this suggests that to crustacea DDE is at least an order less toxic than DDT.

Vertebrates

The range of short-term LC50 type data for marine fish spans a substantial numerical range and, although most of the data fall in the range 1-100 $\mu g\ l^{-1}$, a few species appear to be sensitive to concentrations below 1 $\mu g\ l^{-1}$ (Portmann, 1979). This relatively wide range of toxicity is explained by Pritchard et al. (1973) as being attributable to the difference in overall lipid content of different species and the relative distribution of lipid in different tissues in different species. DDD is somewhat less toxic and DDE is much less toxic than DDT to marine fish (Portmann, 1979). Valentine and Soulé (1973) found that grunnion, which were collected from field situations in which they had been exposed to DDT, were markedly more sensitive to DDT in laboratory bioassays, than fish which had little or no previous history of exposure to DDT - a finding in marked contrast to that with fresh/brackish water fish (Dzuik and Plapp, 1973). Smith and Cole (1973) found that winter flounder exposed to 1 or 2 $\mu g\ l^{-1}$ of DDT and dieldrin in combination, laid eggs containing a mean concentration of DDT of 2.4 $mg\ kg^{-1}$, and that mortality bore a linear relationship to the concentration of DDT in the eggs. Although DDT passed from the female to her eggs it did not pass from males into their milt.

Behavioural and physiological response tests

Although the lethal effects of DDT and of DDD and DDE appear to be registered fairly rapidly, as was apparent with the oyster shell regrowth response, there is the possibility that much lower concentrations than those which prove fatal may affect behavioural or physiological responses in marine invertebrates and fish (Portmann, 1979). Jowett et al. (1978) carried out in vitro tests on the effect of DDT on ATPase activity in the gills of shore crabs. They found that at concentrations of DDT as low as 0.35 $\mu g\ l^{-1}$, Mg^{2+} ATPase was inhibited, but that Na^{+} K^{+} ATPase was slightly stimulated. The overall effect on total ATPase activity was negligible at concentrations below 3.5 $\mu g\ l^{-1}$. Engel et al. (1972) were also able to detect the effects on some of the enzyme systems they examined in class exposed to DDT at 2 $\mu g\ l^{-1}$ for up to 30 weeks. Hansen et al. (1973) investigated the avoidance reaction of grass shrimp to DDT, on the grounds that this species is important in the fish food chain. They found little evidence of a reaction to any concentration in the range 10 to 0.01 $\mu g\ l^{-1}$, although at 0.1 $\mu g\ l^{-1}$ there was statistical evidence of an attraction effect. Valentine and Soulé (1973) studied the developmental stability of pectoral fin rays in grunnion fry and claimed to be able to detect differences in symmetry in those fry which were exposed to concentrations of 0.1 $\mu g\ l^{-1}$ or more.

Data from investigations of the effects of DDT on enzyme activities in Mugil cephalus L. show that in vitro DDT had a statistically significant ($P<0.05$) stimulatory effect on lactate dehydrogenase from liver and on fumarase from red and white muscle and liver. Such an inhibitory effect was recorded at 1 ppm DDT on fumarase from white muscle and 3-hydroxybutyrate dehydrogenase from liver. A statistically significant influence of DDT at 1 ppm was recorded in vivo in the liver lactate dehydrogenase. This means that DDT has strong effects on the respiratory chain and citric acid cycle. Both processes were slowed. In addition, a decrease in the activity of 3-hydroxabutyrate dehydrogenase in the liver could indicate a reduced catabolism of fatty acids and glycols (Tudor and Bannister, 1979).

Organochlorines, such as o,p' DDD and p,p' DDE inhibited the increase of cortisol output in response to ACTH whether administered to the donor fish (Mugil cephalus and Liza remada) or when given in the superfusion medium for at least 5 h (Yaron, 1986).

On Mugil cephalus the DDT in vivo effects showed a strong inhibition of enzyme activities. It was shown that DDT inhibits the activities of enzymes participating to the oxidative phosphorylation and, therefrom, to ATP-ase. It is quite possible that the inhibition of metabolic pathways in vivo takes place through an allosteric disactivation. This would explain why a slowing of the citrate cycle and respiratory chain occurs in the in vivo test. (Muzinic et al., 1986).

Factors affecting the acute and chronic toxicity of DDT and its biomagnification in Alexandria region were studied by El-Sebae et al., 1986. In most cases Gambusia were more susceptible than Tilapia zillii, thus suggesting its use as a sensitive indicator for the evaluation of hazardous levels of such pollutants.

The permeability of DDT through gills, skin and intestinal wall is lower for euryhaline fish (Tilapia zillii) in fresh water; i.e. fish in polluted salt water may take up more DDT, resulting in high mortality (Saleh, 1981). The results of these tests also indicated a strong correlation between adsorption rate and environmental concentration of DDT.

6.1.3 Marine birds

Zitko (1976) followed the decline in the concentration of total DDT residues in the eggs he collected from a colony of double crested cormorants from 1971-1975. Almost all the residue was as DDE, but whereas in 1971 it was 9.7 mg kg^{-1} (wet weight) by 1973 it had declined to 2.9 mg kg^{-1}, a level which he considered to be comfortably below the level which might affect development of the young. At the earlier higher concentrations, DDE in the fish was less than 0.1 mg kg^{-1}, in the eggs it ranged from 1.4 to 45 mg kg^{-1}. The association of DDE with the thinning of egg-shells in birds is well documented (Portmann, 1979). An excellent review of the subject with a special bias towards marine birds was prepared by Ohlendorf et al. (1978).

The association of DDE with the thinning of eggshells in heron (Bubulcus ibis) from Ebro estuary was investigated by Ruiz et al. (1983). A significant negative correlation coefficient was found ($r = -0.7$ at $p<0.05$ statistical significance) between concentration of DDE in eggs and eggshell thickness.

6.2 Hexachlorocyclohexane

6.2.1 Marine flora

At the maximum solubility of 1.4 mg l^{-1} the alpha isomer of hexachlorocyclohexane had no effect on two species over two days and still had no effect on growth of one species over four days (Canton et al., 1978). In contrast isomer (lindane) proved lethal to two species of marine phytoplankton at concentrations 4 and 8 mg l^{-1}

(Neuville et al., 1974). In his report on short-term tests with lindane on natural communities of phytoplankton, Butler (1963) comments that lindane was the least harmful of the organochlorine pesticides he had tested in this way.

6.2.2 Marine fauna

Concentrations which would cause the death of marine molluscs in relatively short term experiments were estimated to be in excess of 10 mg l^{-1}. Even tests on reproductive success, usually one of the more sensitive parameters which can readily be measured, indicated effect concentrations for most species of the order of 1 mg l^{-1}.

In contrast to the comparatively low toxicity of the alpha isomer of hexachlorocyclohexane the tests with gamma isomer reveal that it is markedly more toxic to crustacea (Portmann, 1979). Most of the data suggests that concentrations in the range 0.1 to 1 µg l^{-1} would be lethal to various species of shrimp. The concentrations of gamma HCH at which marine crustacea might be expected to suffer a reduction in reproductive success would be between 0.01 and 0.1 µg l^{-1} (Portmann, 1979). Canton et al. (1978) found that guppies which had been acclimatised to salt water of full sea water salinity, were not killed in short term tests by exposure to concentrations of up to 1400 µg l^{-1} of alpha HCH. Most of the true LC50 values of gamma HCH fall in a 1-50 µg l^{-1} range for marine fishes (Portmann, 1979). None of the reported experiments with marine fishes and gamma HCH appear to have been taken to the stage where threshold LC50 could be quoted. The longest test lasted only 10 days and produced an LC50 for mummichogs of 1.6 µg l^{-1} (Eisler, 1970b). This might perhaps indicate that 1.6 g l^{-1} is fairly close to the median lethal threshold concentration (Portmann, 1979).

El-Sebae et al. (1986) studied factors affecting the acute and chronic toxicity of lindane and its biomagnification in fishes from Alexandria region. In most cases Gambusia were more susceptible than Tilapia zillii.

6.2.3 Marine birds

Hexachlorocyclohexane does not appear to be very toxic to birds. It also appears to be fairly readily excreted or metabolised by them with the result that usually low concentrations of HCH are found in avian tissues and eggs (Portmann, 1979).

6.3 Polychlorinated biphenyls

6.3.1 Marine flora

PCBs generally inhibit the growth of aquatic plants at concentrations of 10-100 µg l^{-1}, but reduction in photosynthesis and carbon uptake in sensitive species may occur at 0.1-1.0 µg l^{-1} (Fisher and Wurster, 1973). Plants growing under sub-optimal conditions may be more vulnerable to PCB-induced stress than those growing under optimal conditions.

6.3.2 Marina fauna

The effects on the copepod Tisbe bulbisetosa of Aroclor 1254 suspensions stabilized with Corexit 7664 in the concentration range 0.1 to 500 µg l^{-1} were studied by Dalla Venezia et al. (1981). No mortality was noted in adults exposed to PCB concentrations of up to 100 µg l^{-1} for one week. Mortality was observed in 500 µg l^{-1} of PCB. Cumulative mortality was much higher in males than in females: for example for individuals originating from control samples, the mortality curves show that 50% of males died after a 4-day exposure to 500 µg l^{-1}, while less than 50% females died after a ten-day exposure. Fecundity experiments indicated that the duration of the entire biological cycle is lengthened in polluted conditions; thus, in polluted and in control media females produced on average 0.93 and 1.26 nauplii per day respectively. Survival of nauplii was lowered significantly at 1.6 µg l^{-1} PCB concentration. The authors concluded that selection probably occurs in Tisbe bulbisetosa at the nauplius stage, consequently the surviving individuals tolerate polluted conditions just as well as control individuals tolerate normal conditions; on the other hand, PCB retards the biological cycle of survivors, probably by affecting some metabolic process.

Preliminary research has been performed by Krsinic et al. (1979) on the influence of Diesel oil D-2 the synergistic effect of Aroclor 1242 on the isopod Euridice truncata. In the course of a series of four-day experiments, concentrations of under 1 ppm Diesel oil D-2 mixed with Aroclor 1242 at 0.2 ppb did not cause any mortality. However, in concentrations of 10 ppm D-2, more than 50% of the organisms died within 48 hours; however mortality did not increase when Aroclor 1242 (0.2 ppb) was added.

Marine invertebrates are also highly sensitive to PCBs. Nimmo et al. (1975) recorded toxicities of Aroclor 1254 to several species of shrimp and oysters of 0.1-12.5 µg l^{-1} in testing that lasted 30 weeks.

Using Aroclor 1016, Hansen et al. (1974) reported 96-h LC50 of 10.5 and 12.5 µg l^{-1} for two species of shrimp, whereas Stahl (1979) found no acute effect of Aroclor 1254 on hermit crabs at concentrations of up to 30 µg 1-1.

As with aquatic plants, toxicity to marine invertebrates of the different Aroclors, differs considerably (Nebeker and Puglishi, 1974). It has also been shown that the juvenile/immature stages of many invertebrates are often more sensitive than adults. Under natural conditions this probably means there is a seasonal cycle in the sensitivity of invertebrate populations to PCB-containing wastes.

Effects of Aroclor 1254 on crustacean decapod Leander (syn. Palaemon) adspersus (toxicity, bioaccumulation, oxygen consumption and osmoregulation) were studied by Dalla Venezia and Fossato (1986). The 96-hour LC50 ranged from 10 to 100 µg l^{-1} PCB at 50°/oo and at 10°/oo. Oxygen consumption was not affected when animals were pre-exposed to PCBs in water at up to 1 µg l^{-1} concentration. Leander adspersus is an exceptional osmoregulator and its osmoregulatory ability is almost independent of both temperature and PCB pollution at 1 ppb

concentration. The ability of shrimps to concentrate the PCBs from food was confirmed. However, when mussels with high levels of PCBs, were used as food PCB uptake did occur in the shrimps, but not at a rate proportional to that in the food.

Dalla Venezia et al. (1983) reported on the physiological and behavioural response of mussel Mytilus galloprovincialis taken from the Gulf of Venice. Their experiments involved a three-day acclimation period in 34.0 + 0.5 salinity clean seawater, followed by a five day period in PCB (Aroclor 1254) concentrations ranging from 10 to 1000 $\mu g\ l^{-1}$. No dead individual was recorded in any treatment during the 10-day experimental period. Mussels were normally active in all PCB suspensions, but unusually elongated feet were observed at 100 $\mu g\ l^{-1}$ PCB concentration. Concentrations of 10 $\mu g\ l^{-1}$ of Aroclor 1254 produced no effect on oxygen consumption within five days of exposure. However, significant increase in oxygen consumption was found at concentrations of 100 $\mu g\ l^{-1}$ and above.

Most species and life stages of fish are sensitive to PCBs. De Foe et al. (1978) calculated that the 30 day LC50 in fathead minnows exposed to Aroclor 1260 was 3.3 $\mu g\ l^{-1}$ compared with 4.7 $\mu g\ l^{-1}$ for Aroclor 1248. Although reproduction occurred at concentrations as high as 3 $\mu g\ l^{-1}$, there was a 20% reduction in the standing crop of second-generation fish exposed to much lower levels (0.1 $\mu g\ l^{-1}$). This was mainly due to the death of larvae soon after hatching. Enhanced sensitivity of juvenile stages is widespread among fish. Nebeker et al. (1974) reported a 96-h LC50 of 15 $\mu g\ l^{-1}$ for newly hatched fathead minnows exposed to Aroclor 1242 and 300 $\mu g\ l^{-1}$ for 3-months.

PCBs are strong inducers of mixed function oxygenases (MFO) in various marine organisms (Duinker and Boon, 1985). Low levels of MFO enzyme systems are constantly present, but they can be increased by the presence of certain xenobiotics. PCB mixtures also act as a substrate to be hydroxylated, but more often they only induce the systems, resulting in an increased and/or altered metabolism of other compounds. An increased activity of MFO systems in marine organisms by PCBs was also demonstrated under field conditions in fishes and invertebrates.

6.3.3 Marine birds

PCBs have been implicated in reducing eggshell thickness in water fowl in laboratory experiments (Heseltine et al., 1981). Although a comparable response is likely to occur under natural conditions, it has not been possible to separate the effects of PCBs from those of DDTs on eggshell thickness. It is known, however that PCB residues in bird eggs have recently declined over wide geographic areas. Ingestion of PCBs may also produce generalized oedema and hypopericardium in birds.

Other pathological changes include enlargement and damage to the kidneys and livers, internal haemorrhages and spleenic atrophy. Exposure to levels below those causing acute toxicity may result in increased susceptibility to viral infection.

6.4 Hexachlorobenzene

The main use of hexachlorobenzene as a fungicide on wheat and its low solubility in water perhaps explains the apparent lack of interest in the toxicity of hexachlorobenzene to aquatic organisms (Portmann, 1979). For instance there does not appear to have been any attempt to assess the potential impact of HCB on marine flora. The amount of work done with marine fauna is also very limited. The relatively short term tests conducted by Parish et al. (1974) with invertebrates, suggest that at least over short exposure, pink and grass shrimps are more sensitive than fish, since mortalities of up to 33% and 10% respectively were observed at the highest exposure concentrations for each species, i.e. 25 and 17 $\mu g\ l^{-1}$ respectively. At the lowest exposure concentrations, 0.67 and 1.87 $\mu g\ l^{-1}$, there was still no evidence that uptake was levelling off; at 0.06 and 0.15 $\mu g\ l^{-1}$ they had almost certainly reached a plateau in all tissues except possibly liver. As these concentrations caused no ill effects, they might reasonably be regarded as no effect levels for adult fish.

Laseter et al. (1976) attempted to relate the results of their laboratory tests with HCB to the levels which were associated with adverse effects in the field. The laboratory work suggested that 1-5 $\mu g\ l^{-1}$ would cause no effects but that accumulation by fish at such exposure levels might reach 10 $mg\ kg^{-1}$. In practice they found most species present in the field at concentrations of between 2 and 20 $\mu g\ l^{-1}$ but that the concentration of HCB in the fish was much lower than expected. This perhaps reflects the lower bioavailability of the HCB under field conditions due to strong adsorption on particulate matter and sediments. Thus to fish, concentrations of around 1 $\mu g\ l^{-1}$ are probably safe whereas for crustacea the safe concentration would appear to be around 0.1 $\mu g\ l^{-1}$.

6.5 The Drins (aldrin, dieldrin and endrin)

Research work on the effects of aldrin and dieldrin on adults mollusca Monodonta articulata from Malta coastal waters was performed by University of Malta (Saliba and Axiak, 1986). The results indicated that up to 5 $mg\ l^{-1}$ seawater concentration of aldrin and dieldrin have no apparent effect on the copper binding property of haemocyanin. Since this is involved in oxygen binding, this infers that these pesticides show no effect on oxygen transport in animals having haemocyanin as the oxygen carrier.

Butijn and Koeman (1977) carried out a comprehensive review of the available literature on the toxicity of the drins. They concluded that for most species dieldrin was more toxic than aldrin and that endrin was usually a similar or perhaps slightly greater toxicity than dieldrin. Since aldrin is readily converted to dieldrin in the aquatic environment and in marine organisms, and because there seem to be virtually no reports of endrin concentrations for the Mediterranean area this assessment of the toxicological data on drins is confined to data on dieldrin.

Short-term (96hrs) LC50 tests with marine and estuarine fish suggest that the lethal concentration of dieldrin to these species are usually around 10 $\mu g\ l^{-1}$ with a minimum of 1 $\mu g\ l^{-1}$ (Butijn and Koeman, 1977). The review of Butijn and Koeman (1977) also suggests that shellfish (molluscs) are less sensitive to dieldrin than fish, but that crustacea may be somewhat more sensitive. Their review indicates that the concentration factor in fish relative to water is around 6×10^4. Their overall conclusions suggest that the non-toxic level of dieldrin to all species of fish is 0.001 $\mu g\ l^{-1}$, but that a reasonable level for general environmental protection purposes is probably 0.05 $\mu g\ l^{-1}$. An examination of the data (Craig, 1977; Shannon, 1977; Butijn and Koeman, 1977) on which Butijn and Koeman base their conclusions suggest that their 0.001 $\mu g\ l^{-1}$ figure is set very cautiously and that an average concentration of 0.05 $\mu g\ l^{-1}$ or even 0.1 $\mu g\ l^{-1}$ would probably not result in widely detectable effects.

6.6 Heptachlor and Heptachlor epoxide

Very little work appears to have been carried out to investigate the toxicity of heptachlor or heptachlor epoxide to marine phytoplankton but the range of concentrations reported to have caused effects ranges from 1 mg l^{-1} (almost total inhibition of productivity) (Butler, 1963) to as low as 1 $\mu g\ l^{-1}$ (killed three species of phytoplankton) (Konar, 1970).

Portmann (1979) reviewed the available data on the toxicity of heptachlor and heptachlor epoxide to marine organisms and found the majority of the short-term lethality tests were reported to have produced LC50 values for fish in the range 10-100 $\mu g\ l^{-1}$. However, most of the tests related to added rather than measured concentrations. Work by Schimmel et al. (1976) suggested that the true lethal concentrations are probably around 1 $\mu g\ l^{-1}$ or in the longer term perhaps as low as 0.1 $\mu g\ l^{-1}$. Work by the same authors suggested that this sort of concentration would be about the lowest likely to affect crustacea. Based largely on these results Portmann (1979) suggested a no effect concentration for both heptachlor and heptachlor epoxide of 0.01 $\mu g\ l^{-1}$. The concentration factor for heptachlor and heptachlor epoxide in marine organisms relative to sea water is relatively low for invertebrates according to Schimmel et al. (1976), ranging from 200 to 700 fold but is markedly higher in fish (maximum ca 10,000 fold).

7. RISK ASSESSMENT

In this section of the report a comparison is made of the concentrations that are likely to be harmful to either marine organisms or to man, relative to those that have been found in the Mediterranean environment. The risk of harmful effects in marine organisms will be related to concentrations in water. This simplification may be justified on two grounds. Firstly entry into the food chain depends to a certain degree on the concentration of the harmful substance in water, and ultimately this first step determines even the exposure of predators. Secondly, at present it would be impossible to define other exposure parameters for the complex marine ecological system. Man's exposure to organochlorines is also complex (from the atmosphere,

drink, food, occupation), but the report will consider only whether organochlorines in seafood present a health risk to the consumer. Both risk assessment is hampered by common problems concerning both sampling and the accuracy and precision of analyses which together make difficult to discover trends or compare data.

The comparison of PCB concentrations measured in 1974-1978 and 1978-1982 in the water, planktons and sediments of the Mediterranean Sea indicated some decline (Table XXI), but it seems that PCB concentrations in Mytilus galloprovincialis actually increased from 1975 to 1979 in the Aegean sea (Fig. 11). Though some data indicate that DDT levels are falling (Fig. 10), the decline is not consistent (Fig. 11) and there is a possibility that the changes are due to variations in the sampling and analytical techniques. Thus seasonal variations in the concentrations of DDT and PCB in Sarda sarda, Engraulis encrasicolus, Nephrops norvegicus and Mytilus galloprovincialis can be of one order of magnitude (Fig. 12). Altogether, concentration changes are equivocal for these two organochlorines and this ambiguity in itself indicates that DDT and PCB inputs either remained unchanged or the decrease was not sufficient to elicit consistent reductions in mussels, crustaceans or fish. There is even less data for organochlorines that are present at lower concentrations than DDT and PCB.

7.1 Risk to organisms

7.1.1 Concentration in water and sediments

The regional means of the aquatic concentrations of DDT, PCB and HCH were mostly below 10 ng l^{-1}, though DDT and PCB concentrations occasionally reached or exceeded 100 ng l^{-1}. The maximum concentration for PCB was around 550 ng l^{-1}. Only few values are available for dieldrin and these show that concentration in water is below 1 ng l^{-1} (Table XVIII). In sediments the concentration of PCB is higher than the concentration of DDT, 40 and 20 µg kg^{-1} dry weight respectively. Only few values are available for HCB and dieldrin. In two areas the concentration of HCB was around 10 µg kg^{-1}, and the concentration of dieldrin measured only in one area was only 0.1 µg kg^{-1} dry weight (Table XXII).

7.1.2 Risk assessment

7.1.2.1 DDT

There has been a great deal of work conducted to establish the levels of DDT that might be harmful to marine organisms and the range of concentrations reported to cause mortality in virtually all groups of species is considerable. Phytoplankton were reported to be affected at concentrations of 1 µg l^{-1} but crustacea were killed in concentrations of 10 µg l^{-1} and suffered sub-lethal effects at concentrations down to 0.01 µg l^{-1}. The range of lower concentrations reported to affect fish is from 0.1-1 µg l^{-1}. These figures suggest that concentrations below about 0.01 µg l^{-1} are unlikely to cause serious effects to populations of marine species. This figure coincides with the assessment of the no effect concentration conducted by Portmann (1979) based on an extensive review of the world literature. The environmental quality objective set by the European Community is 10 ng l^{-1} pp DDT and 25 ng l^{-1} total DDT.

The concentrations of DDT found in marine organisms are, not surprisingly, markedly higher than in sea water, but comparison of the maximum concentrations typically encountered in Mediterranean species suggests that they are comfortably below those reported to cause effects on reproduction and other sub-lethal effects. There have in the past been many suggestions that DDT or its metabolite DDE is associated with failure in reproductive success of marine birds due to thinning of shells of their eggs. However, the concentrations associated with this phenomenon were quite high and there is no suggestion that populations of marine birds in the Mediterranean are at risk, or that their numbers are in decline.

7.1.2.2 HCH

The lowest concentrations reported to affect fish are 1.6 $\mu g\ l^{-1}$, with crustacea apparently being slightly more sensitive. The European Community have agreed that the environmental quality objective for total HCH should be set at 20 $ng\ l^{-1}$ and such a concentration should ensure that no marine species are adversely affected. This concentration is about double than normally reported as being found in Mediterranean sea waters.

HCH is, by comparison to most other organochlorine pesticides, relatively soluble in water and is not therefore so markedly accumulated by marine organisms as some other organochlorine compounds e.g. DDT. A concentration factor of about 1000 fold is probably about the maximum encountered (this report and Portmann, 1979). On that basis one might expect the typical concentrations of HCH found in marine fish ($<20\ \mu g\ kg^{-1}$) to be associated with concentrations in sea water of $<20\ ng\ l^{-1}$, which in fact appears to be the case. HCH is not generally considered to present a hazard to avian species or marine mammals in other parts of the world. There is no reason to suppose that present levels of HCH present any risk to marine birds or mammals in the Mediterranean.

7.1.2.3 PCBs

The available toxicity data, as reported in section 6.3 suggest that the toxicity of PCBs differ somewhat according to formulation. It is also apparent that in the field the pattern of residues actually present in marine waters and biota is not strictly analogous to any one formulation. This makes an accurate assessment of the risks to marine organisms rather difficult. However, it appears that the concentration of PCBs, as a formulation, likely to be lethal in the short-term to marine organisms is about 500 $\mu g\ l^{-1}$ and that the lowest recorded effect is in relation to larval survival at 1.6 $\mu g\ l^{-1}$. Sub-lethal effects have been recorded at around 0.1 $\mu g\ l^{-1}$ or 100 $ng\ l^{-1}$. This is well above the concentrations likely to be found in the marine environment at the present time, suggesting that, at least in relation to marine fish and shellfish, the risk is minimal.

Concentrations of PCBs in marine fish and shellfish are markdely higher than in sea water, due to the lipophilic nature of these compounds. Typical concentrations were 50-500 $\mu g\ kg^{-1}$ but occasional concentrations of up to 10.000 $\mu g\ kg^{-1}$ (Table XXIX). There have been suggestions from other parts of the world that these highest concentrations might be associated with effects on marine mammals (ICES, 1988), and perhaps on marine birds, though for the latter the link was more tenuous.

7.1.2.4 HCB

The limited toxicity data suggest that concentrations of 100 ng l^{-1} would probably not cause any ill-effects to marine species. This is well above the concentrations apparently likely to be found in Mediterranean species, suggesting that there is little cause for concern in relation to the potential impact of HCB on marine organisms in the sea.

7.1.2.5 Drins

The only toxicity data collected using Mediterranean species suggest simply that 5 mg l^{-1} did not affect the oxygen carrying capability of bivalve molluscs. A report produced by Butijn and Koeman (1977) reviewed the world literature on all three drins and suggested that the no effect concentration could be set at 5 ng l^{-1} although the actually proposed figure for aldrin and dieldrin was 1 ng l^{-1}. The European Community has not yet achieved agreement on an environmental quality standard for marine species but has suggested a maximum for all three drins in total of 30 ng l^{-1}, 10 ng l^{-1} each for aldrin and dieldrin and 5 ng l^{-1} for endrin. These concentrations seem to be above those currently reported for Mediterranean waters. It therefore seems unlikely, on the basis of the limited data available, that present levels of drins in the Mediterranean are likely to adversely affect marine organisms. It seems equally unlikely that marine mammals or sea-birds are likely to be at risk.

7.1.2.6 Heptachlor

The no effect concentration for all marine species has been suggested to be between 10 and 100 ng l^{-1} which seems to be well above those likely to occur in the Mediterranean. If this is correct there would be no cause for concern over present levels but the data base is very small indeed. Consequently it would be unwise to give much credence to such a conclusion.

7.2 Risk to man

7.2.1 Concentrations in mussels, crustaceans and fish

PCB concentration in seafood consistently exceeded the concentration of DDT. In mussels DDT concentration of 47 $\mu g\ kg^{-1}$ was associated with 236 $\mu g\ kg^{-1}$ PCB (Table XXV). In crustaceans 1.7 - 10.2 $\mu g\ kg^{-1}$ DDT was associated with 21 - 157 $\mu g\ kg^{-1}$ PCB and 0.2 - 2.35 $\mu g\ kg^{-1}$ HCH (Table XXVI). In fish the concentrations of these

three organochlorines follow the same order. In striped mullet (Mullus barbatus) collected from different areas of the Mediterranean Sea the average of area means were 64 μg kg^{-1} for DDT, 187 μg kg^{-1} for PCB and 4.0 μg kg^{-1} for HCH. The corresponding numbers for anchovies (Engraulis encrasicolus) were 38, 128 and 9.8 μg kg^{-1}. In various species, including tuna (Thunnus thynnus), the order was the same. The concentration of dieldrin was in the order of HCH. When DDT concentration in striped mullet ranged from 4 to 85 μg kg^{-1}, dieldrin concentration ranged from 0.1 to 1.6 μg kg^{-1}. In the same area (Mediterranean region VI) there was hardly any difference between striped mullet, anchovies and tuna. In various fish species grouped together the means, with one exceptions, were similar. The one exception was 1,756 μg kg^{-1}, PCB in Region II. HCB concentration in fish was in the range of 0.1 to 1.0 μg kg^{-1} (Table XIX).

The Marine Biological Association of the United Kingdom (1988) gives some values for aldrin, dieldrin, chlordane and heptachlor (which is 3-chlordane) in fish:

Aldrin or dieldrin

striped mullet (Mullus barbatus), Israel,	2.3	μg kg^{-1}
" " Saronikos Gulf, Greece,	17.0	μg kg^{-1}
bream (Sargus vulgaris) Abu Qir Bay, Egypt,	20	μg kg^{-1}

Chlordane

Sprat (Sprattus sprattus), Port Said, Egypt,	108	μg kg^{-1}

Heptachlor

pandora (Pagellus erythrinus), Abu Qir Bay, Egypt,	5.3	μg kg^{-1}
striped mullet Saronikos Gulf, Greece,	0.5	μg kg^{-1}
" " Pagassitikos Gulf, Greece,	0.1	μg kg^{-1}

7.2.2 The use of data for intake estimates

Data tabulated in the document indicate large variations in organochlorine concentrations in fish, mussels and crustaceans from the same region. It is typical that the maximum value is 2-4 fold higher and the minimum value is 3 to 10 times lower than the mean. Though regional means differ, the between regions variation is not more than the within region variation. Such variations may have different origin and may be explained with differences in pollution and the selection of sampling sites. It is most likely that fish caught near the estuaries of rivers, loaded with agricultural and industrial waste, contain more organochlorines than fish caught in the same region but far from the main local input. Assuming a bias in the selection of sampling sites towards polluted areas, the mean values overestimate concentrations in seafood. Such a bias is likely, because a polluted area attracts more attention than a relatively clean area. This point is illustrated by the following example. The seven data sources selected for aldrin by the Library and Information Services of the Marine Biological Association of the United Kingdom (1988) consist of Valparaiso and Conception Bays (Chile) twice, Port Said (Egypt), Abu Qir Bay (Egypt), Caspian Sea, Thames Estuary (U.K.) and the Mediterranean Coast of Israel. It is most likely that data presented in this report are similarly biased towards the heavily polluted areas and therefore the real (unbiased) means are lower than the observed means. However, even if this assumption is correct, the observed range may cover the whole spectrum of concentrations.

7.2.3 Estimates of daily intake

For the purpose of risk assessement low, medium, and high concentration values in fish and molluscs will be set for DDT as 8, 50 and 150 μg kg^{-1}, for PCBs as 25, 150 and 450, for HCH as 1.0, 6.0 and 18. The value for HCH may be valid for the 'drins' (aldrin, dieldrin), while for HCB and heptachlor the chosen concentration categories are 0.1, 1.0 and 10.0 μg kg^{-1}. Risk will be calculated for three seafood consumption patterns: one seafood meal weekly (20 g day^{-1}), three seafood meals weekly (60 g day^{-1}) and one seafood meal (150g day^{-1}) daily. Thus owing to variations in concentrations and food consumption the risk assessment will cover 120 fold differences in exposure.

7.2.4 Risk related to acceptable daily intakes

Acceptable daily intake (ADI) denotes the dose, expressed on a body weight basis, of a substance which can be accepted over a lifetime without appreciable health risk. The starting point is usually the no observed adverse effect level (NOAEL) estimated in 90-day animal studies and extrapolated to man with some margin of safety (WHO, 1987a). The FAO/WHO recommended acceptable daily intakes converted to 70 kg body weights are: dieldrin + aldrin, 7 μg; heptachlor, 350 μg (FAO/WHO, 1971); DDT, 350 μg; HCH, 700 μg (FAO/WHO, 1979). As the 420 μg ADI for HCB had been cancelled as too high (FAO/WHO, 1979), Table XXXIII gives one tenth of the cancelled conditional ADI. Table XXXIII gives one tenth of the cancelled conditional ADI as an arbitrary value. For PCB no ADI has been proposed by FAO/WHO. The value for PCB in Table XXXIII is the tolerable daily intake based on the Yusho (Japan) incident (Kolbye, 1983).

Table XXXIII shows how the consumption of fish containing several times the average concentrations of the listed organochlorines contribute to the ADI of high fish consumers. The range is from 0.4 to 38.5%. The contribution of aldrin+dieldrin and PCB to their ADI is the highest, while the contribution of HCH and heptachlor does not reach the 1% level. As dietary studies indicate that the daily intake of aldrin and dieldrin can be as high as the ADI value (IARC, 1974), the daily consumption of one fish-meal containing 18 μg kg^{-1} 'drins' can shift intake above the acceptable level. This effect is less likely with PCB. In the more industrialized countries the daily dietary intake of PCB is usually not less than 5 μg and not more than 100 μg, and this includes fish (WHO, 1976). However irrespective of any other source of 'drins' or PCB, the daily consumption of 500 g fish containing 18 μg kg^{-1} 'drins' or 450 μg kg^{-1} PCB results in intake in excess of the relevant ADI. On the other hand 3 times a week consumption of fish with medium contamination delivers only 10-15% of the ADIs of drins and PCB.

7.3 Daily intake and the acceptable level of cancerogenic risk

Though none of the organochlorines listed in Table XXXIII have sufficient evidence for human carcinogenicity (Group 1), all have evidence of carcinogenicity in animals. The animal experimental carcinogenicity data are sufficient for DDT, HCB, HCH and PCB, and limited to aldrin, dieldrin, and heptachlor. It is widely accepted that in the absence of adequate data on humans, it is biologically plausible and prudent to regard agents for which there is sufficient evidence of carcinogenicity in experimental animals as if they

Table XXXIII

The comparison of ADI values with the daily intake of high fish consumers (150 g seafood day^{-1}).

	ADI µg 70 kg^{-1}	conc. in fish µg kg^{-1}	daily intake µg kg^{-1}	in % of ADI
aldrin + dieldrin	7	18	2.7	38.5
DDT	350	150	22.5	6.4
HCB	42	10	1.5	3.6
HCH	700	18	2.7	0.4
heptachlor	350	10	1.5	0.4
PCB	200	450	67.5	33.8

ADIs for HCB and PCB are not FAO/WHO recommendations. See text.

presented carcinogenic risk to humans (IARC, 1987). Thus though the evidence of human carcinogenicity data is limited for PCB and inadequate for DDT, HCB and HCH, these four organohalogens must be treated as potential human carcinogens. Nevertheless as animals studies on aldrin, dieldrin and heptachlor can not be interpreted as showing either the presence or absence of carcinogenicity, the following risk assessment will also include these three organochlorines.

There is a very wide gap between ADI values set by FAO/WHO and the daily intake which assures that the life-time risk attributable for a carcinogenic organochlorine does not exceed the acceptable level. According to WHO (1987b) the risk is acceptable if not more than one in every 100,000 people (10^{-5} risk) develop cancer as a result of life time exposure to a cancerogen. The choice of 10^{-5} as an acceptable or reference risk level has been based on an arbitrary or 'default' assumption.

As animal experiments are carried out with very much larger doses than would even be experienced by a human population, risk assessment based on animal experiments requires not only interspecies, but high dose to low dose extrapolation. WHO (1987b) has adapted for extrapolation the linearized multi-stage model. This model employs enough arbitrary constants to be able to fit almost any monotically increasing dose-response data, and it incorporates a procedure for estimating the largest possible linear slope (in the 95% confidence limit sense) at low extrapolated doses (Anderson, 1985). A slope of 1 mg kg^{-1} day^{-1} indicates 1:1 life-time risk (100%) at this dose level; slope below this value indicates that only a proportion of those exposed to this dose would develop cancer, while a steeper slope indicates 1:1 cancer risk at some lower dose level.

The upper bound slopes are used for the calculation of the daily intake which is equivalent with the one-sided upper bound 95% confidence limit of 10^{-5} life-time risk. The upper bound 95% confidence limit means that the true value (which is unknown) is not likely to exceed the upper bound risk and may be much lower, with the lower bound approaching zero. From the upper bound slope (B_H) (listed by Anderson, 1985) the daily intake (DI) associated with 10^{-5} cancer risk is calculated for 70 kg body weight by the equation:

$$70: \quad (B_H) \times 100{,}000 = \text{DI in mg day}^{-1}$$

and DI in mg day^{-1} multiplied by 1,000 gives the DI in µg day^{-1} for the 10^{-5} risk.

Table XXXIV shows that differences between ADIs and daily intakes associated with 10^{-5} life-time riks are in the order of 2 to 3 magnitudes. The table also shows the maximum organohalogen concentrations, which, if there were no other sources of exposure (from the atmosphere, drink, other foodtuffs), could keep intake at the acceptable risk level for low, medium and high fish consumption.

Table XXXV shows risk associated with the consumption of fish in the low, medium and high contamination categories. At present HCB, HCH and heptachlor is safe for low, and mostly safe, for medium consumption, while the intake of DDT or PCB from one fish meal per week elevates life-time risk above 10^{-5}. The quantified risk presented by aldrin and dieldrin is lower than the risk presented by DDT or PCB and higher than the risk presented by HCB, HCH and heptachlor. For aldrin, dieldrin and heptachlor the evidence of carcinogenicity is weak even in animal experiments.

Though these numbers are alarming, they must be considered in perspective. First of all, evidence of carcinogenicity in animals is not a proof of carcinogenicity in man, but based on animal experiments it is prudent to regard PCB and DDT as potential human carcinogens. In the case of PCB this view is supported by limited evidence of human carcinogenicity. Secondly every model, including the linear multi-stage model, have inherent uncertainties. It must also be emphasized that decimal points of risk estimates do not indicate precision or accuracy, but rather they help to trace the derivation of these numbers through the various extrapolation and mathematical calculations. However imprecise the linearized multistage model is, this quantification approach represents the best available scientific tool currently available to estimate risk (Anderson, 1985).

Table XXXIV

Acceptable daily intake, daily intake associated with 10^{-5} life risk and concentrations of organochlorines which present the same acceptable risk at three different fish consumption levels.

	ADI µg	upper bound slope mg kg^{-1} day^{-1}	daily intake resulting in 10^{-5} risk µg day^{-1}	concentration (µg kg^{-1}) in seafood with 10^{-1} risk		
				one meal weekly	three meal weekly	one meal daily
aldrin	7	11.44	0.0612	3.1	1.0	0.4
dieldrin	7	30.37	0.023	1.2	0.4	0.15
DDT	350	8.42	0.083	4.2	1.4	0.55
HCB	42	1.68	0.417	21	7	2.8
HCH (gamma)	700	1.33	0.526	26	9	3.5
heptachlor	350	3.37	0.208	10	3.5	1.4
PCB	200	4.43	0.158	8	2.6	1.0

ADI for aldrin + dieldrin is 7 µg. ADIs for HCB and PCB are not FAO/WHO recommended ones. See text above

Table XXXV

The association between organochlorine contamination in seafood and life-time cancer risk.

	conc. in µg kg^{-1}	cancer risk		
		one meal weekly	three meal weekly	one meal daily
aldrin	1	$<10^{-5}$	10^{-5}	2.4×10^{-5}
	6	2×10^{-5}	5.9×10^{-5}	1.5×10^{-4}
	18	5.9×10^{-5}	1.8×10^{-4}	4.4×10^{-4}
dieldrin	1	$<10^{-5}$	2.6×10^{-5}	6.5×10^{-5}
	6	5.2×10^{-5}	1.5×10^{-4}	3.9×10^{-4}
	18	1.6×10^{-4}	4.7×10^{-4}	1.2×10^{-3}
DDT	8	1.9×10^{-5}	5.8×10^{-5}	1.4×10^{-4}
	50	1.2×10^{-4}	3.6×10^{-5}	9.0×10^{-5}
	150	3.6×10^{-4}	1.1×10^{-3}	2.7×10^{-3}

Table XXXV (continued)

	conc. in $\mu g\ kg^{-1}$	cancer risk one meal weekly	three meal weekly	one meal daily
HCB	0.1	$<10^{-5}$	$<10^{-5}$	$<10^{-5}$
	1	$<10^{-5}$	$<10^{-5}$	$<10^{-5}$
	10	$<10^{-5}$	$1.4x10^{-5}$	$3.6x10^{-5}$
HCH	1	$<10^{-5}$	$<10^{-5}$	$<10^{-5}$
	6	$<10^{-5}$	$<10^{-5}$	$1.7x10^{-5}$
	18	$<10^{-5}$	$2x10^{-5}$	$5.1x10^{-5}$
heptachlor	0.1	$<10^{-5}$	$<10^{-5}$	$<10^{-5}$
	1.0	$<10^{-5}$	$<10^{-5}$	$<10^{-5}$
	10.0	10^{-5}	$2.9x10^{-5}$	$7.2x10^{-5}$
PCB	25	$3.2x10^{-5}$	$9.5x10^{-5}$	$2.4x10^{-4}$
	150	$1.9x10^{-4}$	$5.6x10^{-4}$	$1.4x10^{-3}$
	450	$5.7x10^{-4}$	$1.7x10^{-3}$	$4.3x10^{-3}$

8. CONTROL MEASURES

8.1 Present national and international provisions and recommendations

DDT was the first chlorinated organic compound which, owing to its persistence, toxic potential, and ubiquity in both environment and food, was recognised as a global risk to man's ecosystem and his health. In 1972 this awareness led to a nearly complete ban on its use in many countries. The present legal provisions applying in the Mediterranean countries are shown in Table XXXVI.

At a regional level the European Economic Community took the following measures. By Council directive 76/769/EEC of 27 July 1976 the use of PCB and PCT was restricted to closed-system electrical equipment, hydraulic fluids, condensers etc. In the same year a directive was issued (76/403/EEC of 6 April 1976) to regulate the disposal of these substances. This directive will soon be succeeded by a new and more detailed one which will include instructions for collection, storage, disposal, transport, labelling etc.

The policy of the Community so far has been to set limits of discharge for industrial plants. Table XXXVII indicates the limit set for certain organohalogens. Quality objectives have also been set for those countries wishing to apply this option. Table XXXVIII shows these quality objectives for the various organohalogens.

Table XXXVI

Legal provisions for organohalogens in Mediterranean countries.

Country	Provisions
Algeria	Total ban on PCB, DDT and lindane
Cyprus	Control use of pesticides, ban on use of aldrin/dieldrin, DDT, chlordane and PCB. Lindane used only as wood preservative. DDT in fish should not exceed 5 mg kg^{-1}
Egypt	*
France	EEC directives apply. Control on production. Ban use of drins, DDT, HCH, HCB, toxaphene and DBCP in agriculture
Greece	EEC directives apply
Israel	Industrial effluent standard of 0.02 mg l^{-1} for sewage systems
Italy	EEC directives apply. Indicative figure for PCB in fish of 5 mg kg^{-1}. Effluent standard of 0.05 mg l^{-1} for organohalogen pesticides
Lebanon	*
Libya	Control on import and manufacture of all organohalogens
Malta	PCBs, PCTs and chlorinated pesticides are not manufactured and their importation and use is prohibited
Monaco	EEC directives apply
Morocco	*
Spain	EEC directives apply
Syria	*
Tunisia	*
Turkey	*
Yugoslavia	EQC for all organohalogens varying from 0.001-0.1 mg l^{-1} depending on the category of water. For seafood, PCB 3 mg kg^{-1}, DDT 1.0 mg kg^{-1}, HCH (alpha, beta, gamma) 0.1 mg kg^{-1}, HCH(gamma) 0.5 mg kg^{-1} (pesticides on a fat wt basis).

* No information supplied

Table XXXVII

EEC limits set for industrial discharges
(mg l^{-1}, monthly averages).

Industrial sector	Limit	Date of application	Directive
1) Production of HCH	2	1.10.88	84/491/EEC
2) Extraction of lindane	2	"	"
3) Production of HCH and extraction of lindane	2	"	"
4) Production of CCl_4	1.5	1.1.88	86/280/EEC
5) Production of chloromethanes	1.5	1.1.88	"
6) Production of CFCs	No limit	set	
7) Production of DDT	0.7	1.1.88	"
	0.2	1.1.91	"
8) Production of PCP	1	1.1.88	"
9) Production of drins	2	1.1.89	88/347/EEC
10) HCB production and processing	1	1.1.90	"

Table XXXVIII

EEC quality objectives for certain organohalogens.

Compound	Quality objectives
HCH (total)	20 ng l^{-1} in territorial waters close to discharge points. 100 ng l^{-1} in inland surface waters affected by discharges
CCl_4	12 µg l^{-1} in all types of waters
DDT	10 µg l^{-1} for pp DDT and 25 µg l^{-1} for total DDT applies from 1.1.88 for all types of waters
PCP	2 µg l^{-1} from 1.1.88 for all types of waters
Drins	30 ng l^{-1} for all with a maximum of 5 ng for endrin
HCB	0.03 µg l^{-1} from 1.1.90 for all waters

Note: The phrase "The concentration of (organohalogen) in sediments and/or molluscs and/or shellfish and/or fish must not increase significantly with time" accompanies the objectives.

Other organizations have also taken a keen interest in the reduction of organohalogen emission into the marine environment. In 1983 the Fifth Meeting of the Paris Commission (1984) decided to encourage the Contracting Parties to retrofill PCB-containing transformers with substitues and to accelerate the phasing out of PCB in heat transmitting fluids. The Eight Meeting of the Paris Commission (1986) agreed to phase out the existing use of PCBs and PCTs (polychlorinated terphenyls). The Helsinki (Baltic Marine Environment Protection) Commission (1982) recommended to prohibit the introduction of new articles and equipments containing PCB, to reduce discharges from existing sources of PCBs, to identify diffuse sources of PCBs, to introduce national regulations for both the safe handling and the destruction of PCBs, to ban the production and marketing of DDT and its derivatives, to take measures for the prevention of their accidental introduction to the Baltic Sea Area and finally to monitor DDT in sediments and organisms. Later the Helsinki Commission recommended more stringent restrictions on the emission of PCBs and PCTs (1985) and in 1988 recommended the reduction of organochlorine discharge from the pulp and paper industry (1988).

8.2 Scientific rationale for establishing common control measures in the Mediterranean region

The scientific rationale for control depends on whether (i) the levels actually being encountered in a particular environment are close to those which are likely to prove harmful to the ecosystem or are human health hazards; or (ii) if inputs remain unchecked harmful levels will be reached.

The data included in this review is somewhat inhomogenous and of variable quality. However, for DDT, HCH and PCBs there are probably sufficient data to establish, with some measure of reliability, whether the ecological balance in the Mediterranean, or even in any individual species, is likely to be at risk. The available data suggests that only PCBs on marine mammals and birds and DDT on particularly sensitive species of crustacea may be harmful at the highest concentrations reported. However this view may be untenable if further studies does not confirm the presence of these high concentrations or require extension if research will establish that organochlorines have an additive or even synergistic effect on marine organisms.

The assessment of risk to human health must consider that organochlorines in seafood are only one part of the total exposure. If the daily intake from other sources is near to the hazardous level, organochlorines in seafood products may elevate daily intake above the tolerable level. Moreover most of the organochlorines in seafood are carcinogenic. As it is assumed that cancer initiating agents have no threshold dose and their effects is irreversible and additive, it is possible that the combination of several carcinogens in seafood is more carcinogenic than the most potent one alone. However the concentration of some organohalogen carcinogen in marine food is so high that fish consumption alone, without any additional intake and a single carcinogen without any additive effect, can increase the life-time risk of cancer above the acceptable level. PCB and DDT are the two

organochlorines which have such an influence on cancer risk. They increase the cancer risk even in the lower range of concentrations observed in Mediterranean fish and not only the risk of high, but also that of low fish (one meal per week) consumers.

The prospect for both the viability of the ecosystem and the human health depends not only on the present situation, but on trends, which can not be established without monitoring. The maritime organizations' interest in the reduction of organochlorine pollution is reflected by the investigations of monitoring programmes. The Annex 12 of the Twelve Annual Report of the Oslo Commission (1987) describes a base line study in which 16 countries participated. Besides metals, the base line study covered organochlorine compounds in cod, plaice, flounder, dab and blue mussels. The annual meetings of the Joint Monitoring Group of the Oslo and Paris Commissions reported studies on DDT, PCB, or other organochlorines in fish from Swedish (1984), U.K. (1984), FRG (1985) and Danish (1988) coastal waters. The present report is also a demonstration of this interest, while the problem of carcinogenic risk to man is underlined by the publication of 'Levels of Carcinogens in the Marine Biota' by the Library and Information Services of the Marine Biological Association of the United Kingdom (1988).

The second scientific rationale concerns the efficiency of control measures. Though input into the sea derives from local sources and from atmospheric precipitation, the highest organochlorine tissue residues are found in organisms from high direct input areas and the lowest from areas remote from direct input. The concentrations or organochlorine pesticides and PCBs were highest in striped mullet (Mullus barbatus) near the main sewage outfall in the Saronikos Gulf, and decreased with distance (Table X). The concentrations of organochlorines (e.g. lindane) in sediments were also the highest near the mouth of rivers (such as the Rhône, Po, Danube and Ebro) draining major agricultural and near to important agricultural areas of northern Italy, Sicily and northern Africa (section 5.2.2). Thus any restriction on direct input must have a significant effect on local pollution levels.

The infuence of input on the pollution of nearby waters is also shown by the effects of bans or restrictions on the use of organochlorines. The ban on the use of hexachlorobenzene and hexachlorocyclohexane in Japan did not influence concentrations in the open ocean surrounding Japan, but decreased levels in the coastal marine environment (GESAMP WG.26, 1988). Similarly from 1962 to 1982 the ban on DDT resulted in a 90% and restrictions on the use of PCB a 50% decline in concentrations of the respective chemicals in fish from the Baltic Sea and in Kattegat (Olson and Reutergard, 1984). The ban on the production and restrictions imposed on the use of PCB in North America resulted in a decline in PCB levels in seals from the Canadian east and west coast. The ban on the use on DDT had the same effect on DDT concentrations in seals from the east coast, but the effect on west coast seals was neutralised by the increased use of DDT in South-East Asia (GESAMP WG.26, 1988). This later example demonstrates the need for concerted regulatory policy.

8.3 Requirement for control and reduction of organochlorine pollution

Information is available on levels of a few, though important, organochlorine compounds in the Mediterranean Sea area. Though only the highest observed level of DDT and PCB may affect the most sensitive species, both the concentrations of PCB and DDT are sufficently high to increase the cancer risk of all consumers who eat at least one fish meal per week, while the life-time risk of those who eat one fish meal daily from the high pollution stock is increased by PCB and DDT from one in the 100,000 to 2-4 in 1,000. The cancer risk from aldrin and dieldrin is not only lower but questionable, while the level HCB, HCH and heptachlor can increase the risk only in extreme circumstances. Thus, based on presently available information, there is a need to control and reduce the input of DDT and PCB, and keep other organochlorines monitored.

(a) Thus monitoring programmes, which are able to follow trends in pollution, must be actively encouraged.

(b) Since 1970 the use of DDT in many countries has been either banned or severly restricted. Thus the United States eliminated the use of DDT for shade trees, tobacco, domestic applications, and for the aquatic environments, marshes, etc., except where specifically authorised by public health officers for vector control. A similar restriction by all Mediterranean countries would significantly decrease DDT input into the marine environment.

(c) The EEC, the Paris Commission and the Helsinki Commission made steps for the elimination of PCB and PCT (polychlorinated terphenyls) from transformers, large and small capacitors, heat-transmitting fluids, hydraulic mining equipment, as intermediates in synthesis processes, and in tooling compounds during the manufacture of jet engine turbine blades, semi conductors and optical equipment. The first steps are:

(i) to prohibit the use of PCB and PCT in any new equipment;

(ii) to promote the policy of retrofilling PCB-containing transformers with substitutes;

(iii) to ensure good management of existing PCB-filled units, retrofilling operations and the disposal of all PCB-containing fluids and equipments, e.g. transformer cores which may be contaminated with PCBs;

(iv) to establish national programmes to find out and define diffuse sources of PCB and PCT discharges.

(d) Specific control measures can be proposed, based on the Directives of EEC which limit the discharge of organochlorines from industrial plants. Discharge is restricted to a limit value for each tonne produced (or treated) and to a limit value for concentration in effluents.

(e) The environmentally sound use of pesticides ought to be encouraged in order to prevent run-off to water by protection zones between application and bodies of water. Application of pesticides by aircraft should be strictly controlled.

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