Bull. Environm. Contam. Toxicol. 26, 496-501 (1981)

Monitoring of DDT, PCBs, and Other Organochlorine Compounds in Marine Organisms from the North Aegean Sea

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It is well established that human activities have resulted in serious environmental changes, especially in the coastal marine environment. Organochlorine insecticides and polychlorinated biphenyls are among the most persistent and toxic pollutants in aquatic and terrestrial ecosystems. The organochlorine insecticides can enter into the marine ecosystem, mainly, from the atmosphere. However,there is frequently a relationship between the presence of some specific insecticides and local pollution sources such as agricultural or municipal wastes. On the other hand, PCBs are related to industrial pollution. The distribution of these micropollutants has been extensively studied in the last decade, and considerable efforts have been made to understand the mechanisms of their transport through the biotic community. While the level of organochlorine residues in any organisms is a static index of a dynamic process, it identifies the presence and relative amounts of particular compounds (KERR & VASS 1973).

A comparison of residues level in predator and prey organisms in such an environment could establish present day background level typical of unpolluted coastal marine waters and indicate those animals most susceptible to accumulation through food chain transfer.

This paper describes the monitoring of organochlorine compounds in several biota species of coastal waters of North Aegean Sea.

MATERIALS AND METHODS

Areas studied: The Aegean Sea, especially its northern part, being a semi-enclosed formation and relatively shallow and fairly small water body, belongs to those marine ecosystems whose coastal waters offer a suitable location for investigations into the fate of organochlorine compounds.

The survey of DDT, PCBs and other organochlorine in marine organisms covered the whole of the north coast of the Aegean Sea, and sampling stations were located in the three important, industrial and agricultural, areas. The areas covered correspond to an anomalous coastline, formed by the deltas of the six main rivers namely Aliakmon, Loudias, Axios, Gallikos, Strymon and Nestos. These rivers flowing in the N.Aegean Sea, are the main sources of pesticides and PCBs contamination of the N.Greece coast. From this area three main gulfs were selected for study: The Thermaikos (40° 30'N-21° 50'E), the Strymonikos (40° 50'N-23° 60'E) and the Kavala gulf (40° 55'N - 24° 24'E) (Fig. 1).

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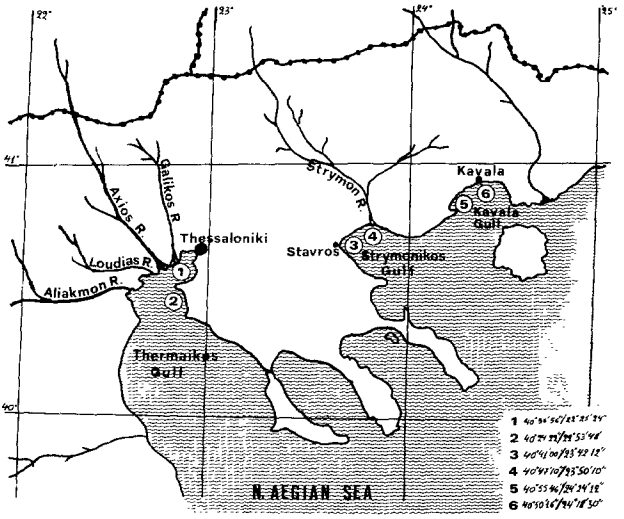

Fig. 1. Map of N.Aegean Sea.

The Thermaikos gulf rèceives the wastes of the city of Thessaloniki, industrial wastes (west coast) and agricultural wastes (east coast). The west coast is not suitable for swimming. The Strymonikos gulf receives mainly agricultural wastes, while the gulf of Kavala receives the wastes of the city of Kavala and agricultural wastes.

Sampling: To investigate the pollution of marine organisms a total of 142 samples (fish and shellfish) were collected from the above mentioned areas.

Sampling started in Sept. 1975 and continued through Dec. 1979. To monitor organochlorine insecticides (HCB, HCH and its metabolites, all DDT's, aldrin, dieldrin, heptachlor and heptachlor epoxide) and PCBs we started by collecting *Mytilus galloprovincialis*, *Mullus barbatus*, *Xiphias gladius*, *Thunnus thynnus* and *Merluccius merluccius*. *M.galloprovincialis* samples from six sampling stations indicated on the enclosed map (Fig. 1), while the samples of fish caught in the three above mentioned gulfs. The Kind and the number of samples are summarised in table 1.

Table 1. Sampling Stations and Number of Samples

FISH AND SHELLFISH	SAMPLING STATIONS			T O T A L
	THERMAIKOS gulf	STRYMONIKOS gulf	KAVALA gulf	(N.AEGEAN SEA)
M.galloprovincialis	39	18	39	96
M.barbatus	12	13	9	34
T.thynnus	2	1	1	4
X.gladius	2	-	-	2
M.merluccius	2	2	2	6
T O T A L	57	34	51	142

All organisms were placed in glass jars and held at -20°C until analysed. Containers were prerinsed with hexane and acetone and similarly rinsed aluminium foil was used to line caps to prevent contamination.

Handling samples and analytical techniques: Samples were treated with sodium sulfate and then Soxhlet-extracted, using petroleum ether, bp 40-60°C. The extractable organic organic matter was treated by the JOHNSON's (1965), and JENSEN et al (1973) methods.

In analyzing fish and shellfish for organochlorine insecticides and PCBs, chromatographic meyhods were used. A gas-chromatograph with a ^{63}Ni detector was used. The column was a coiled pyrex glass of 2 m (id, 2 mm), packed with 15% QF-1 and 10% DC-200 on 80-100 mesh Chromosorb W. Operation conditions were as follows:
a) Temperatures: Detector and injector 300°C; Column 210°C,
b) Flow rate of nitrogen: 14 mℓ/min.

All determinations were conducted in duplicate, and mean values were calculated.

RESULTS AND DISCUSSION

The mean analytical results for organochlorine residues in five species of fish and shellfish studied are presented in Tables 2 and 3, along with the necessary suplementary information. Those results are presented as concentration on a wet weight basis.

Table 2. Organochlorinesin *Mytilus galloprovincialis* (M.G.) and *Mullus barbatus* (M.B.) (ppb wet weight).

Compound	THERMAIKOS GULF		STRYMONIKOS GULF		KAVALA GULF	
	(M.G.)	(M.B.)	(M.G.)	(M.B.)	(M.G.)	(M.B.)
	(40 sampl.)	(12 sampl.)	(20 sampl.)	(12 sampl.)	(36 sampl.)	(10 sampl.)
DDE	6 (100)*	30 (100)*	8 (100)*	31 (100)*	14 (100)*	57 (100)*
DDD	4 (89)	9 (83)	7 (95)	11 (92)	9 (86)	26 (90)
DDT	5 (80)	12 (83)	6 (90)	12 (92)	11 (92)	33 (90)
Total DDT	14	51	22	54	33	120
Aldrin	0.5 (17)	Ø	0.7 (85)	Ø	3 (38)	Ø
HCB	1 (47)	1 (77)	2 (20)	3 (67)	0.6 (42)	3 (80)
PCBs	340 (100)	230 (100)	261 (100)	1600 (100)	290 (100)	180 (100)

* Positiveness per cent.

Table 3. Organochlorinesin Marine Organisms from N.Aegean Sea (ppb wet weight).

Compound	*Mytilus galloprovincialis* (96 samples)	*Mullus barbatus* (34 samples)	*Merluccius merluccius* (6 samples)	*Xiphias gladius* (2 samples)	*Thunnus thynnus* (4 samples)
DDT	9	38	18	190	600
DDD	6	15	10	46	320
DDT	8	19	16	210	320
Total DDT	23	71	43	450	1200
HCB	0.9	4	2	2	37
Aldrin	1	Ø	Ø	Ø	Ø
PCBs	310	700	510	360	2600

Three DDT related compound (pp'-DDE, pp'-DDT and pp'-DDD) were present in sufficient quantities for reliable determination. No peak corresponding to op'-DDT, dieldrin or heptachlor was observed in any samples. In the case of aldrin in fish, all samples had concentra-

tion lower than the detection limit (0.01 ng). Also, peaks attributable to PCBs, some of which have a column retention time similar to that of pp'-DDD and pp'-DDT (ADDISON et al. 1972), were absent.

All samples analyzed contained PCBs and DDE. PCB residues are found as ubiquitous contaminants of aquatic life (PEAKALL 1975) and DDE is, under reducing conditions, the most persistent metabolite of the previously widely used insecticide DDT. Usually DDE represents between 60 and 90% of the total DDT (DDT plus all DDT metabolites) (KAISER 1977). This is in agreement with our data from the tables 2 and 3. Residues of pp'-DDE present in all organisms examined ranged in concentrations from 1 ppb, wet weight, in *M.galloprovincialis* to over 1,000 ppb in samples from *T.thynnus*. On the other hand, residues of pp'-DDT were not found in every sample and when present, concentrations were usually equal to or less than those of pp'-DDE (Tables 2 and 3).

As can be seen from the results of Table 2, no significant difference was found in the distribution of total organochlorines in the organisms investigated (*M.galloprovincialis*, *M.barbatus*), except of PCBs of *M.barbatus* from the Strymonikos gulf. This high concentration of PCBs is attributed not only to local sources of pollution but to the inflow effect of the Strymon river.

The means of total organochlorines were higher in *T.thynnus* than in *X.gladius*, *M.merluccius* and *M.barbatus* (Fig. 2). This may be par-

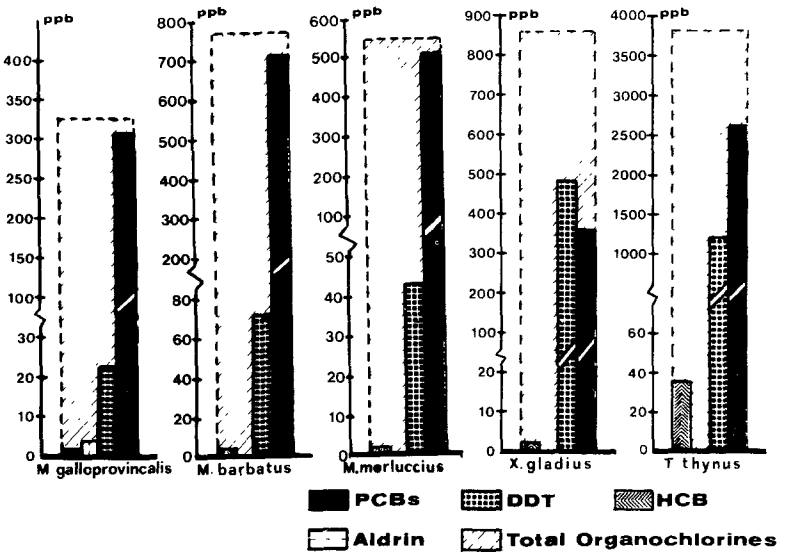

Fig. 2. Concentration of Organochlorine Compounds in examined marine organisms. (ppb wet weight).

tly due to differences in their body chemistry and location in the food chain. Data from diverse geographic locations do indicate, however, a relative uniformity in total DDT residue levels in widely separated marine habitats (FOWLER et al. 1978, BALKAS et al. 1978, NAZANSKY et al. 1978). What has been established from the data di-

scussed here, however, is that a minimum level of contamination may exist, which can be considered a background level, in all marine food chains.

From the results obtained (Table 2) it can be observed that the N.Aegean Sea is characterized by high value of PCBs (340 ppb wet weight in *M.galloprovincialis*), while the value of total DDT in the same organisms is low (14 ppb wet weight).

Generally, local urban and industrial wastes seem to be the main sources of the pollution in the areas investigated.

M.galloprovincialis samples show significant differences of organochlorine pesticides and PCBs, during the period of investigation (Table 4). The concentration of PCBs in *M.galloprovincialis* increased in the last year of investigation (1979), two times more than the first two year-period (1975-76). In Fig. 3 it is possible to see that, how the concentration of pesticides and PCB in *M.galloprovincialis* varied annually.

Table 4. Annual Variations in the Level of Organochlorine Compounds in *Mytilus galloprovincialis* (ppb wet weight).

Compound	1975-76 (40 samples)	1977 (10 samples)	1978 (23 samples)	1979 (23 samples)
DDE	9	9	11	9
DDD	3	9	11	6
DDT	8	4	8	10
Total DDT	20	22	30	25
HCB	Ø	2	2	2
Aldrin	3	Ø	Ø	0.8
PCBs	270	350	340	580

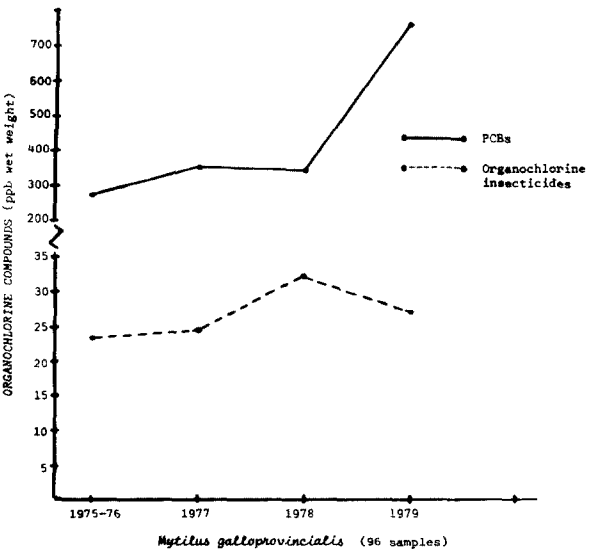

Fig. 3. Annual variation of Organochlorine Compounds in *M.galloprovincialis*.

There are few results reported for the organochlorine residues in *M.galloprovincialis* and *M.barbatus* from the Mediterranean. The total DDT values reported from Saronikos Bay, from France and from the Adriatic Sea vary between 3 and 120 ppb for *M.galloprovincialis* and between 8 and 140 for *M.barbatus*, while PCBs concentration varied from 300 to 9,800 ppb (SATSMADJIS & GABRIELIDES 1977, MESTRES 1978, NAZANSKY et al. 1978, DUJMOV 1978).

Finally, marine organisms from the heigher trophic level (e.g. *T.thynnus*) were found more contaminated than those from lower (e.g. *M.galloprovincialis*) levels.

It can be thus concluded that an understanding of organochlorine pollutants, as regards their types and concentrations, depends on background information on the compounds consumed, their tendency for biomagnification or biodegradation and, perhaps, seasonal variations.

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