Chapter IV

Study of the contamination of fish and shell fish

by

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Based on work by Fisheries Research Station, Ostend (Biometry); Institute for Chemical Research, Tervuren (Heavy metals); Station for Phytopharmacy, Gembloux (Pesticides, P.C.B.); all from Ministry of Agriculture (D.G. Research).

1.- Heavy metals

The results mentioned in the present report concern work that has been done in 1974 and that succeeds to the report 1973 *Study of the pollution in sea fish and shell fish.*

Taken in a whole, the activities of 1974 may be subdivised in the continuation of the research of 1973 — observation of the Belgian Coast and study of the Belgian fishery with regard to the contents of heavy metals and organic forms of mercury in the fillets of different species of fish and in shrimps — and in new activities :

- the systematical determination of the contents of methylmercury in different species of fish (fillets) and shrimps;
- determination of heavy metals contents in the liver and the stomach content of different fish species.

The fish and shrimps studied by the Institute of Chemical Research are furnished by the Station for Maritime Fishery that makes biometric studies on them.

- A third activity is the determination of heavy metals contents in organisms collected by the team Van der Ben on the breakwaters of the Belgian Coast.

The results of the work that has been done in 1974 are successively presented as follows.

1.1.- Heavy metals in the fillets

1.1.1.- Determination intended to get together a statistical series of 50 individuals for each species

In shore fishery (Fisheries 1972, 6 species)

Table 1 : mean Hg, Cu, Pb and Zn content in plaice , whiting, sprat, herring and shrimps for n = 50 .

Off shore fishery (Belgian fishery products from July 1972 till end 1973)

Table 2,3 : mean Hg, Cu, Pb and Zn content in plaices and soles of the northern North Sea and the Bristol Channel.

1.1.2.- Evolution of the percentage of heavy metals in fish and shell fish since end 1971 (Initial study)

In shore fishery (Fishing periods from end 1-71 till end 1973)

Table 4 : mean periodical Hg and Cu content (4 fish species and shrimps).

Off shore fishery (Fishing in four regions during the years 1972 and 1973)

Table 5,6 : mean Hg and Cu content per periods 72-73 in plaices and soles (Northern North Sea, Irish Sea, Bristol Channel, English Channel).

1.2.- Methylmercury

First series of determinations on species with different origines (Belgian Coast and other places).

Table 7 : individual relations methylmercury / total mercury.

Table 8 : mean relations methylmercury / total mercury.

1.3.- Heavy metals in the liver, the stomach content and the fillets

Table 9 : Hg and Cu content (individual and mean) in fillets, liver and stomach content of whiting (1974 fishing, Belgian Coast).

1.4.- Heavy metals in marine organisms

Table 10 : mean Hg and Cu contents in marine organisms collected on the breakwaters of the Belgian Coast (1974).

Table 1

Mean levels of Hg, Cu, Pb, Zn (ppm)
Belgian coast : Plaices - Whiting - Cod - Sprats - Herring - Shrimps
(Fisheries 1972)

n = 50	Hg			Cu			Pb			Zn		
	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)
Plaices	0.19	0.08	42	0.77	0.33	42	0.30	0.07	23	6.40	1.60	25
Whiting	0.21	0.10	48	1.07	0.44	41	1.04	0.98	94	10.6	8.82	83
Cod	0.19	0.17	89	0.74	0.39	53	0.33	0.14	42	5.11	1.36	27
Sprats	0.15	0.06	40	1.32	0.49	37	1.67	1.4	84	24.3	5.7	23
Herring (1973)	0.05	0.02	40	0.88	0.26	30	0.28	0.07	25	8.7	2.6	30
Shrimps	0.10	0.03	30	14.6	3.26	22	3.42	3.25	98	26.5	6.47	24

Table 2

Mean levels of Hg, Cu, Pb, Zn (ppm)
Off shore Fisheries (1972) : Plaices

n = 50	Hg			Cu			Pb			Zn		
	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)
Irish Sea	0.35	0.23	66	0.79	0.35	44	0.38	0.47	124	5.98	1.67	28
Bristol Channel	0.20	0.12	60	0.62	0.36	58	0.33	0.22	67	6.58	3.74	57
North Sea	0.20	0.14	70	0.58	0.23	40	0.40	0.58	145	6.33	2.54	40

Table 3

Mean levels of Hg, Cu, Pb, Zn (ppm)
Off shore Fisheries (July 1972 till end June 1973) : Soles

n = 50	Hg			Cu			Pb			Zn		
	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)	$\bar{X}$	σ	$\sigma/\bar{X}$ (%)
Bristol Channel	0.17	0.12	68	0.86	0.46	53	0.38	0.13	34	10.1	6.55	65
North Sea	0.31	0.21	69	1.06	0.65	61	0.38	0.22	59	9.1	3.44	38

Table 4

Mean levels : Hg, Cu (ppm)
Belgian coast : Plaices - Whiting - Cod - Sprats - Shrimps (71-72-73)

Quarter	Plaice			Whiting			Sprats			Cod			Shrimps		
	Hg	Cu	n	Hg	Cu	n	Hg	Cu	n	Hg	Cu	n	Hg	Cu	n
IV/71	0.14	-	46	0.14	-	67	0.14	-	12	0.10	-	34	0.10	-	10
I /72	0.14	0.67	57	0.17	0.84	25	0.15	1.20	23	0.14	0.70	43	0.10	12.2	57
II/72	0.16	0.81	41	0.17	0.86	59	0.11	1.97	9	0.16	0.48	5	0.12	12.5	27
III/72	0.22	0.77	86	0.23	1.49	59	0.17	1.25	16	-	-	-	0.10	16	13
IV/72	0.18	0.90	80	0.18	1.51	107	0.14	1.74	21	0.29	1.09	15	0.09	15	51
II/73	0.19	-	16	0.20	-	30	-	-	-	-	-	-	-	-	-
IV/73	0.12	-	15	0.21	-	10	-	-	-	-	-	-	-	-	-

Table 5

Mean levels of Hg, Cu (ppm)
Off shore Fisheries : Plaices (1972)

Quarter	Southern North Sea			Bristol Channel		
	Hg	Cu	n	Hg	Cu	n
I /72	0.17	0.60	8	0.16	0.73	12
II/72	0.25	0.62	10	0.20	0.76	5
III/72	0.27	0.48	10	0.25	0.70	15
IV/72	0.30	0.78	14	0.23	0.74	14

Table 6

Mean levels of Hg, Cu (ppm)
Off shore Fisheries : Soles (72-73)

Quarter	North Sea			Bristol Channel			English Channel		
	Hg	Cu	n	Hg	Cu	n	Hg	Cu	n
III/72	-	-	-	0.15	0.64	10	-	-	-
IV/72	-	-	-	0.20	1.43	9	-	-	-
I /73	-	-	-	0.15	0.60	33	0.20	0.63	24
II/73	-	-	-	0.13	0.69	13	0.33	0.89	26
III/73	0.35 0.18	1.21 -	22 21	0.20	1.15	40	0.40	1.03	14
IV/73	0.14	-	30	0.16	1.39	13	0.24	-	14

Table 7

Mercury contents and % methylmercury

Species	Hg (total) (ppm)	Methylmercury Hg (total) (%)
Soles North Sea IV/73	0.04	75
	0.05	80
	0.09	66
	0.15	53
	0.16	50
	0.22	63
	0.30	66
Plaices Bristol Channel IV/72	0.11	81
	0.14	100
	0.14	93
	0.15	93
	0.15	86
	0.16	68
	0.21	71
	0.39	56
	0.46	32

Table 7

(continuation)

Species	Hg (total) (ppm)	Methylmercury Hg (total) (%)
Whiting Belgian coast IV/72	0.11	91
	0.13	100
	0.16	100
	0.17	76
	0.34	65
	0.38	53
	0.49	37
Shrimps Belgian Coast IV/72	0.10	60
	0.10	60
	0.10	40
	0.10	40
	0.10	40
	0.13	35
	0.15	27
	0.18	17

Table 8

Mean levels : Mercury contents and % methylmercury

Area	Quarter	Hg (total) (ppm)	Methylmercury Hg (total)	n
Soles				
North Sea	IV/73	0.15 (0.05-0.30)	65 (80-50)	7
Bristol Channel	IV/73	0.22 (0.12-0.30)	44 (65-13)	10
Plaices				
Bristol Channel	IV/72	0.21 (0.16-0.46)	77 (100-32)	10
Belgian coast	IV/72	0.20 (0.12-0.39)	36 (40-20)	13
Whiting				
Belgian coast	IV/72	0.24 (0.13-0.49)	74 (100-37)	10
Sprats				
Belgian coast	IV/72	0.14 (0.09-0.20)	45 (90-26)	10
Shrimps				
Belgian coast	IV/72	0.12 (0.10-0.18)	37 (60-17)	10

Table 9

Fillet - Liver - Stomach content
Belgian coast : Whiting (April 1974)

N° Spec.	Fillet		Liver		Stomach content		
	Hg ppm	Cu ppm	Hg ppm	Cu ppm	Hg ppm	Cu ppm	Nature of the content
49	0.13	1.0	0.16	15.6	0.24	4.2	sprat
50	0.19	0.7	0.11	8	0.17	3.4	!
51	0.10	1.7	0.13	4.2	0.12	2.5	!
52	0.23	0.6	0.09	6.4	0.15	2.2	Shrimps
53	0.23	2.0	0.12	7.1	0.22	4.9	Shrimps
54	0.62	1.2	0.27	4.4	0.11	2.2	!
55	0.17	2.6	0.08	6.4	0.12	3.8	!
56	0.23	1.6	0.10	6.9	0.12	10.2	!
58	0.15	0.8	0.04	5.4	0.13	1.7	!
59	0.19	1.5	0.05	9.6	0.08	3.3	Shrimps
60	0.23	1.8	0.12	6.2	0.10	0.81	!
61	0.20	0.9	0.13	10.1	0.14	3.4	Shrimps
$\bar{X}$	0.22	1.4	0.12	7.5	0.14	3.6	
σ	0.13	0.61	0.06	3.14	0.05	2.4	
$\sigma/\bar{X}$	68	44	50	42	36	67	

Table 10

Average content of Hg, Cu, Zn, Pb
(ppm, dry matter)
Belgian coast : marine organisms (breakwaters - 1974)

Species	n	Hg	Cu	Pb	Zn
Ulva lactuca	12	0.13	8.1	6.3	44
Fucus spiralis	7	0.11	5.5	5	200
Porphyra umbilicalis	2	0.03	22.3	2.4	85
Navicula	1	0.21	86	20.4	127
Asterias rubens	1	0.34	6.1	3.9	210
Mytilus edulis	12	0.44	10	6.8	185
Littorina littorea	13	0.24	73	2.9	80

1.5.- Conclusions

1.5.1.- Heavy metals in fish (fillets) and in shrimps

Factors having an influence

In brief, the conclusions of previous reports have been confirmed : the mean contents of heavy metals may vary between classes and species from one region to the other and according to the period (tables 1, 2, 3 and 10). *In the same species* there is a clear cut correlation between the total Hg content and the age (weight) and the mean contents may be very different according to the regions (tables 2, 3, 4, 6).

The new results strengthen the assumption of a variation of the contents according to the seasons, with higher contents in summer (tables 4, 5, 6). We suggest connecting these fluctuations with those of the primary productivity. Abdullah and Royle (1973) found a similar variation for cadmium in plankton.

Levels of contents

If the Hg levels were already well defined, it is also the case in this moment for Cu, Pb and Zn. It has been confirmed that Zn and Pb contents (25 and 3 ppm) are higher in sprats and shrimps and that shrimps have a higher Cu content (15 ppm).

As for Hg, there should be a fluctuation in function of the seasons.

As for Hg, Cu, Pb and Zn contents of a same species are distributed according to a normal log way, with a variation coefficient of about 50 % . In some species however, such as whiting, plaices, sprats and shrimps (tables 1, 2), this coefficient is nearly 100 % or higher for Pb.

As far as Pb distribution is concerned, we obtain rather curious results : *plaices*, captured in four different regions, have very closely related mean contents (0.3 to 0.4 ppm Pb) but, according to the regions the variation coefficients are very divergent — from 23 % (Belgian Coast) to 145 % (North Sea); *soles*, on the other hand, from three of the same regions have mean contents of the same rate (0.38 to 0.39 ppm of Pb), but the variation coefficients are not very divergent and smaller than those of plaices (tables 1, 2, 3).

In short, same mean Pb content in plaices as in soles, in all cases a correlation between the variation coefficients and the region, 2 to 3 times higher variation coefficients in plaices (in every case there is a series of 50 samples). There seems to be a different physiological reaction.

Cadmium

We have had a great number of cadmium determinations, but notwithstanding several restatements of the question, we are not pleased with the absolute value of the results. The levels we found are nearly 0.2 to 0.4 ppm Cd for soles and 0.7 ppm for whiting; they are considered to be too high and research continues in better conditions on biological material; determination on a great series will follow afterwards.

Nevertheless, the results have a comparative value.

According to the series of 50 samples that have already been analysed, it seems to be evident :

- that for a same species, the means vary in function of the region (soles : North Sea 0.2 ppm; Irish Sea 0.4; Bristol Channel 0.2);
- that the means vary according to the species (soles 0.2 to 0.4 ppm; whiting 0.7 ppm);
- that the variation coefficients vary between 30 and 55 % .

1.5.2.- Methylmercury

Variations according to the species

As appears from table 8, the ratio methylmercury/total mercury differs from one species to another.

In short for the Belgian coast it varies between 36 % for plaices and 74 % for whiting, whereas for the Bristol Channel it varies between 44 % for soles and 77 % for plaices, the total Hg contents being the same. It should be interesting to compare these fluctuations with those of the sulphurated amino acid contents of the same species, those contents may be correlated with the Hg retention.

Variation in the same species

Generally the relation Me-Hg/total Hg varies in inverse ratio to the total mercury contents.

The results are given in table 7.

For *whiting*, the relation reaches 100 % for contents of about 0.1 ppm total Hg and 37 % for ± 0.5 ppm . For *plaices* nearly 100 % for 0.1 ppm total Hg and 32 % for ± 0.5 ppm ; for shrimps 60 % for 0.1 ppm total Hg and nearly 17 % for ± 0.2 ppm . Kosta *et al.* (1974) made a similar observation for a Hg polluted river : "The reduction of total Hg in trout keeps pace with the increase of the methylmercury fraction."

As it is known that the total Hg content is correlated with the age, we may say that the degree of methylmercury increase lessens with the age.

Variations according to the region

For an almost equal mean content of total mercury, a same species may give, according to the regions, totally different relations Me.Hg/ total Hg. Examples are given in table 8.

Plaices of the Bristol Channel and the Belgian Coast have mean contents of total mercury of respectively 0.21 and 0.20 ppm , while the corresponding relation Me-Hg/total Hg are 77 and 36 % , for soles of the southern part of the North Sea and the Irish Sea the contents are 0.40 and 0.37 ppm , the relation 34 and 47 % .

The relative value of the methylation degree of mercury seems important enough to be considered in order to differentiate the regional pollution.

Remarks

After these considerations it becomes apparent that the above mentioned seasonal variations of the total mercury contents should be mainly imputable to the mineral mercury. Indeed, an increase of the content generally keeps pace with a decrease of the methylmercury proportion, while the phenomenon of subsequent elimination of Hg for plaices

is certainly more complicated with methylmercury as CH_3-Hg-proteinate, the half life of which having been rated at 780 days by Hasanen (1973).

In view of the high toxicity of Me-Hg and of the fact that the relation Me-Hg/total Hg presents a high variability, a low content of total mercury, from the point of view of fish consumption, could present the same risks as a higher one.

1.5.3.- Distribution of heavy metals in fillets, liver and stomach content of whiting (Belgian Coast)

These are the first results, for Hg and Cu (table 9) of the new development of our studies.

With regard to the comparison of the contents of the different organs :

- on the average and in most cases copper is more abundant in liver, next in the stomach content;
- on the average and in several cases total mercury is more abundant in fillets.

Those first trials seem to confirm some data of the literature according to which there should be a greater accumulation of Hg in the muscles than in the liver [Gilles *et al.* (1973)] in less polluted areas. A higher Cu-content in the liver is probably not at all an exception, in view of the function of this organ.

The research concerning the relations between the content of the muscle and that of the liver and the stomach content have been unsuccessful, except for Hg between muscle and liver where a correlation $r = 0.75$ implicates a 99 % significative correlation.

New series are already examined, and also new elements such as Me-Hg.

1.5.4.- Marine organisms captured on the breakwaters

This study, started in 1974, is based upon four campaigns during which marine organisms (sea-weed, diatoms, mussels, littorines, etc.) are captured on the breakwaters of the Belgian coast. Only heavy metals are studied.

Table 10 gives the mean contents, calculated on the dry material (the water content is generally ± 70 %).

Concerning the three animal species that already have been studied (mussels, littorines and star-fish), we may admit that, pro element, the Hg-, Cu-, Pb- and Zn-contents are nearly the same; nevertheless an exception should be made for littorines with a Cu-content of 73 ppm and for mussels and starfish with a Zn-content of ± 200 ppm .

Compared with the heavy metal contents in fish and shellfish, calculated on dry material (nearly 3.5 times the values calculated on fresh material), the Hg and Pb contents are nearly the same. The contents are higher for copper in littorines (that contain hemocyanine) and rank above those of shrimps (nearly 73 against 50 ppm). Starfish and mussels have a nearly three times higher Zn content than the high value found for this element in sprats and shrimps.

2.- Pesticides and P.C.B. [Henriet]

As for the heavy metals — continuation of the determination of pesticides and P.C.B. intended to get together a statistical series for each studied species (plaice, sole, whiting, cod, sprats, shrimps, herring) and different fishing groups — the results confirm that the contents are relatively low and there is no differentiation between regions. The means are : pp'DDT : 0.004 ppm ; DDD : 0.002 ppm ; DDE : 0.002 ppm ; Lindane : 0.003 ppm ; Dieldrine : 0.002 ppm ; P.C.B. : 0.04 ppm .

For recall the amounts of the different kinds of pesticides and P.C.B. are clearly higher in the sprats.

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