Trace Metals and Organochlorine Residue Content of Mullidae Family Fishes and Sediments in the Vicinity of Erdemli (Icel), Turkey

by

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Abstract

The organochlorine residue content of three members of the mullidae family, i.e., *Mullus barbatus, Mullus surmuletus* and *Upenus moluccensis* caught in the vicinity of Erdemli has been investigated with the aid of gas chromatography. Some trace metals such as Hg, Cu, Cd, Zn, and Pb in the same species have also been investigated with atomic absorption spectrometry. Sediment samples of the area were analysed and their organochlorine residue and trace metal contents determinated.

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Introduction

It is now well established that man's activities in recent years have resulted in serious environmental changes, especially in the coastal marine environment. Among the major pollutants recognized to have important environmental effects are the chlorinated hydrocarbons, i.e., DDT and its derivatives and PCB's and heavy metals, particularly mercury.

Perhaps an area which has suffered more than any other is the Mediterranean Sea. This essentially closed sea is bounded by many nations, some of whom are highly industrially developed. The Mediterranean basin receives annually large inputs of sewage, industrial wastes and agriculture run-off (OSTERBERG & KECKES, 1977). In addition, petroleum contamination is a serious problem.

Recognizing this pollution threat, the states bordering the Mediterranean in 1975 agreed to initiate a program to clean up the marine environment. A first step was the initiation of a series of pilot projects to monitor and determine the baseline levels of major pollutants and distribution in biological organisms.

Sediment analysis is also important because sediments can play an important role in the distribution of toxic substances in the marine environment. The concentrations of these substances in the water can be regulated by adsorption and desorption processes and by the sediment-water interface (PIERCE *et al.*, 1974, PRESLEY *et al.*, 1972).

In view of the above-mentioned factors, a monitoring program of organochlorine residues, including aldrin, dieldrin, heptachlor, heptachlor epoxide, all isomers of BHC, all DDT's and PCB's, and heavy metals, including Hg, Cd, Cu, Zn and Pb in marine samples was carried out in the region near Erdemli, Turkey.

IV^me Journées Étud. Pollutions, pp. 159-163, Antalya, C.I.E.S.M. (1978).

Materials and methods

Reagents : Care was taken to use only extremely pure reagents throughout.

Sampling : Fish samples taken by deep trawl or gill net were placed in plastic bags (for metal analysis) or wrapped in aluminium foil (for analysis of organochlorine residues) and frozen at -40°C. Sediment samples collected with a grab sampler were stored in plastic bags (for metals) or glass containers (for chlorinated hydrocarbons). Samples for organochlorine residue and mercury analysis were frozen wet ; the others were dried at 110°C after rinsing with distilled, deionized water and ground to a powder which was passed through a 70 mesh (0.2 mm) mesh sieve.

Digestion and Extraction of Samples

a. Heavy metals - Fish muscle tissue, circa 1 g, was digested by 3 ml HNO_3 in PRFE-lined closed vessels and diluted with distilled, deionized water. 0.05 g dried sediment was digested by 3 ml HNO_3-$HC1O_4$-HF (1:1:1: ratio). For analysis of mercury content, between 0.05 and 0.3 g wet sediment was digested by 2 to 5 ml HNO_3 for 9 hours.

b. Organochlorine residues - Fish muscle tissue was digested by a mixture of perchloric and acetic acids (1:1 V/V). For 1 g sample 3 ml of cold acid mixture was used. The digested samples were diluted with doubly distilled water and extracted with 4 x 25 ml of hexane. The combined extract was dried over andhydrous Na_2SO_4, the volume reduced to an appropriate volume, and H_2SO_4 cleanup (MURPHY, 1972) applied. Sediment samples were extracted with methanol-benzene mixture (10:90 V/V), then acetonitrile partitioning performed and the residues extracted into the hexane fraction. Samples containing high sulfer were sulfer were subjected to Cu treatment (HARVEY & STEINHAUER, 1976). Dehydrochlorisation and/or oxidation confirmatory tests (PAM, 1976) were applied to bothe fish and sediment extracts.

Analysis Techniques : All metal analyses were performed by atomic absoption spectrometry. Mercury was analyzed by the cold-vapor method. Zinc in fish and all metals in sediment were analyzed using flame atomization. Cd, Cu, and Pb in fish required the use of flameless atomization (carbon rod) and background correction.

Organochlorine residue analysis was perfomed by GLC with ECD detector (Ni-63 source). The separation column was a coiled pyrex glass of 10 ft lenght (i.d. 2 mm) packed with 1.5 % OV 17 - 2% OV - 110 on Chromasorb W (80-100 mesh).

Results and discussion

a. Trace Metals

The average analytical results and ranges for Hg, Cd, Cu, Zn and Pb in the three species of fish studied and sediments are presented in Table I along with the necessary suplementary information. In the case of lead in fish, all samples had concentrations less than the detection limit of the carbon rod flameless technique used (0.1 ug/g).

A comparison of the values obtained in this work with those from other Mediterranean regions is difficult because of the lack of published data (ROTH & HORNUNG, 1975 ; STOEPPLER *et al.* 1977). In general the mercury values obtained are lower than those from other regions. For the other metals studied, only a comparison with data from the Israel coast (ROTH & HORNUNG, 1977) is possible. Again our values are lower in all cases, with the exception of zinc in *Mullus barbatus*. The lead content of the Israel samples was 5-10 times the amount in the Erdemli samples.

A limited amount of data on heavy metals in sediments from other Mediterranean regions (ROTH & HORNUNG, 1975 ; GRIMANIS, *et al,* 1977 ; STIRN, *et al.*, 1974 ; PAUL & MEISCHNER, 1976 ; RENZONI, *et al.*, 1973 ; ROBERTSON, *et al.*, 1972) allows a comparison with the present values to be made. In the case of mercury it can be concluded that the level of mercury in the Erdemli sediment is low. This may be considered as the background level in the region since there is no industrial activity in the area. This conclusion is reinforced by the observations of similarly low mercury levels in other nearby coastal sediments and high values (about 10 times higher) in sediments taken from Mersin harbour, a busy port and industrial area.

For the other metals studied the results obtained in the present work are approximately in the same range as those from other regions, despite different geological characteristics, with the exception of the data from the Israel coast which are consistently lower.

TABLE I. Heavy Metals in Mullidae Family and Sediment (μg/g wet weight).

	Mullus barbatus	*Mullus surmuletus*	*Upenus moluccensis*	Sediment
Fork length (mm)	146-190	125-255	117-169	—
Fresh/Dry	4.25	4.02	4.46	—
Hg	0.04	0.04	0.22	0.03
Cd	0.03	(0.01-0.06)	0.02	—
Cu	0.48	0.54	0.4	31.0
Zn	4.5	4.0	2.5	65.0
Pb	0.1	0.1	0.1	57.1

b. Organochlorine Residues

A total of 20 *Mullus barbatus*, 6 *Mullus surmuletus* and 16 *Upenus moluccensis* samples were individually analyzed for organochlorine residues. The average results together with the results obtained from sediment analysis are given in Table II. The average standard deviations were 16%, 30%, 11%, 9%, 12 % and 21 % for Lindane, aldrin, DDE, DDD, DDT and PCB's, respectively. These deviations varied between 1 and 30%, depending on the concentration.

The extractable organic matter (E.O.M.), determined with the aid of soxhlet extraction of the samples with hexane, was found to be 9.3% for *Mullus barbatus*, 6.7% for *Upenus moluccensis* and 4.3% for *Mullus surmuletus*. As can be seen from Table II, the total t-DDT showed the same trend with E.O.M., 136.4 ppb in *Mullus barbatus*, 89.2 ppb in *Upenus moluccensis* and 33.8 ppb in *Mullus surmuletus*. The contribution of DDE, which is a metabolic product of DDT, to t-DDT is at least 50%. The other chlorinated hydrocarbons such as PCB's, aldrin, dieldrin, BHC, heptachlor and heptachlor epoxide, in all fish samples were in minute concentrations.

There are few results reported for the organochlorine residues in *Mullus barbatus* obtained from the Mediterranean. The t-DDT values reported from Saranikos Bay, in Greece, (SATSMADJIS & GABRIELIDES, 1977) and from France (MESTRES, 1978) are in between 8 and 138 ppb, while PCB concentrations varied from 30 to 9770 ppb.

Due to the lack of reported data for organochlorine residues in *Mullus surmuletus* and *Upenus moluccensis*, the results are compared with the same species E.O.M. ALZIEU (1976) reported t-DDT twice that of *Mullus surmuletus*. The t-DDT content of the fish samples from the North Adriatic (REVELANTE & GILMARTIN, 1975) is much higher than that of *Upenus moluccensis*.

Although residue content of the sediment samples, are qualitatively the same as fish samples, the concentrations are lower. The t-DDT values in the sediment reported from the North Adriatic (SALIHOGLU *et al.*, 1977) are on the average twice the values of this work.

TABLE II. Organochlorine Residues in *Mullus Barbatus*, *Upenus moluccensis*, *Mullus surmuletus* and sediments (ppb wet weight).

	Mullus barbatus	*Upenus moluccensis*	*Mullus surmuletus*	Sediment
Fork length (mm)	125-230	120-143	120-208	—
wet wt.	4.6	4.2	4.5	—
dry wt.	9.3	6.7	4.3	1.0
% E.O.M.	1.8	1.2	1.0	ND
BHC	1.0	1.1	1.0	0.8
Aldrin	1.0	T	T	ND
Dieldrin	ND	ND	ND	ND
Heptachlor	1.7	1.0	ND	ND
Hept. Epoxide	1.2	2.0	T	0.5
PCB	4.5	2.4	1.4	0.6
op-DDE	64.2	48.7	15.5	2.1
pp-DDE	2.0	2.6	T	4.6
op-DDD	23.1	26.5	7.4	4.1
pp-DDD	1.3	2.1	1.7	ND
op-DDT	47.9	6.9	7.8	51
pp-DDT	136.4	89.2	33.8	13.6
DDT				

ND : Not detectable.
T : Trace.

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