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Technical Report

Mathematical Model of Marine
Pollution in the North Sea

1972/BIOL./SYNTHESE 06

INTERIM REPORT ON THE AMOUNT OF HEAVY METALS
AND PESTICIDES RESIDUES IN FISH AND
SHRIMPS.

by

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1. Introduction.

An investigation on the amount of heavy metals, pesticides and other organic components in commercial fish (plaice, whiting, cod and sprat) and in shrimps was carried out on catches from the research vessel "Hinders". Experimental fisheries took place during the period September 1971 - June 1972 off the Belgian coast.

A similar investigation was undertaken on market samples from commercial catches of different fishing grounds.

The determination of mercury was carried out during the whole period under survey, while the other analyses started in January 1972.

This report mentions the preliminary results of this investigation. A complete statistical analysis will be carried out when the programmed period of investigation will come to an end (end December 1972).

2. Methods.

2.1. Chemical methods.

Hg-determination : Digestion method with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$; Reduction of Hg with NaBH_4 . Determination with A. A. (M. A. S. 50).

Cu- determination : As for Hg but without reduction. Determination with A. A. (oven).

Zn- and Pb- determination : Calcination till 450°C . Digestion of the ash with $\text{HNO}_3/\text{H}_2\text{O}_2$. Determination A. A. (Zn- flame) (Pb- oven).

Pesticides-determination : Same methos as for the sediments with a supplementary purification technique.

2.2. Sampling.

The following species were investigated :

- shrimps (*Crangon crangon* L.),
- plaice (*Pleuronectes platessa* L.),
- cod (*Gadus morhua* L.),
- whiting (*Merlangus merlangus* L.),
- sprat (*Sprattus sprattus* L.).

The individual biological parameters of plaice, cod and whiting were :

- length (in cm),
- weight (in g),
- age (otolith readings),
- sex (gonads and testes).

The samples of sprat consisted of 1 till 10 specimens, depending upon the abundancy.

For shrimps a sample of 250 g was taken.

2.2.1. Belgian coast.

Two areas were sampled on a monthly basis viz. "Westdiep" (5 stations) and "Vlakte van de Raan" (5 stations). On the other hand an overall survey of 30 stations in September 1971 and May 1972 was undertaken (Figure 1).

Table 1 shows the sampling procedure.

Figure 2 gives the age distribution of the samples.

Table 1 - Sampling procedure off the Belgian coast.

Area	Amount of samples of				Sprat
	Shrimps	Plaice	Cod	Whiting	
"Westdiep" (5 stations)	28	33	43	42	20
"Vlakte van de Raan" (5 stations)	14	61	32	17	17
Belgian coast (30 stations)	60	63	-	92	9

2.2.2. Market samples.

The plaice was investigated on 5 fishing grounds (figure 3). The sampling was carried out weekly in the three national fish markets (Ostend, Zeebrugge and Nieuport). An additions limited investigation on sole took place in 1971.

Table 2 gives the sampling procedure.

Figure 4 shows the age distribution of the samples.

Table 2 - Sampling procedure on the commercial species.

Area	Amount of samples of	
	Plaice	Sole
Southern North Sea	29	23
Central North Sea	15	14
English Channel	18	-
Bristol Channel	16	-
Irish Sea	28	-

3. Mercury content in fish and shrimps.

3.1. Belgian coast.

The results of the analysis are listed in table 3.

Table 3 - Mercury in fish and shrimps off the Belgian coast (ppm).

Species	n	Min.	Max.	Mean	s	v(%)
Shrimps	93	0,040	0,250	0,106	0,044	42
Plaice	139	0,030	0,360	0,148	0,062	42
Whiting	131	0,020	0,350	0,157	0,058	37
Cod	75	0,031	0,270	0,122	0,062	51
Sprat	44	0,050	0,370	0,140	0,063	45

No important differences in mercury content were found between the species studied.

Three additional factors were studied for shrimps : the area (West and East coast) (table 4), the distance to the coastline (more or less than 5 miles) (table 5) and the season (table 6).

Table 4 - Differences in mercury content for shrimps from the East - and West coast (ppm).

Area	n	Min.	Max.	Mean	s	v(%)
Eastern	14	0,040	0,220	0,114	0,054	47
Western	28	0,060	0,183	0,094	0,033	35

Table 5 - Differences in mercury content of shrimps from more or less than 5 miles (ppm).

Distance of the sample to the coast	n	Min.	Max.	Mean	s	v(%)
< 5 miles	44	0,040	0,250	0,112	0,048	43
> 5 miles	49	0,050	0,190	0,100	0,034	34

Table 6 - Differences in mercury content of shrimps by season (ppm).

Season	n	Min.	Max.	Mean	s	v(%)
Autumn	33	0,040	0,190	0,097	0,035	36
Winter	23	0,040	0,183	0,105	0,043	41
Spring	37	0,050	0,250	0,114	0,046	40

A specific investigation was performed on the mercury distribution in the body of the shrimps. The results showed a distribution of 56 % in the flesh, 32 % in the cephalothorax, 12 % in the shell and 0 % in the telson.

The t-tests gave with a probability of 95 % no significant differences between the mercury contents per season, as listed in table 6.

3.2. Fishing areas.

Table 7 shows the mercury contents of the different species from different fishing areas. The data of the Belgian coast are grouped with the data of the Southern North Sea area.

Plaice from the Irish Sea seems to have a rather high mercury content. The other areas and species did not differ very much.

Table 7 - Mercury content in fish and shrimps from different fishing areas (ppm).

Species and areas	n	Min.	Max.	Mean	s	v(%)
Plaice						
Southern North Sea	168	0,015	0,500	0,168	0,074	44
Central North Sea	15	0,034	0,430	0,116	0,095	82
English Channel	18	0,060	0,340	0,174	0,081	47
Bristol Channel	16	0,082	0,280	0,161	0,058	36
Irish Sea	28	0,070	0,840	0,317	0,191	60
Sole						
Southern North Sea	23	0,036	0,403	0,204	0,107	53
Central North Sea	14	0,042	0,660	0,144	0,160	100
Whiting						
Southern North Sea	131	0,020	0,350	0,157	0,058	37
Cod						
Southern North Sea	80	0,031	0,270	0,125	0,051	41
Sprat						
Southern North Sea	44	0,050	0,370	0,140	0,063	45
Shrimps						
Southern North Sea	93	0,040	0,250	0,106	0,044	42

3.3. Mercury content and biological parameters.

The mercury content was correlated with 4 biological parameters, i. e. : age (table 8), length (table 9), weight and sex (table 10).

Between mercury content and age as well as length 4 positive correlations were found. No significant correlations between mercury and weight were found. The mercury content between males and females did not differ very much.

Table 8 - Correlation between mercury content and age.

Species	Area	n	r(a)	Regression
Plaice	Southern North Sea	168	0,406 ***	$y = 13,9 \cdot 10^{-3}x + 110 \cdot 10^{-3}$
	Central North Sea	15	0,311	-
	Bristol Channel	16	0,090	-
	English Channel	18	0,114	-
	Irish Sea	28	0,273	-
Sole	Southern North Sea	23	0,316	-
	Central North Sea	14	0,595*	$y = 21 \cdot 10^{-3}x + 24 \cdot 10^{-3}$
Whiting	Southern North Sea	130	0,232*	$y = 19 \cdot 10^{-3}x + 129 \cdot 10^{-3}$
Cod	Southern North Sea	80	0,383***	$y = 27 \cdot 10^{-3}x + 79 \cdot 10^{-3}$

(a) Significance of the correlation coefficients : * = 95 % ; *** = 99,9%.

Table 9 - Correlation between mercury content and length.

Species	Area	n	r(a)	Regression
Plaice	Southern North Sea	168	0,368***	$y = 4,1 \cdot 10^{-3}x + 43 \cdot 10^{-3}$
	Central North Sea	15	0,264	-
	Bristol Channel	16	0,144	-
	English Channel	18	0,202	-
	Irish Sea	28	0,010	-
Sole	Southern North Sea	23	0,044	-
	Central North Sea	14	0,516*	$y = 13,3 \cdot 10^{-3}x + 293 \cdot 10^{-3}$
Whiting	Southern North Sea	131	0,604***	$y = 7,5 \cdot 10^{-3}x + 9 \cdot 10^{-3}$
Cod	Southern North Sea	80	0,370***	$y = 2,0 \cdot 10^{-3}x + 46 \cdot 10^{-3}$

(a) Significance of the correlation coefficients : * = 95 % ; *** = 99,9%.

Table 10 - Mercury content in males and females (ppm).

Species and areas	sex	n	mean	s	v(%)
Plaice					
Southern North Sea	female	86	0,159	0,082	52
	male	82	0,14	0,066	45
Central North Sea	female	8	0,101	0,052	51
	male	7	0,133	0,126	95
Bristol Channel	female	11	0,169	0,065	38
	male	5	0,144	0,037	26
English Channel	female	9	0,164	0,070	43
	male	9	0,183	0,091	50
Irish Sea	female	20	0,317	0,209	66
	male	8	0,316	0,138	44
<hr/>					
Sole					
Southern North Sea	female	11	0,157	0,078	50
	male	12	0,248	0,109	44
Central North Sea	female	12	0,154	0,171	100
	male	2	0,084	0,025	30
<hr/>					
Cod					
Southern North Sea	female	44	0,116	0,049	42
	male	31	0,131	0,053	40
<hr/>					
Whiting					
Southern North Sea	female	73	0,161	0,060	37
	male	58	0,151	0,056	37

4. Other heavy metals in fish and shrimps.4.1. Copper.

The preliminary results of the copper investigations are listed in tables 11 and 12.

Tabel 11 - Copper content in fish and shrimps (first trimester 1972). (ppm).

Species	Area	n	Min.	Max.	Mean	s	v(%)
Plaice	Westdiep	39	0,38	1,33	0,71	0,24	34
		18	0,24	1,30	0,59	0,28	46
	Bristol Channel	12	0,26	1,66	0,73	0,50	68
	English Channel	9	0,26	0,91	0,54	0,22	40
	Irish Sea	19	0,25	1,17	0,66	0,26	39
Whiting	North Sea	18	0,31	0,95	0,57	0,17	29
	Westdiep	11	0,32	1,98	1,02	0,51	50
Sprat	Vlakte van de Raan	14	0,39	0,95	0,55	0,22	39
	Westdiep	15	0,78	1,41	1,29	0,19	17
Cod	Vlakte van de Raan	8	0,84	1,42	1	0,24	24
	Westdiep	28	0,27	1,24	0,70	0,26	40
Shrimps	Vlakte van de Raan	15	0,25	1,30	0,74	0,38	52
	Westdiep	13	8,56	21,9	13,3	3,25	25
	Vlakte van de Raan	11	7,4	19,7	13,1	3,53	27
	Belgian Coast	33	6,6	16,8	11,4	2,4	21

Table 12 - Copper content in fish and shrimps meand trimester 1972(ppm)

Species	Area	n	Min.	Max.	Mean	s	v(%)
Plaice	Belgian coast	41	0,41	1,67	0,81	0,34 ^o	42
	Bristol Channel + English Channel	14	0,31	1,20	0,67	0,30	45
	Irish Sea	5	0,32	0,82	0,51		
	North Sea	5	0,34	0,81	0,52		
Whiting	Belgian coast	59	0,34	1,69	0,86	0,35	41
Sprat	Belgian coast	9	1,38	2,41	1,97	0,32	16
Cod	Norths Sea	5	0,33	0,69	0,48	0,04	28
Shrimp	Belgian coast	27	8,00	19,30	12,50	3,17	25
Sole	North Sea	3	0,42	1,36	0,83	0,48	58

From the results it seems that higher copper contents are found in sprat than in other fish. Very high amounts are noted in shrimps.

A specific investigation was carried out to study the distribution of the copper in the shrimp body. The results show a distribution of 54 % in the ocephalothorax, 28,5 % in the flesh, 13 % in the shell and 4,5 % in the telson.

4.2. Zinc and lead.

The results of the analyses on zinc and lead are given in table 13.

It seems that sprat from the Belgian coast contains much higher values of zinc and lead (4 - 5 times more) than plaice and whiting.

Table 13 - Zinc and lead content in fish (first trimester 1972) (ppm).

Species	Area		Zinc					Lead				
			Min.	Max.	Gem.	s	v(%)	Min.	Max.	Gem.	s	v(%)
Whiting	Vlakte van de Raan	10	4,75	6,85	5,37	0,73	14	0,19	2,40	0,76	0,79	103
	Westdiep	6	5,70	8,00	6,64	1,10	17	0,26	4,01	0,97	1,50	154
Sprat	Vlakte van de Raan	8	21,30	28,00	24,00	2,20	9	0,10	5,29	2,40	1,95	82
	Westdiep	15	16,70	29,30	23,80	3,46	14	0,15	4,12	1,50	1,12	75
Plaice	North Sea	5	4,50	5,52	5,10	0,45	9	0,14	0,17	0,15	0,01	7
	Bristol Ch.	9	3,62	13,80	5,76	3,08	53	0,11	0,25	0,17	0,05	30
	Irish Sea	11	3,66	6,46	5,44	0,81	15	0,13	2,88	0,61	0,89	145
	English Channel	3	5,39	6,02	5,8	0,36	6	0,20	0,29	0,25	0,05	20

5. Pesticides and PCB in fish and shrimps.

The investigations concerning the amount of pesticides and PCB in fish and shrimps were carried out by the "Station de Phyto-pharmacie de l'état" at Gembloux (J. Henriët).

5.1. Pesticides and PCB in fish and shrimps off the Belgian coast.

An investigation on DDT, DDE, DDD, Dieldrine, Lindane and PCB in cod, whiting, plaice, sprat and shrimps was undertaken. The results are given in table 14.

Table 14 - Pesticides and PCB in fish and shrimps off the Belgian coast (ppb).

Species	Area	n	DDT	DDE	DDD	Dieldrine	Lindane	PCB
Cod	Vlakte van de Raan	4	42,4 till 74,2	6,9 till 13,8	2,3 till 5,1	8,6 till 14,7	3,5 till 9,4	119 till 254
		2	28 till 41,2	10,4 till 16,7	2,5 till 2,6	6,3 till 19,2	4,3 till 7,4	116 till 437
Whiting	Vlakte van de Raan	3	2,1 till 21	2,1 till 4,6	1,3(3x)	6,6 till 13,6	3,5 till 7	34 till 136
		3	17,1 till 41,5	5,4 till 7,5	tr. till 2,2	6,7 till 9,7	7,1 till 9,2	65 till 132
Plaice	Vlakte van de Raan	4	12,6 till 55	tr. till 11,3	tr. till 8,7	7,4 till 14	2,7 till 9,5	80 till 466
		3	4,3 till 71,3	3,9 till 11,8	tr. till 6,6	8,3 till 13,2	8,4 till 10,3	142 till 390
Sprat	Vlakte van de Raan	1	66,2	42,0	25,4	26,4	16,2 till	857
Shrimps	Vlakte van de Raan	2	57,0 till 60,7	12,4 till 12,5	0 till tr.	11,8 till 12,0	7,0 till 11,3	(x)

(*) Not determinated.

From this preliminary investigation it seems that on the Belgian coast sprat contains more DDT, DDE, DDD, Dieldrine, Lindane and PCB than cod, plaice and whiting.

5.2. Pesticides and PCB in plaice and sole of the Southern North Sea.

On a limited amount of samples a first investigation was undertaken on pesticides and PCB in plaice and sole samples from commercial catches off the Southern North Sea. The results are shown in table 15.

Table 15 - Pesticides and PCB in plaice and sole from the Southern North Sea (ppb).

	Plaice				Sole			
	n	Mean	s	v %	n	Mean	s	v %
DDT	7	28	16,2	58,6	7	40,3	18,7	46,4
DDE	7	12,4	3,87	32,3	7	12,4	4,1	33
DDD	7	1,87	1,48	80	7	2,99	2,92	98
Dieldrine	7	6,43	3,84	60	7	7,87	3,78	46,7
Lindane	7	6,63	2,53	38,2	7	4,31	2,48	57,5
PCB	5	166	35,2	21,2	7	225,3	66,6	29,5

A peak of Endrine was found in several samples. To this end a method of identification of Endrine will be developed. Aldrine, Heptachlore and Heptaepoxide were never found.

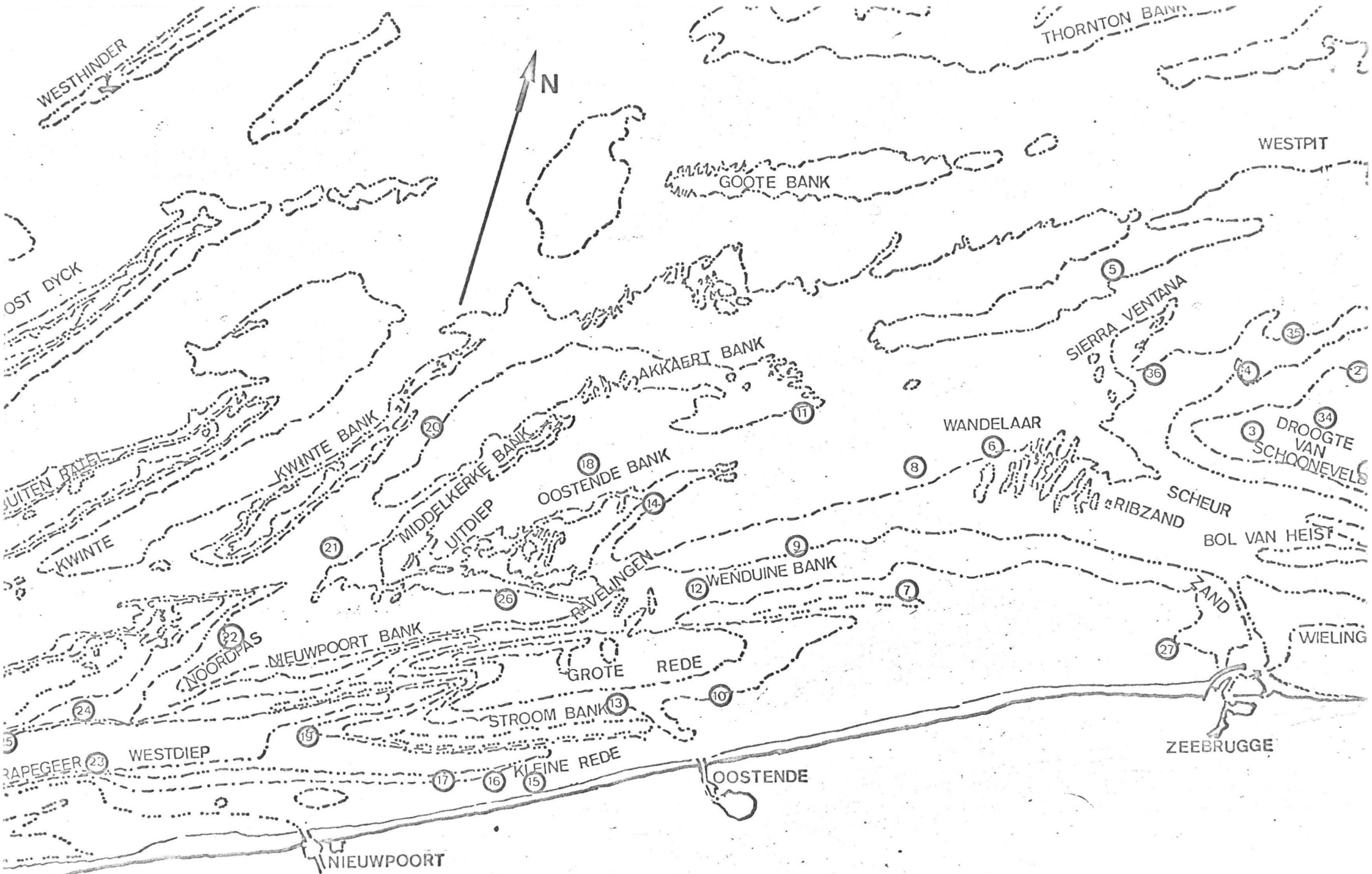


Figure 1 : Positions of the stations off the Belgian coast.

"Westdiep" : Stations 17, 19, 23, 24 en 25 ; "Vlakte van de Raan" : Stations 2, 4, 34, 35 en 36.

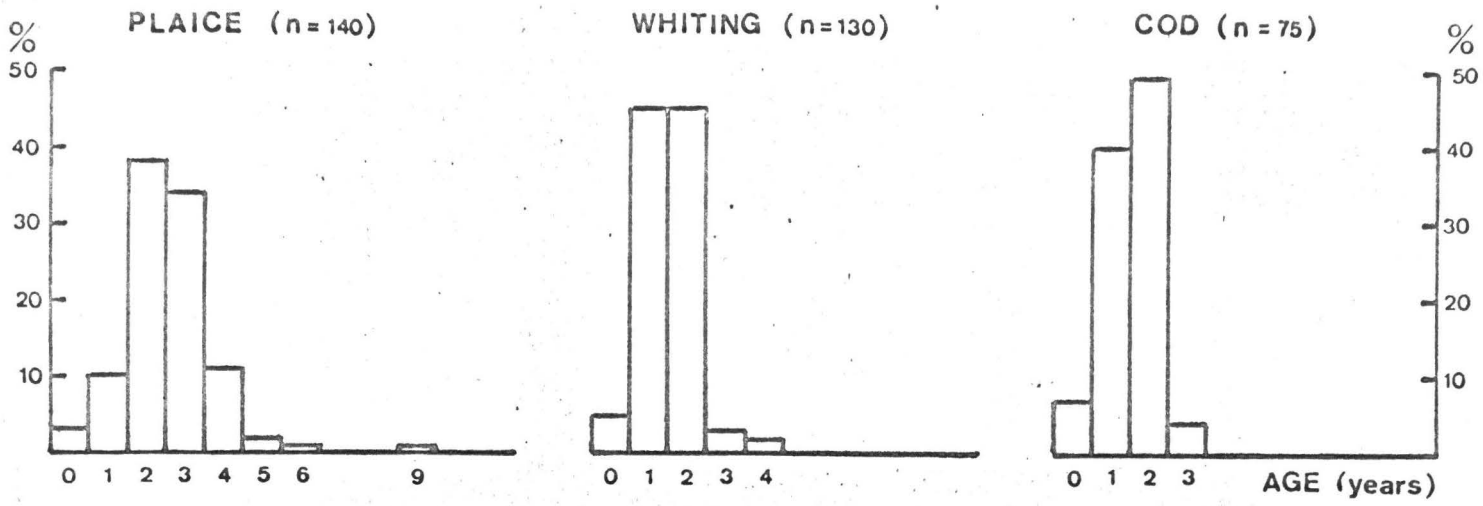


FIGURE 2.

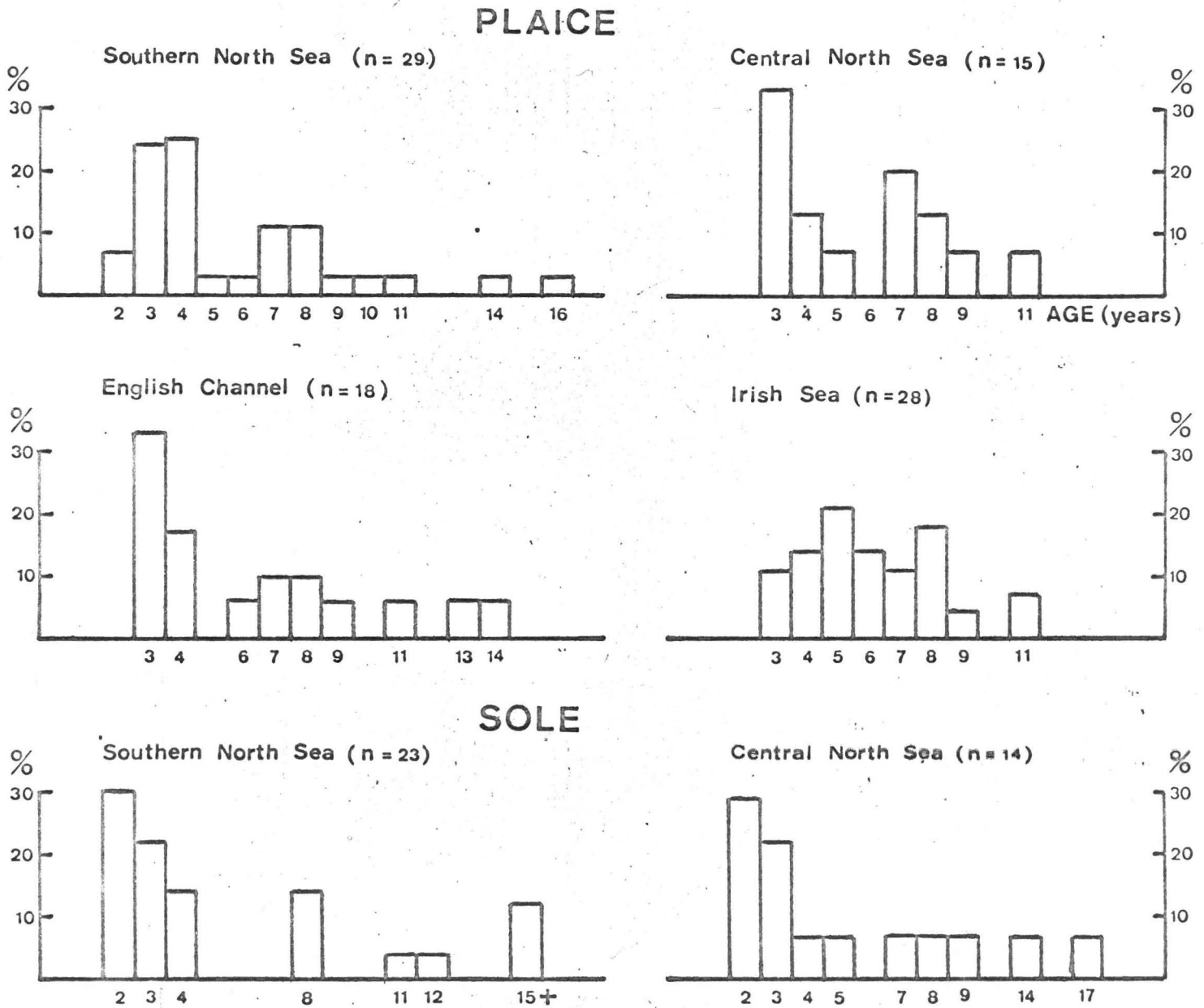


FIGURE 4.

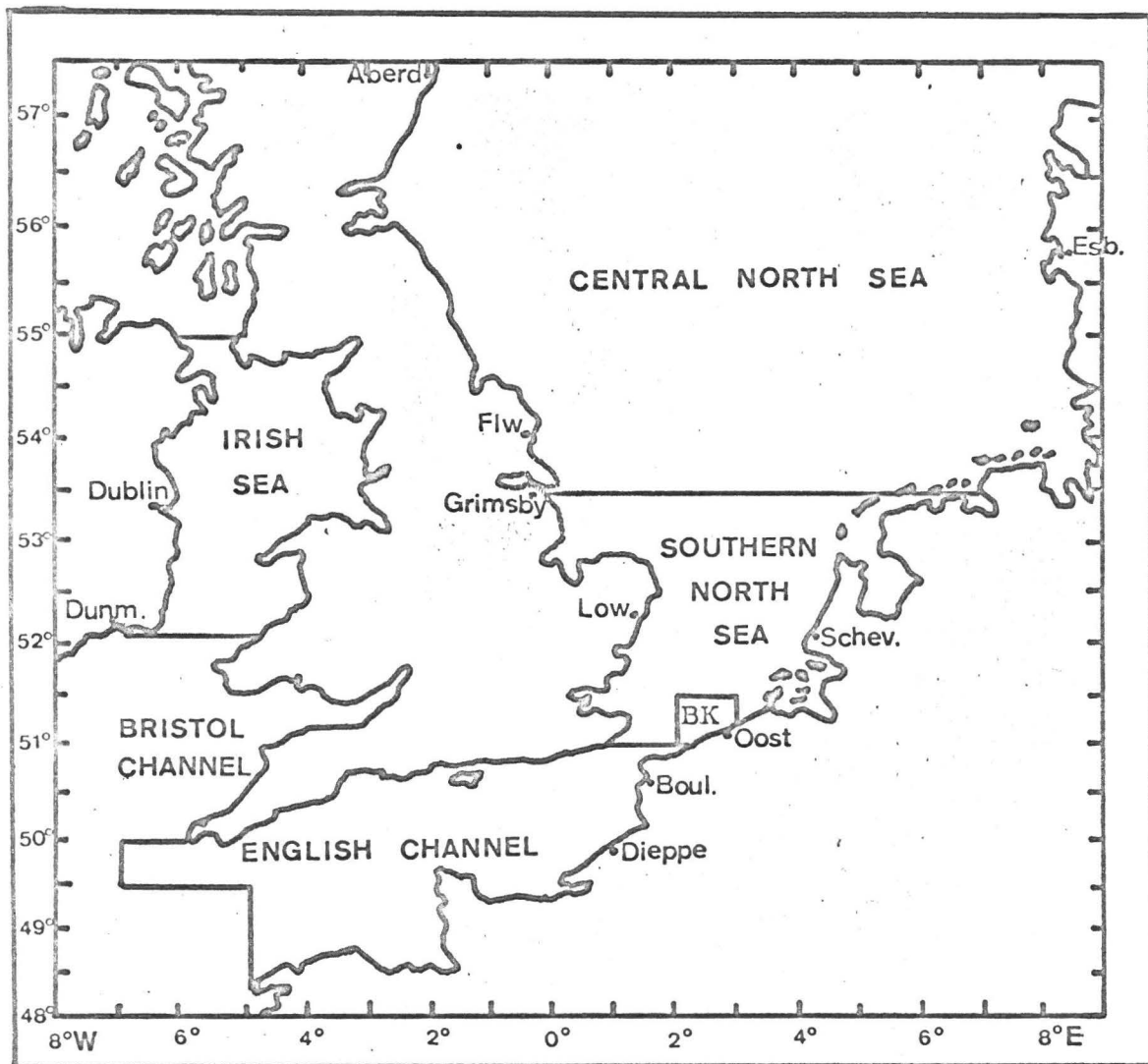


Figure 3 : The five fishing grounds of plaice.

B.K. : Belgian coast.