Distribution of Trace Elements and Chlorinated Hydrocarbons in *Mugil auratus* (Grey Mullet)*

by

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Abstract

Analyses are reported for *Mugil auratus* caught between 1978 and 1980 in the Cilician Basin, northeastern Mediterranean. The concentration of trace metals (Hg, Zn, Cu, Cr, Ni, Pb, Cd and Fe) and of chlorinated hydrocarbons (DDT, DDD, DDE, Aldrin and PCBs) are presented as a function of age, sex and size of fish. The concentrations of heavy metals are lower than those reported by workers in other regions of the Medirranean. Zn concentrations show an unusual increase or decrease with increase in the size of fish depending on the season, which has been interpreted in terms of physiological changes.

Concentrations of PCBs have generally been below the limits of detection. Concentrations of other chlorinated hydrocarbons are generally similar to those reported for fish in the Adriatic. The main constituent of total DDT was found to be DDE, which is a metabolite of DDT.

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Introduction

Most Mediterranean countries have agreed to a programme coordinated by FAO/UNEP, for monitoring pollutants present in their coastal areas. Such pollutants include the heavy metals Hg, Cd, Zn, Pb, etc.; chlorinated hydrocarbons, especially chlorinated pesticides DDT, endrin, lindane, etc.; and polychlorinated biphenyls. According to the programme the species of Mediterranean fish which must be analysed as indicators of pollution include *Mytil* sp., *Mullus barbatus, Parapenaeus longirostris, Carcinus mediterraneus* and *Thunnus thynnus thynnus* (FAO/UNEP, 1977). The mugilidae family has been cited as an alternative to *Mullus barbatus*, while *Mugil auratus*, a member of the mugilidae family, has also been studied extensively since in addition to being commercially valuable, it survives and lives in waters having a wide range in hydrographic parameters.

In this paper, results of heavy metal analysis and organochlorine residues found in *Mugil auratus* caught during 1978-1980 in the north-eastern Mediterranean are presented. The fish were inhabitants of the Cilician basin, which is bounded by the Toros mountains of Turkey in the north and the Kyrenia range of Cyprus in the south. The fertile coastal areas support well established agriculture and also include a busy harbour (Mersin) and agrichemical, petrochemical and textile complexes

* Communication présentée par le modérateur de la séance.

V^es^ *Journées Étud. Pollutions*, pp. 235-242, Cagliari, C.I.E.S.M. (1980).

TABLE I

Analysis of Trace Metals and Organochlorine Residues in Fish Homogenate Intercalibration Exercise Coordinated by IAEA Monaco Laboratories

Fish tissue homogenate MA-A-2				Fish fillet homogenate MAM-2			
Element	This work (μg/g dry weight)	Overall average* (μg/g dry weight)	Trials	Organochlorine residue	This work (ng/g dry weight)	Overall average* (ng/g dry weight)	Trials
Cr	1.7	2.9 ± 0.6	25	α-BHC	18	21 ± 11	6
Mn	1.24	1.0 ± 0.1	28	β-BHC	64	—	—
Fe	50 ± 2	61 ± 4	35	γ-BHC	43	51 ± 23	7
Ni	1.0	1.2 ± 0.2	18	Aldrin	16	9 ± 5	5
Cu	6.5 ± 0.2	4.6 ± 0.4	44	pp-DDE	149	330 ± 230	10
Zn	32 ± 1	36 ± 3	53	pp-DDD	52	350 ± 290	9
Cd	0.05 ± 0.01	0.16 ± 0.04	27	pp-DDT	374	360 ± 240	9
Hg	0.49	0.48 ± 0.02	37	Aroclor 1254	1900	3460 ± 2420	8
Pb	0.45	0.7 ± 0.2	24				

* The values are the overall average of the results reported to IAEA Monaco Lab. and does not necessarily reflect the true concentrations in the samples ; ± indicates the standard deviation.

Materials and methods

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

Sampling : The samples were collected by gill net, and placed in plastic bags (for metal analysis) or wrapped in aluminium foil (for analysis of organochlorine residue analysis) and frozen at − 20° C.

Digestion, Extraction and Analysis of Samples.

a. *Heavy metals :* Approximately 1 g of fish muscle tissue was digested with concentrated HNO_3 in the high pressure decomposition vessels according to the procedure given in FAO Technical Paper No. 158 (FAO/UNEP, 1976). The digested samples were then analysed by atomic absorption spectrophotometry.

Mercury analyses were performed by a cold-vapour technique using a system of our own design. Flame measurements were made with the usual air-acetylene flame using standard techniques. Flameless measurements were carried out with the Varian CRA-90 carbon rod atomizer.

b. ***Organochlorine residues :*** About 5 g of fish muscle tissue was ground with unhydrous Na_2SO_4, and soxhlet extracted with 50 ml of hexane for at least 24 cycles. Half of the extract was used for % EOM determinations. The volume of the other half was reduced to 2 ml under reduced pressure at 30° C. The concentrated extract was eluted from a 1 g alumina column (deactivated with 2.5 % water) by hexane and its volume reduced to 1 ml by a nitrogen stream. 2.5 μ 1 was injected into a GC. Whenever necessary, KOH-alcohol de-hydrochlorination and Cr_2O_3-acid oxidation confirmatory tests were applied.

Analysis was performed by GLC with an ECD detector (Ni-63 source). The 6 ft separation column was of coiled pyrex glass (2 mm id), packed with 5 % DC — 200 absorbed on Varaport 30 (100-120 mesh).

The lowest detection limit of the method was 1 ng for total PCBs and 2 ng for DDTs.

Intercalibration

The validity of both heavy metal and organochlorine residue analyses presented in the next section were justified by the results obtained on the intercalibration samples supplied by the IAEA, Monaco Laboratories. The procedures adopted here have results within the range of the averages obtained by other laboratories as is shown in Table I.

Results and Discussion

Organochlorine residues and heavy metal analyses together with biological data of *Mugil auratus* are given in Tables II and III. Fig. 1 and 2 show the results of t-DDT and Zn analyses in more detail. The average trace metal and organochlorine residue analyses together with their standard deviations are given in Table IV. In this table, results obtained from other parts of the Mediterranean are also included.

TABLE II

Organochlorine Residues (ng/g wet weight) for individual *Mugil auratus*

Catch date	Standard length (mm)	Total weight (g)	DDE	t-DDT (ng/g wet weight)	Aldrin
31. 7.78	167	75	7	27	1
29. 9.78	155	62	7	21	2
29. 9.78	200	125	21	36	1
29. 9.78	356	488	45	72	—
29. 9.78	210	140	18	28	1
28.10.78	250	175	23	32	2
29.11.78	210	93	3	5	1
29.11.78	200	85	7	10	2
29.11.78	215	94	9	15	—
29.11.78	195	77	2	3	1
29.11.78	210	105	22	35	1
30.11.78	360	576	2	3	1
30.11.78	345	485	19	42	1
3. 2.79	375	625	26	75	—
3. 2.79	335	449	24	26	2
3. 2.79	270	213	19	36	2
3. 2.79	310	364	16	17	1

TABLE III

Trace metal concentrations (μg/kg wet weight) for individual *Mugil auratus*

Date of catch	Fork length (mm)	Total weight (g)	Hg	Zn	Cu	Ni	Cr	Fe	Mn	Pb	Cd
13. 7.78	370	706	20	-	-	-	-	-	-	-	-
" "	195	84	10	-	-	-	-	-	-	-	-
14. 7.78	300	335	120	-	-	-	-	-	-	-	-
" "	340	507	10	-	-	-	-	-	-	-	-
19. 4.78	150	30	20	-	-	-	-	-	-	-	-
" "	149	35	40	-	-	-	-	-	-	-	-
" "	163	42	20	-	-	-	-	-	-	-	-
" "	165	47	30	-	-	-	-	-	-	-	-
" "	198	89	20	-	-	-	-	-	-	-	-
" "	215	117	30	-	-	-	-	-	-	-	-
20. 7.78	340	507	-	3100	480	540	850	5800	840	790	<10
19. 4.78	215	117	-	5200	610	210	70	5700	160	540	<10
" "	198	89	-	3700	380	100	70	2300	580	170	<10
" "	165	47	-	3700	310	60	40	3300	400	<100	60
" "	163	42	-	4800	410	230	270	2800	180	<100	<10
" "	150	30	-	6000	290	230	70	4300	180	<100	<10
" "	149	35	-	4500	410	340	70	2400	740	<100	<10
28.10.78	300	314	22	3580	420	-	10	5300	-	-	-
" "	325	425	13	3300	420	-	35	4800	-	-	-
" "	380	696	17	4600	440 (1200)	-	39	2400	-	-	-
" "	280	269	26	2700	400	-	12	1400	-	-	-
" "	250	174	18	5200	440	-	12	4200	-	-	-
29.11.78	220	104	27	3100	410	-	33	4500	-	-	-
" "	215	94	16	2900	400	-	115	6000	-	-	-
" "	195	77	22	2800	400	-	30	3400	-	-	-
30.11.78	345	484	27	5900	820	-	-	8200	-	-	-
" "	360	576	25	4600	660	-	-	7200	-	-	-
3. 2.79	335	449	23	5000	820	-	-	12600	-	-	-
30.11.78	395	655	29	4400	-	-	-	6700	-	-	-
2. 2.79	270	213	17	3700	-	-	-	4700	-	-	-
" "	375	625	22	3800	-	-	-	4700	-	-	-
" "	310	364	19	4000	540	-	-	3400	-	-	-
" "	275	263	40	4500	660	-	-	5200	-	-	-
17. 5.79	160	42	33	6500	290	-	-	2900	-	-	-
" "	152	32	54	7800	1850	-	-	3500	-	-	-
" "	188	76	44	6700	460	-	-	3200	-	-	-
" "	207	107	17	5200	680	-	-	3400	-	-	-
" "	170	52	42	5700	-	-	-	2000	-	-	-
" "	152	40	23	8200	460	-	-	2800	-	-	-
7. 2.79	240	168	12	4100	-	-	-	3000	-	-	-
18. 9.79	250	179	16	4300	-	-	-	4100	-	-	-
" "	205	94	20	4100	-	-	-	2800	-	-	-
" "	182	69	19	3900	-	-	-	2500	-	-	-
" "	137	25	19	5500	-	-	-	4600	-	-	-
" "	140	26	22	6100	1060	-	-	4000	-	-	-
" "	242	155	9	4500	620	-	-	4100	-	-	-
" "	185	69	16	4100	560	-	-	4700	-	-	-
5. 6.80	350	407	20	3800	-	-	-	1800	-	-	-
" "	305	315	18	2300	-	-	-	400	-	-	-
" "	360	416	14	5000	-	-	-	3100	-	-	-

TABLE IV

Trace Metal Concentrations (μg/g wet weight) & Organochlorine Residues (ng/g wet weight) for *Mugil auratus*

	Fresh wt (g)	Length (mm)	Hg (ppb[b])	Zn	Cu	Cr	Ni	Fe	Mn	Pb	Cd
This work [a]	30 149	696 395	27 ± 17 (42)[c]	4.3 ± 1.3 (40)	0.50 ± 0.18 (18)	0.12 ± 0.21 (15)	0.24 ± 0.15 (7)	4.4 ± 2.0 (38)	0.44 ± 0.26 (7)	0.1 ± 0.79 (7)	0.01 ± 0.06 (7)
Aegean [d] coast of Turkey	—	—	124—383	17.8—37.9	5.1 9	5.3—8.2	—	7.3—25.5	5.2—8.1	12.5—17.9	1.4—2.8
Gulf of [e] Trieste	—	—	27—104	8.5 9.7	0.78 0.88	—	—	6.8—8.7	0.36—0.59	0.67—0.68	0.16—0.17
Adriatic [f]	—	—	260 M[g] 80—1000	450 M 50—10000	65 M 270—1250	—	—	—	—	950 50—2100	—
			Aldrin	DDE	t-DDT	PCB					
This work	175 62	375 625	2 ± 1 (17)	15.5 ± 11 (17)	28 ± 20 (17)	Not detectable					

(a) : $\frac{\text{wet wt.}}{\text{dry wt.}} = 4.56$ (32) **(b)** : Hg values (ppb, dry wt.) **(c)** : No. in parenthesis shows the numbers of individuals analysed

(d) : UYSAL (1979) **(e)** : MAJORI *et al.*, (1979) **(f)** : BERNHARD (1978) **(g)** : mean

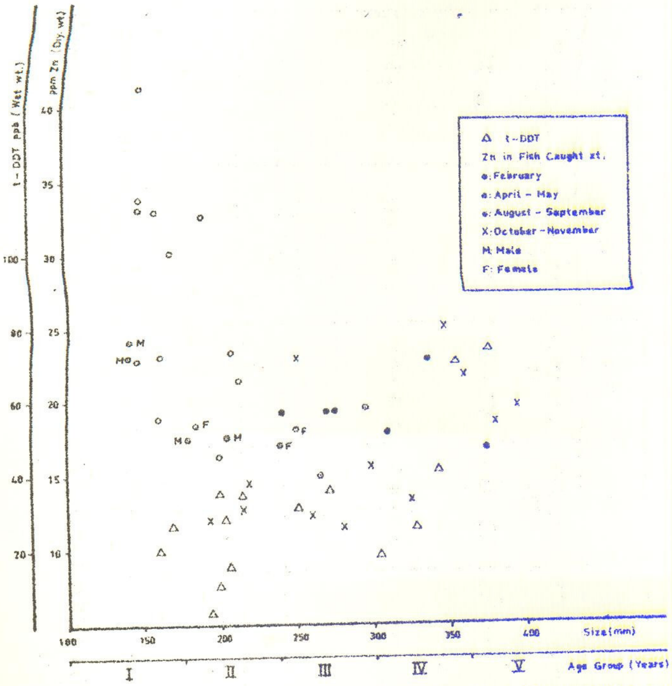

Figure 1. Total DDT ppb (wet weight) and Zinc ppm (dry weight) concentrations as a function of age and fork length of *Mugil auratus*

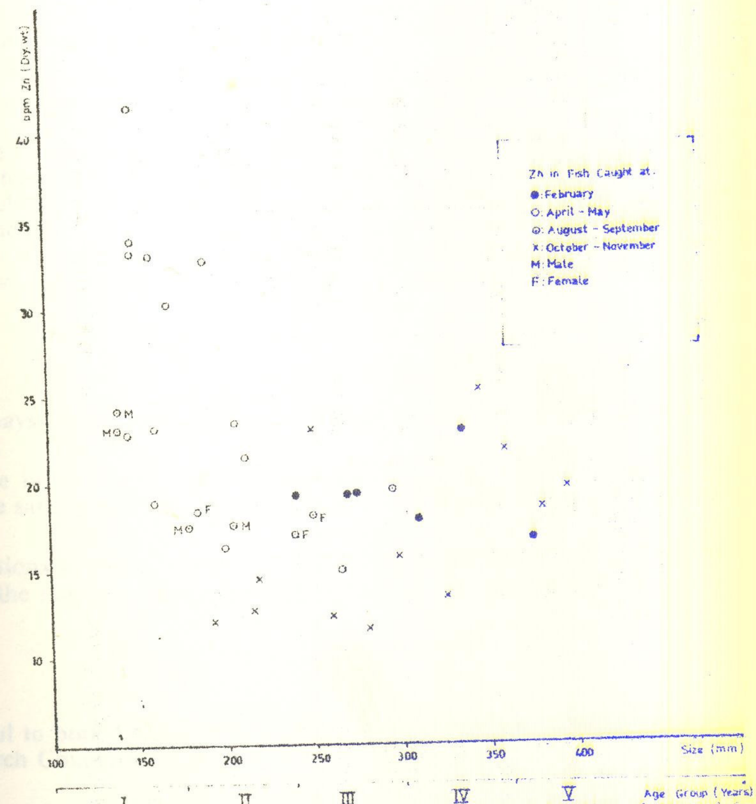

Figure 2. Zinc (ppm, dry weight) concentration as a function of age and fork length of *Mugil auratus*

Results of PCB analyses are not shown in table II or Fig. 1 since the concentrations of PCB were insignificant in all sample examined. PCBs are not used extensively in the area studied. This observation is also consistent with the results reported by ELDER & VILLENEUVE (1977) who observed a decrease in PCB concentrations from the western towards the eastern Mediterranean. It has been shown that in those areas where evaporation exceeds precipitation, as is the case in the eastern Mediterranean, co-distillation of PCBs results in their rapid removal from the water column (HARVEY *et al.*, 1974; BIDELMAN & OLNEY, 1974). This provides another reason for the absence of PCBs in the analysed samples. The total DDT concentrations obtained in this work are comparable with those reported from the north Adriatic. PICER *et al.* (1978) and REVELANTE & GILMARTIN (1975) reported total DDT values between 28 and 409 ng/g fresh weight. As with PCBs, co-distillation of DDTs from the sea at the temperatures prevailing in the north eastern Mediterranean implies that DDTs remain in the water column for less than a day. In each of the 17 samples studied 50-70 % of the t-DDTs consisted of pp'DDE, a metabolite of pp'DDT. Metabolism of DDT in plankton is known to take some years although on land, especially in the presence of Al or basic minerals, it may be a more rapid process (FREAR, 1955). Thus the evidence of our analyses is that the DDT found in *Mugil auratus* had been recycled between the sea, air and land very many times before its ingestion.

As can be seen from Table III and IV, the concentrations of Cr and Ni found in the fish were very low. These results are suprising, since the concentrations of the metals in the sediment from the sampling sites were comparatively high (330-560 ppm Ni, 530-595 ppm Cr dry OZKAN, 1978). This is a reminder that *Mugil auratus* does not become polluted merely because it lives among a significant concentration of pollutants, but the pollutant has to be actively taken in by and subsequently discharged from the organism.

The Hg values obtained here are of the same order of magnitude as those found in the Atlantic (STERNER & NICKLESS, 1975) and in Australian water (BEBBINGTON *et al.* 1977) but less than Hg concentrations found in the other parts of the Mediterranean (UYSAL, 1979; MAJORI, 1979; BERNHARD, 1978). At the moment, Hg concentrations in the north eastern Mediterranean could be used as a reference level against which values from other parts of the Mediterranean could be compared. However, there has been an increase of phenyl Hg due to agriculture in the coastal region and Hg concentrations must continue to be monitored carefully. Possibly due to the relatively high temperatures observed on the north eastern Mediterranean, concentrations of Hg compounds in the atmosphere may be higher than their concentrations in *Mugil auratus* would indicate.

The Zn, Cu and Cd values presented in Table IV are lower than those reported from the Gulf of Trieste but Zn and Cu values appear to be higher than those found near the Adriatic coast, although the latter coast is generally thought to be rather polluted (HELMER, 1978). Our Zn values are shown in Fig. 2. Although there is considerable scatter, the figure suggests that Zn levels are highest in the youngest fish. There may be a tendency, yet to be confirmed, for Zn concentrations in fish caught in October and November to be correlated with the age and size of the fish. These variations may indicate a connection between Zn uptake and physiology and feeding habitat of the fish. *Mugil auratus* reach sexual maturity at about two years old and they spawn in November and December (BINGEL, 1980). The implication that Zn concentrations may be high in the roe and newly spawned fish needs to be tested.

Conclusions

Laboratory assays of intercalibration samples have produced results in good agreement with those of other laboratories.

No PCBs have been found in *Mugil auratus* caught in the north eastern Mediterranean during 1978-1980. During the same period the levels of t-DDT and its residues were comparable with those found by other workers.

The concentrations of heavy metals, including Hg found in *Mugil auratus* during 1978-1979, were significantly lower in the northeast than elsewhere in the Mediterranean region.

Acknowledgement

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