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DDT, DDE, and PCB Residues in Fish, Crustaceans and Sediments from the Eastern Mediterranean Coast of Turkey

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Residues of DDE, DDT and PCBs were determined in four different commercial bony fishes: grey mullet, red mullet, striped mullet and gold bandgoat fish, as well as in shrimps, limpets and sediments obtained from the eastern Mediterranean coast of Turkey. The PCB levels in living organisms and sediments were found to be very low, and in most cases below the detection limits. The DDE and DDT values were relatively high compared to PCBs and there was a linear correlation between the organochlorine residue concentrations and the extractable organic material of the analysed samples.

To date a considerable amount of effort has been spent in the determination of the levels of organochlorine residues in organisms, sea water and sediments of the Mediterranean (IAEA, 1976). However, very little work has been done in the eastern Mediterranean, especially on the Turkish coast (Balkas *et al.*, 1978).

In the present work organochlorine residues, i.e. chlorinated pesticides and polychlorinated biphenyls, present in marine organisms caught on the eastern Mediterranean coast of Turkey, as well as sediment samples obtained nearby, have been investigated. The location of the samples is shown in Fig. 1. The bony fishes selected were those which have commercial value and may be found throughout the area. The species studied were, *Mugil auratus* (golden grey mullet), *Mullus barbatus* (striped mullet), *Mullus surmuletus* (red mullet) and *Upeneus mollucensis* (gold band goat fish), *Panaeus kerathurus* (shrimp) and *Patella caerulea* (limpet) were also analysed, since they have different feeding habits to bony fishes. *Patella caerulea* is a

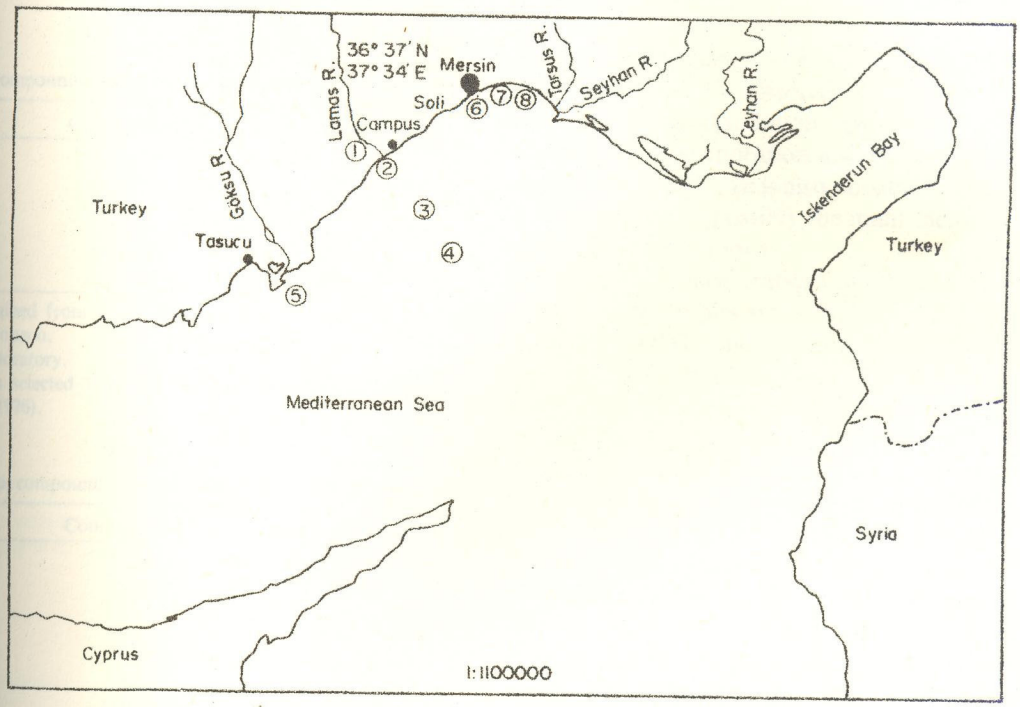

Fig. 1 Location of sampling stations on the eastern Mediterranean coast of Turkey.

filter feeder (Riedl, 1973) so it might be an indicator of the levels of organochlorine residues in sea water (Goldberg *et al.*, 1978).

Samples and Methods

The samples of fish and shrimp were caught by gill nets and identified according to the FAO identification Directory (FAO, 1973). Limpets were collected from the rocks with the aid of metal knives. Samples were rinsed with distilled water, weighed and measured then wrapped in ethanol-prewashed aluminium foil and frozen at −25°C until analysis.

Sediment samples were taken with the aid of a grab sampler and immediately transferred into ethyl alcohol prewashed glass jars and finally deep frozen until analysis.

About 10 g of the muscle tissue of the living organisms was mixed with an equal amount of anhydrous Na_2SO_4 and soxhlet extracted with 75 ml of hexane which had been distilled over NaOH in an all-Pyrex 1 m fractional distillation column. After at least 20 cycles of extraction, half of the aliquot was used for EOM (extractable organic material) determinations. The other half of the extract was cleaned as described elsewhere (Holden & Marsden, 1969), its volume reduced to 1 ml and eluted with 45 ml of hexane from an aluminium column. In order to separate PCBs and DDTs a further elution from a silica column (Snyder & Reinert, 1971) was necessary.

The homogenized wet sediment samples were divided into four portions. One of the portions was dried in an oven to determine the dry weight. The second portion was extracted on a shaker with 3 × 100 ml of methanol–benzene mixture (50:50 by volume). The combined extracts were partitioned with hexane. Half of the hexane fraction was used for the determination of per cent EOM and the other half cleaned and eluted over alumina and silica columns as described for the organisms. Mean time blank experiments were also carried out and background correction for the residues was made.

Sediment extracts containing sulphur were treated with metallic Cu prior to GC analysis in order to remove sulphur.

The volumes of both eluates from living organisms and sediment were reduced to 1 and 2 ml, and 1 μl aliquots were injected to GC. A Varian Model 2700 gas chromatogram equipped with a ^{63}Ni electron capture detector was used during GLC analysis. The separation was achieved by a 3 m (2 mm i.d.) coiled glass column filled with 1.5% OV17 and 2% OV 210 on Varaport 30 (80–100 mesh). The injection port, column and detector temperatures were 250, 225 and 275°C, respectively. Nitrogen flowing at 20 ml min^{-1} was the carrier gas.

Identification of PCBs was achieved by matching the standard Aroclor (supplied by International Laboratory Inc., USA) peaks with the unknowns. The quantification was based on five major peaks of Aroclor 1254. The pesticide peaks were compared with the standards. Whenever necessary, i.e. especially in the case of intercalibration samples, where the PCB peaks in the chromatograms were dominant, dehydrochlorination with alcoholic KOH and oxidation with acidic Cr_2O_3 were performed as confirmatory tests for DDTs.

Our laboratory is also participating in the intercalibration exercise organized by the International Laboratory of Marine Radioactivity (IAEA), Monaco. Tables 1 and 2 consists of analysis results obtained from the analysis of the Mediterranean sediment and fish homogenate supplied by IAEA during the intercalibration. The extraction, clean up and analysis procedure for the intercalibration were exactly the same as applied to the analysis of fish and sediment samples. As can be seen from Table 1 and Table 2 there is no systematic difference in the DDT and PCB concentrations reported by our laboratory and average values given by IAEA (IAEA, 1976).

TABLE 1

Organochlorine compound concentrations in Mediterranean sediment.[a]

Residue	Concentration[b]	ng g^{-1} dry weight[c]
α-BHC	1.8	0.1
β-BHC	0.2	0.7
pp'-DDE	1.9	2.7 ± 0.7
pp'-DDD	9.2	7 ± 4
pp'-DDT	16.1	13 ± 5.3
PCB-1260	208.6	180 ± 39

[a]Sample was obtained from the International Laboratory of Marine Radioactivity, Monaco.
[b]Results of this laboratory.
[c]Results of seven selected laboratories from IAEA intercalibration exercise (IAEA, 1976).

TABLE 2

Organochlorine compound concentrations in fish homogenate.[a]

Residue	Concentration[b]	ng g^{-1} dry weight[c]
α-BHC	7.8	16.0 ± 7.4
β-BHC	37.7	41.3 ± 17.4
Aldrin	11.1	17.2 ± 4.1
pp'-DDE	56.4	296.0 ± 214.0
pp'-DDD	30.7	293.0 ± 227.0
pp'-DDT	40.0	370.0 ± 270.0
PCB-1254	1645.0	3220.0 ± 2830

[a]Sample obtained from the International Laboratory of Marine Radioactivity, Monaco.
[b]Results of this laboratory.
[c]Overall average values reported by the participating laboratories (Laboratories reporting < values have been excluded) (IAEA, 1978).

Results and Discussion

The results obtained from the analysis of marine biota are given in Table 3. As can be seen from this table, there was no appreciable amount of PCB in any of the species analysed, except *Patella caerulea* which showed up to 39 ng g^{-1} (fresh weight) of PCB concentration. Table 4 consists of the results obtained from sediment analysis. Again in sediments as in biota, the PCB levels were low. This observation is consistent with the results reported by Elder & Villeneuve (1977). They observed a decreasing trend in the PCB concentration from the western towards the eastern Mediterranean. Harvey *et al.* (1974a) and Bidelman & Olney (1974) explained low dissolved PCB values in the Sargasso Sea by a co-distillation process. In the eastern Mediterranean evaporation also exceeds precipitation and co-distillation of PCBs is also possible in this area. The lack of local sources is possibly the main factor accounting for low PCB concentrations.

The *t*-DDT concentrations in all analysed marine biota and sediment samples are EOM dependent. With increasing EOM, the *t*-DDT concentration increases. When, using the 'least square method' the mean *t*-DDT values given in Table 3 for different species were plotted against % EOM, a straight line (Fig. 2) with a linear correlation coefficient of 0.83 and a standard error ± 1.1 was obtained. In the case of sediment samples too, with the exception of the result from Station No. 8, *t*-DDT vs % EOM gave a straight line (Fig. 3). The linear correlation coefficient in this case was 0.97 and the standard error ± 0.25. The sampling point No. 8 was very close to an industrial area where agrichemical, petrochemical and some other complexes are located. This might be a reason for the relatively high *t*-DDT concentrations with respect to % EOM.

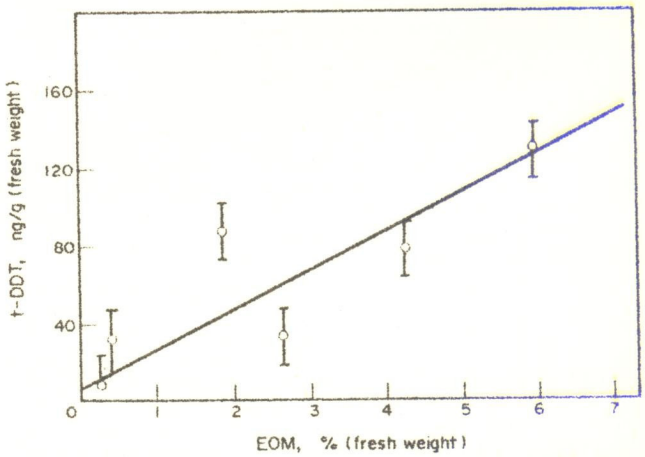

Fig. 2 *t*-DDT in living organisms as a function of % EOM. Curve fitting has been done by using 'least-square method'.

TABLE 3

Organochlorine concentrations in the living organisms.

Species analysed	No. of individuals analysed	% EOM[a]	Organochlorine residue (ng g^{-1} F.W.)			
				t-DDE[d]	*t*-DDT	*t*-PCB[b]
Mugil auratus (golden grey mullet)	20	1.8	min	5	8	T[c]
			max.	173	324	10
			mean	48	89	–
Mullus barbatus (striped mullet)	26	6.0	min.	2	9	T
			max.	122	257	2
			mean	62	130	–
Mullus surmuletus (red mullet)	6	2.6	min.	7	20	–
			max.	35	49	T
			mean	21	34	–
Upeneus mollucensis (gold band goat fish)	30	4.3	min.	31	49	T
			max.	69	94	T
			mean	47	74	–
Parapaneus kerathurus (shrimp)	25	0.4	min.	3	4	T
			max.	61	65	T
			mean	28	34	T
Patella caerulea (limpet)	42	0.3	min.	1	2	2
			max.	4	7	39
			mean	2	5	15

[a]% extractable organic material, based on fresh weight of the living organism.
[b]The PCB calculations were based on Aroclor 1254.
[c]Trace indicates less than 2 ng g^{-1}.
[d]*t*-DDE is the sum of *op*- and *pp*-DDE.

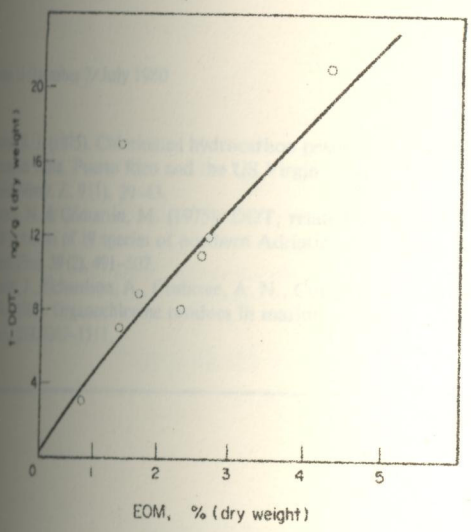

Fig. 3 *t*-DDT in sediment samples as a function of % EOM. Curve fitting has been done by using 'least-square method'.

TABLE 4

Organochlorine concentrations in the sediments.

Sampling point[a]	% EOM[b]	Organochlorine concentration (ng g^{-1} dry weight)		
		t-DDE[d]	*t*-DDT	*t*-PCB
1	4.3	5	21	T[c]
2	2.3	4	8	T
3	1.7	3	9	2
4	1.4	3	7	T
5	0.8	2	3	T
6	2.6	8	11	T
7	2.7	3	12	3
8	1.4	4	17	4

[a] For the sampling points refer to Fig. 1.
[b] Based on the dry weight of the sediments.
[c] Trace indicates less than 2 ng g^{-1}.
[d] *t*-DDE is the sum of *op*- and *pp*-DDE.

The *t*-DDT concentrations observed in *Mugil auratus* in the eastern Mediterranean are comparable with those reported from the North Adriatic. Picer *et al.* (1978) and Bodante & Gilmartin (1975), reported *t*-DDT values of between 28 and 409 ng g^{-1}.

Mullus barbatus, *Mullus surmuletus* and *Upeneus moluccensis* form the family Mullidae. Satsmadjis & Gabrielides (1977, 1979) reported *t*-DDT concentrations of between 9 and 390 ng g^{-1} in *Mullus barbatus* caught from Saranicos Bay, Greece. On the other hand, Reimold (1975) analysed striped mullet from the coast of Puerto Rico and the US Virgin Islands and reported only PCBs but no DDT. The *t*-DDT concentrations from Saranicos Bay are fairly close to the results given in Table 3. Harvey *et al.* (1974b) observed lower *t*-DDT concentrations in shrimps from the Georges Bank (Atlantic Ocean) than we have observed in shrimps from the Eastern Mediterranean; while Giam *et al.* (1972) reported *t*-DDT concentrations about 10 times higher still in the Caribbean Sea. The only available data about *Patella caerulea* (limpet) was reported by Robinson *et al.* (1967) from the Northumberland coast, who showed them to contain about one third of the *t*-DDT found in this work. At this stage it is too early to say anything about the indicator character of *Patella caerulea*; further research is necessary. The *t*-DDT concentrations in the sediment samples given in Table 4 are in the same range as those reported from Southern Greece (Dexter & Pavlou, 1973). In a sequence of deep sea sediments, from 10°N to 43°N in the North Atlantic, due to degradation of DDTs, only PCBs have been observed (Harvey & Steinhauer, 1976).

From the above comparisons, it is readily seen that the *t*-DDT content of living organisms and sediment samples from the eastern Mediterranean coast of Turkey were not much different from those obtained from other parts of the Mediterranean basin. However, in general the *t*-DDT concentrations are higher than those reported from the Atlantic Ocean. On the other hand, PCB concentrations are much lower than those obtained from the Mediterranean Sea and the North Atlantic Ocean.

In all samples, except the sediment sample from Station No. 8 the main constituents of the *t*-DDT was *pp'*-DDE. In the living organisms and in sediments *pp'*-DDE formed about 50% and 30% or more of the total *t*-DDT, respectively. This difference was probably due to metabolic degradation of *pp'*-DDT into *pp'*-DDE (Plimmer *et al.*, 1968).

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