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SEASONAL VARIATION OF MERCURY CONCENTRATIONS IN ORGANISMS OF THE CILICIAN BASIN

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Total mercury concentrations in organisms typical of those found in the Cilician Basin of the northeastern Mediterranean have been measured from 1977 to the present. These concentrations show seasonal variations. Shrimp shows an approximately constant concentration of mercury which might testify to the regulation capacity of shrimp for mercury. Crab, and particular fish, show a seasonal variation which may be correlated with the local application of mercury fungicide, rainfall, and the physiology of the organisms. The rapidity with which mercury applied to the land causes increased concentrations in fish is noteworthy.

Introduction

Many investigations of mercury concentrations in the world oceans (Bernhard and Zettera, 1976) and in the Mediterranean (Bernhard, 1978) have been reported. Tuncel *et al.* (1980) recently showed that concentrations in the sea, in sediment, and in organisms were much lower in the northeastern part than elsewhere in the Mediterranean, although in the northeast Cilician Basin, phenylmercuric chloride, phenylmercuric acetate, methoxymercuric chloride, methoxyethylmercuric chloride, and methoxyethylmercuric silicate are widely used as fungicides (GTHB, 1979). Application usually starts in the middle of January and ceases by the end of June, but this does not necessarily mean that fungicides are not used throughout the whole year. We now extend the work of Tuncel *et al.* (1980) by describing mercury concentrations in a variety of marine organisms, namely, shrimp (*Penaeus kerathurus*), blue crab (*Portunus pelagicus*), grey mullet (*Mugil auratus*), and red mullet (*Mullus surmuletus*), which have been sampled from the Cilician Basin. These species were selected since all have high commercial value and secondly crab, shrimp, and red mullet have been cited as obligatory species to be monitored during the UNEP/MED POL projects (UNEP,1975). Grey mullet is cited as an alternative to red mullet. Frequency of sampling permitted seasonal variations in mercury concentrations to be observed. One has consequently been able to formulate an hypothesis concerning mechanisms of mercury pollution. The potency of mercury in the marine environment and its position on the FAO/UNEP "black list" of the Mediterranean pollutants emphasise the importance of this metal. Excepting bivalves (Goldberg *et al.*,1978), we know of little previous work in which seasonal variations in mercury concentrations were observed.

Materials and Methods

Reagents: Care was taken to use only extremely pure reagents, and before usage, every reagent was checked for purity by running blank experiments.

Sampling: Samples were collected either by net or deep trawl, and immediately taken to the laboratory, identified according to the FAO identification catalogue (FAO,1973), measured, and weighed. They were then placed in plastic bags, marked, and frozen at −30 °C.

Digestion and analysis of samples: Approximately 1 g of fish muscle and/or edible tissue of shrimp and crab was digested with concentrated HNO_3 in high pressure

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Table 1. Intercalibration exercise results of mercury analysis in four different samples (Hg in ng/g dry weight).

Sample	This work	Overall average[a]
Oyster homogenate	0.26 ± 0.01	0.32 ± 0.06
Sea plant	0.362 ± 0.009	0.5 ± 0.2
Copepod	0.27 ± 0.02	0.4 ± 0.2
Fish flesh	0.49	0.48 ± 0.02

[a]Gives the preliminary averages of the results reported by 60 laboratories, but does not indicate "probable concentrations" of trace metals in these samples.

decomposition vessels according to the procedure given in FAO Technical Paper No. 158 (FAO,1976). The digested samples were then analysed by atomic absorption spectroscopy. The details of the method have been given by Tuncel *et al.* (1980).

The validity of the mercury residue analyses presented in the next section were justified by the results obtained on the intercalibration samples supplied by the IAEA, Monoco Laboratories. The procedures adopted here gave results within the range of averages obtained by other laboratories as shown in Table 1.

Results

Table 2 consists of the minimum, maximum, and mean values of the standard lengths of the organisms and the total mercury values together with their standard deviations. Figures 1–4 show the monthly concentrations of mercury found in the organisms; shrimp, red mullet, crab, and grey mullet, respectively. Results are shown on both a wet and a dry weight basis and where lengths are shown on the graphs they represent the standard deviations of the results.

The dry weight values of mercury were obtained by multiplying the fresh weight mercury values by the fresh weight to dry weight ratio of each individual.

Table 2. Minimum, maximum, and mean values of both standard length and mercury concentrations of the analysed species.

Name of specie	Catch date	No. of specimens analysed	Standard length (mm)			Mercury concentration ng/g fresh weight		
			Min.	Max.	Mean	Min.	Max.	Mean
Shrimp[a]	Nov. 78	5	120	225	179	33	104	77 ± 26
(*Penaeus*	Jan. 79	1	–	–	140	–	–	25
kerathurus)	Feb. 79	1	–	–	135	–	–	37
	June 79	1	–	–	140	–	–	14
	Sept. 79	4	95	155	125	17	48	26 ± 13
	Oct. 79	5	110	140	130	10	40	28 ± 11
	Nov. 79	3	130	195	154	24	40	32 ± 8
	Jan. 80	3	130	170	153	12	22	18 ± 5
	Feb. 80	1	–	–	150	–	–	53
	March 80	3	165	175	168	15	38	30 ± 10
Red mullet[b]	Aug. 77	3	98	125	107	16	41	24 ± 12
(*Mullus*	March 78	2	181	192	–	34	78	56
surmuletus)	Feb. 79	4	115	185	138	25	58	40 ± 12
	March 79	4	115	165	140	30	44	37 ± 2
	May 79	3	160	205	183	43	76	56 ± 14
	Aug. 79	4	105	115	110	15	39	27 ± 11
	Sept. 79	5	110	150	134	22	51	36 ± 12
	March 80	5	120	160	133	83	167	131 ± 33
	May 80	6	85	160	125	50	80	66 ± 12
Crab[c]	Nov. 78	5	380	530	460	56	73	64 ± 6
(*Portunus*	April 79	1	–	–	275	–	–	50
pelagicus)	May 79	3	290	440	380	33	170	122 ± 63
	June 79	2	34	36	–	131	269	200 ± 69
	Aug. 79	1	–	–	–	–	–	69
	Sept. 79	4	270	500	405	3–	82	57 ± 31
	Oct. 79	3	120	143	–	32	95	59 ± 8
	March 80	1	–	–	29	–	–	62
Grey mullet[b]	Oct. 78	5	250	380	307	13	26	19 ± 4
(*Mugil*	Nov. 78	6	195	395	288	16	29	24 ± 4
auratus)	Feb. 79	6	240	375	301	12	40	22 ± 9
	May 79	6	152	20–	172	17	54	36 ± 13
	Sept. 79	7	137	250	192	9	22	17 ± 4

[a]Total length. [b]Fork length. [c]Interclaw distance.

Discussion

Whereas the mercury concentrations shown in Fig. 1 (shrimp, *Penaeus keratherus*) show no secular variation since 1978, since 1979 all the other figures consist of a "background" mercury concentration (especially in the summer–autumn months) on which is superimposed a more or less Gaussian maximum leaving its peak in the spring. The inevitable difference in mercury concentration from one orgamism to another results in the averages shown in the figures being associated with rather large standard deviations and, although an analysis of variance shows that the spring levels are indeed higher than the autumn levels, one would wish for further results in future years to confirm the analysis. Nevertheless, one finds that the seasonal variations are interpretable and the interpretation gives insight into the mechanism of pollution in the marine environment. Bertine and Goldberg (1972) showed that mercury content in shrimp carapaces, on a dry weight body burden base, is higher than that in the edible abdomen. Shrimps moult frequently, and in some cases the carapace is changed every 4–7 days (Jerde and Lasker, 1966). On the average, the dry weight of the carapace is about 50% of the whole body. Assuming that mercury is distributed equally in the carapace and the other organs of the shrimp, by moulting the animal gets rid of half of its mercury frequently. Most probably this mechanism controls the accumulation of mercury and the apparent mercury concentrations in the organism do not necessarily reflect the concentrations of mercury in the sea water. We suggest that the constancy of mercury concentrations during the whole year is probably due to moulting.

Figure 2 shows that red mullet (*Mullus surmuletus*) usually possessed similar mercury concentrations to shrimp found in the same or nearby waters. However the concentrations of mercury in the fish caught in the spring appears to exceed concentrations in fish caught in the subsequent summer and autumn. This secular variation is shown to be insignificant by an analysis of variance, but the large standard deviations associated with each average indicates the necessity for seeking the persistence of secular variations in future years. The organic mercury analysis carried out during this work showed that a minimum of 96%, a maximum of 99.5%, and an average of 97.8% of the total mercury observed in red mullet, is in organic form. As was stated in the introductory section, various organic mercury compounds are applied as a fungicide to cotton and other vegetable and fruit plants growing on the coast to the east, north, and west of the Cilician Basin (GTHB,1979). Application starts in the new year and reaches a maximum in February and March, when rainfall is heavy.

Increasing amounts of organic mercury have been applied in successive years from 1977 to 1980 and in the spring of 1980, more precisely March 26, the rainfall was particularly heavy and parts of the coastal region

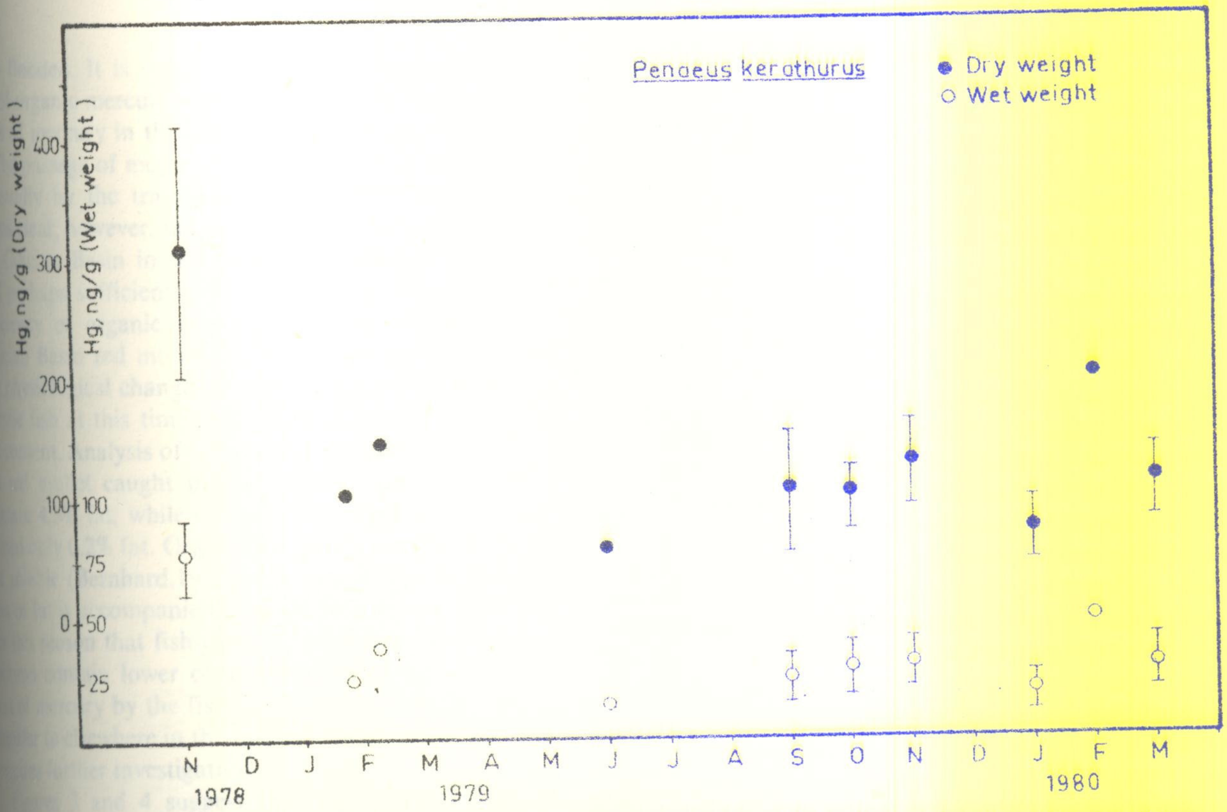

Fig. 1. Mercury concentrations, together with the standard deviations, obtained from the analyses of shrimp as a function of time.

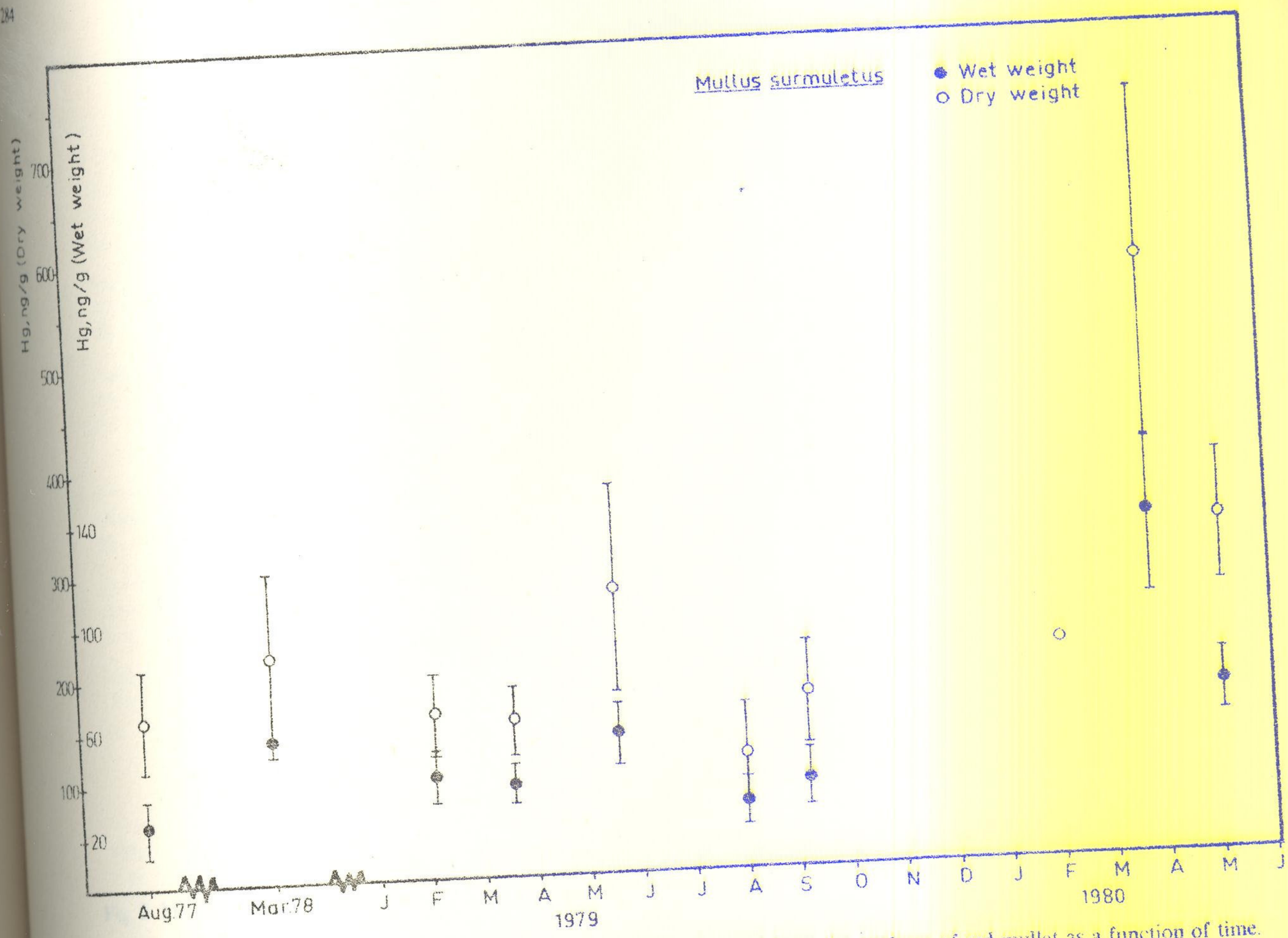

Fig. 2. Mercury concentrations, together with the standard deviations, obtained from the analyses of red mullet as a function of time.

were flooded. It is suggested that it is the agricultural use of organic mercury which causes the high concentrations of mercury in the red mullet caught in the spring.

The passage of mercury compounds from land to sea is usually by the transport of particulate material. It seems clear, however, that in the conditions prevailing in the Cilician Basin in the spring such passage is rapid, and perhaps sufficiently rapid to call into question the efficiency of organic mercury as a fungicide. In the Cilician Basin red mullet spawn in late spring. Among the physiological changes which occur in both male and female fish at this time is a pronounced decline in the fat content. Analysis of the present samples showed that six red mullet caught in March 1980 on the average contain 4.3% fat, while eleven fish caught in May contained only 0.2% fat. Organomercurials are known to be fat soluble (Bernhard,1978), and one suggests that the loss of fat is accompanied by a loss of mercury and it is for this reason that fish caught in the late summer and autumn contain lower concentrations of mercury. The loss of mercury by the fish at spawning time implies its transfer to elsewhere in the marine environment and this requires further investigation.

Figures 3 and 4 suggest that the concentration of mercury in both grey mullet (*Mugil auratus*) and blue crab (*Portunus pelagilus*) may also increase in the late spring and decline again in the subsequent autumn. That is, one would expect the phenomena to be the same as in red mullet and for the same reasons. Unfortunately, the catching of grey mullet and blue crab has occurred less regularly than for red mullet and further confirmatory work is required. One would not expect the peak concentrations of mercury in these organisms and in red mullet to coincide, since the fat concentrations of all organisms do not vary in exactly the same way. However, the results shown in Fig. 4 for the variation of mercury concentrations in blue crab throughout 1979 are of particular interest, since much secular variation, if confirmed, implies that blue crabs are still useful as monitors of mercury pollution.

Mercury concentrations observed in red mullet, grey mullet, shrimp, and crab caught from other regions of the Mediterranean and from other oceans are given in Table 3 together with the average values obtained in this work. Mercury levels in grey mullet, on the average, are within the same order of those obtained from the Israeli coast. The north Adriatic coast is considered as one of the most polluted areas in the Mediterranean (Helmer,1971) and in both the Gulf of Trieste (Major *et al.*,1979) and in the north Adriatic (Bernhard,1978) grey

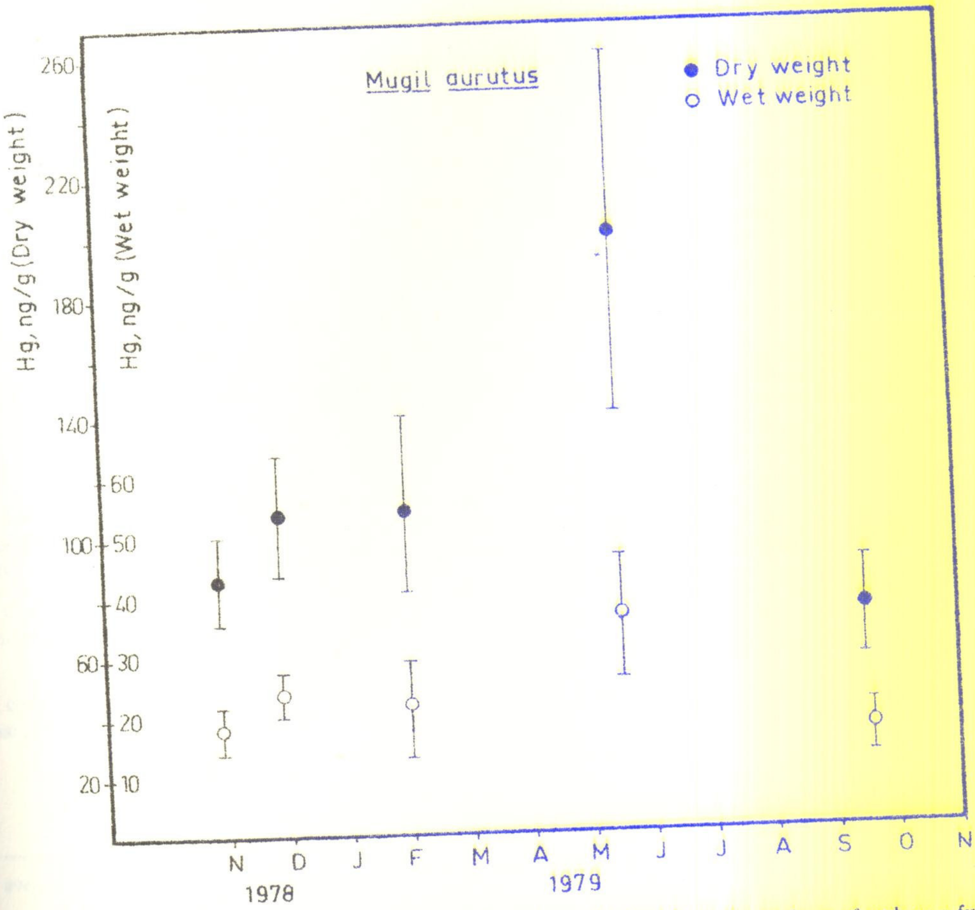

Fig. 3. Mercury concentrations, together with the standard deviations, obtained from the analyses of crab as a function of time.

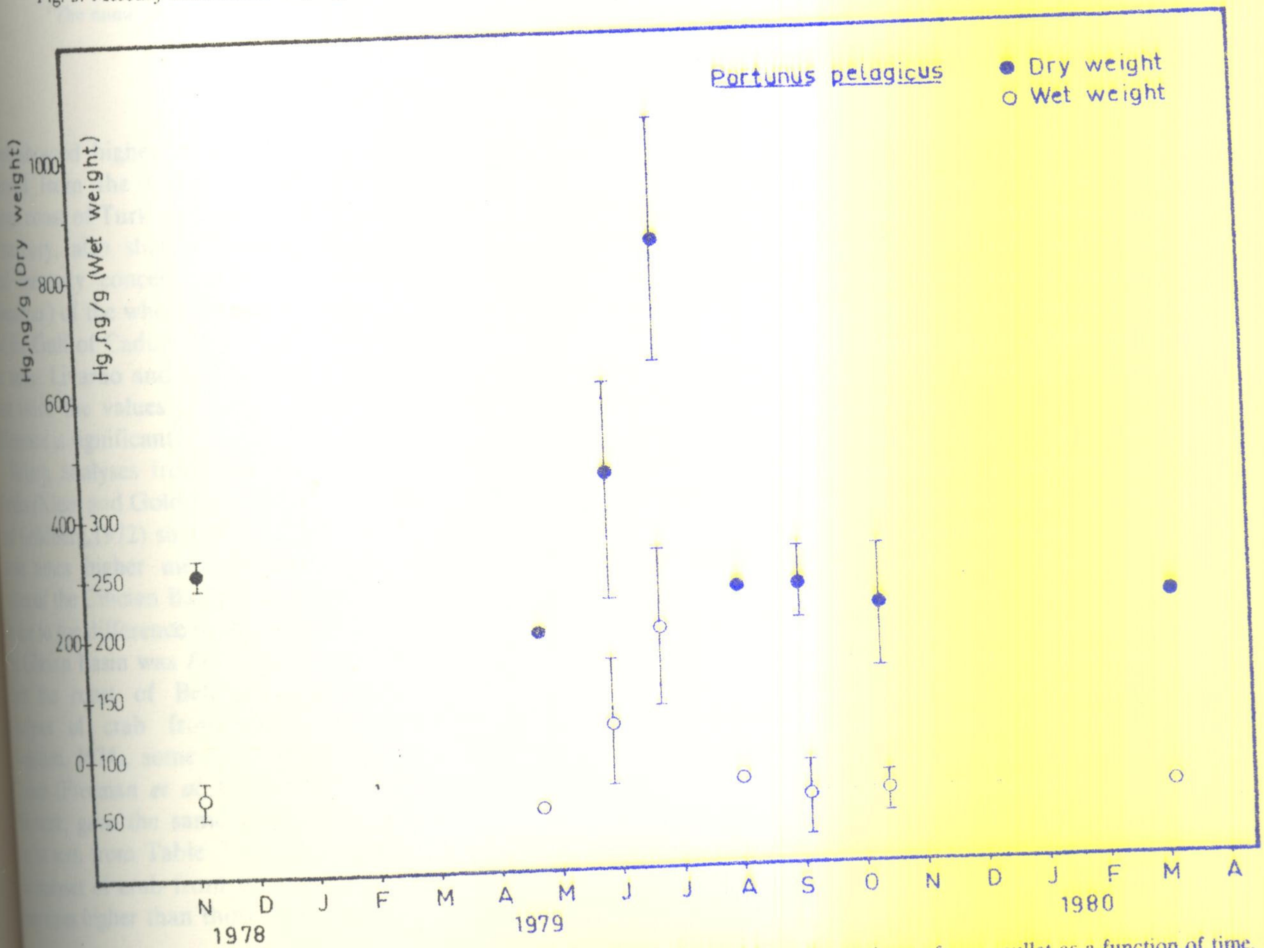

Fig. 4. Mercury concentrations, together with the standard deviations, obtained from the analyses of grey mullet as a function of time.

Table 3. Mercury concentrations obtained from the analysis of various marine organisms from Cilician Basin and other areas (ng/g)[a].

Grey mullet[b] (*Mugil auratus*)	Red mullet[b] (*Mullus surmuletus*)	Shrimp[b]	Crab[b]
This work 7.6–55 (24 ± 12)[c]	This work 15–167 (71 ± 56)	This work 40–420 (152 ± 100)	This work 223–740 (470 ± 277)
Aegean coast of Turkey (Uysal,1979) 124–283	Gulf of Cadiz (Bernhard,1978) 80–800	La Jolla,US. (Klein and Goldberg,1970) 800	Oslofjord (Andersen and Neelactan,1974) 390
Gulf of Trieste (Major *et al.*,1979) 27–104	Straights of Gibralter (Bernhard,1978) 190–390	Palos Verdes, US (Klein and Goldberg,1972) 500–2300	Atlantic coast of Canada (Freeman *et al.*, 1974) 320–640 (480 ± 120)
North Adriatic (Bernhard,1978) 80–1000	Ebro-Blanes (Bernhard,1978) 160–500 (180)	Coast of Belgium (Bertine and Goldberg,1972) 700–1600	840–1860 (1440 ± 460)
Israeli Coast (Levitan *et al.*,1974) 6–81	Secca de Vade (Livarno) (Bernhard,1978) 630 ± 600	Israeli coast (Yannai and Sachs,1973) (90)	
Israeli coast (Yannai and Sachs,1978) 40	Piombino (Bernhard,1978) (360) Trapacni (Bernhard,1978) 70–110 (90)		

[a]The average wet weight/dry weight ratios in this work are grey mullet 4.56, red mullet 4.65, shrimp 4.0, and crab 4.39.

[b]The results of grey and red mullet are in wet weight, and of crab and shrimp, dry weight.

[c]The numbers in parenthesis are the mean values ± standard deviation.

llet showed higher mercury levels than the values tained from the Cilician Basin. Results from the gean coast of Turkey, where there are natural sources f mercury, also showed higher values (Uysal,1979). tal mercury concentrations in red mullet (*Mullus rmuletus*) of the whole Mediterranean, except Livarno d the Gulf of Cadiz (Bernhard,1978) are more or less e same. Livarno and the Gulf of Cadiz values are at st twice the values obtained in this work, and the fference is significant.

Shrimp analyses from the coast of La Jolla, Palos rdes (Klein and Goldberg, 1970) and Belgium (Bertine d Goldberg,1972) showed at least twice, and at most en times higher mercury concentrations than the lues of the Cilician Basin. These big differences might due to the difference in the species, i.e., the type from e Cilician Basin was *Penaeus kerathurus* and the type m the coast of Belgium was *Crangon crangon*. alyses of crab from Oslofjord (Andersen and elakten, 1974), some parts of the Atlantic coast of nada (Freeman *et al.*,1974), and those obtained in s work, gave the same mercury concentrations. As n be seen from Table 3, some values obtained from e analyses of crab from the Canadian coast is about ree times higher than those from the Cilician Basin.

Conclusions

The concentrations of mercury found in shrimp (*Penaeus kerathurus*), crab (*Portunus pelagicus*), grey mullet (*Mugil auratus*), and red mullet (*Mullus surmuletus*) caught in the northeastern Mediterranean during 1978, 1979, and 1980 lay in the range of 12–104, 32–269, 7.6–55, and 15–246 ng/g (fresh weight), respectively, and generally were lower than those found elsewhere in the Mediterranean.

The peak mercury concentrations found in red mullet, and to a lesser extent in grey mullet and blue crab, coincide with a maximum in the local application of mercury fungicides. Local weather conditions appear to ensure that agricultural application of fungicide is followed rather simply by increased mercury concentrations in the marine organisms. The decline in the spring peak is associated with the loss of fat involved in spawning. No secular variation was observed in the mercury concentrations of shrimp (*Penaeus kerathurus*) probably because the carapace, in which most of the mercury is contained, is replaced frequently.

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