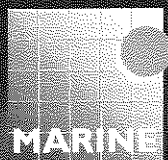


Metal and Organo-Chlorine Concentrations in Fin-Fish from Irish Waters.

FISHERIES LEAFLET 176

by A. Rowe, E. Nixon, E. McGovern, M. McManus & M. Minyth



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METAL AND ORGANO-CHLORINE CONCENTRATIONS IN FIN-FISH FROM IRISH WATERS IN 1995

MARINE ENVIRONMENTAL SERIES 1/98

by
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Fishery Leaflet 176
Marine Institute

February 1998
Dublin 2

Summary

During 1995 a total of 44 samples taken from 16 different species of fin-fish were collected from five Irish fishing ports and analysed for total mercury content in the edible tissue, in accordance with the European Commission's Decision of 19 May 1993. The concentration of mercury ranged from 0.03 to 0.28 with a mean of 0.09 $\mu\text{g}\cdot\text{g}^{-1}$ wet weight. These levels are low and are well within the maximum limits set by the EC for mercury in fisheries products. This survey confirms previous studies that show Irish seafoods are effectively free from mercury contamination.

In addition a number of samples were also analysed for cadmium, copper, lead, zinc, chromium and chlorinated hydrocarbons. Although there are no EU guidelines or standards for these additional contaminants, the levels are well below the strictest standards or guidance values applied by Contracting Parties of the Oslo and Paris Conventions.

Introduction

Following the European Commission's Decision (C (93) 1288) of 19 May 1993 *determining analysis methods, sampling plans and maximum limits for mercury in fisheries products*, the Marine Institute's Fisheries Research Centre set in place a mercury monitoring programme for fish landed at the major fishing ports. Mercury, which occurs naturally in the earth's crust, can also be introduced into the aquatic environment from mining, agricultural, industrial and other human activities. Once in the aquatic environment mercury can be taken up and retained by fish tissue. To protect consumers of marine foodstuffs, the EC set a maximum limit for total mercury of $0.5 \mu\text{g.g}^{-1}$ wet weight in fishery products. For physiological reasons, certain species accumulate mercury more readily than others and for these species a higher acceptable limit of $1.0 \mu\text{g.g}^{-1}$ was set by the EC. These species are listed in Annex 1.

Selected samples were also analysed for other heavy metals and chlorinated hydrocarbon compounds. Samples of fish from four ports (Killybegs, Dunmore East, Howth, Rossaveel) were taken to represent the catch from Irish waters.

The metals analysed were lead, cadmium, chromium, copper and zinc. These are all naturally occurring elements, and their presence in a sample does not necessarily indicate an anthropogenic input.

Polychlorinated biphenyls (PCBs), which originate mainly from electrical transformer oils, and organochlorine pesticides are man-made and tend to be ubiquitous contaminants in the marine environment. Due to their persistence and their lipophilic properties, these contaminants bioconcentrate and bioaccumulate in the marine food chain.

With the exception of mercury, there are no EU standards or guidelines for the elements or compounds monitored here. A number of Contracting Parties to the Oslo and Paris Conventions (OSPAR) have developed standards and guidance values for contaminants in marine foodstuffs and the levels reported here are compared to these values.

Methods

Sample collection and preparation:

Fish landed at the major fishing ports of Killybegs, Rossaveel, Castletownbere, Dunmore East and Howth were sampled during the summer of 1995. Depending on availability, 10 fish of each species landed were sampled at each of these ports. The lengths of the fish were measured and a portion of the edible tissue was removed from each fish, stored in pre-weighed, acid-washed glass jars and returned to the laboratory. In the laboratory the samples were weighed and homogenised and divided into two subsamples. One subsample was freeze-dried for 16 hours and analysed for heavy metals and the second was frozen at

-20°C and analysed for mercury and chlorinated hydrocarbons. The moisture content was determined from a 1g sub-sample of unfrozen tissue dried at 104°C overnight.

Mercury analysis:

Approximately 0.2g of wet tissue was digested by microwave in Teflon pressurised vessels with 4 ml of nitric acid (HNO₃). After cooling, potassium permanganate was added until the solution remained coloured. Sufficient hydroxylamine hydrochloride was added to neutralise the excess potassium permanganate. The solution was diluted to approximately 20 ml with distilled deionised water. Following the reduction of samples with stannous chloride (Hatch and Ott 1968), the mercury was determined by cold vapour flameless atomic absorption using a Varian SpectrAA 20 Plus fitted with a VGA 76 Vapour Generator.

Heavy metal analysis:

Cadmium, chromium, copper, lead and zinc were analysed following microwave digestion in Teflon pressurised vessels with nitric acid and hydrogen peroxide. Metal levels were determined by graphite furnace atomic absorption and flame atomic absorption spectrometry.

Chlorinated hydrocarbon analysis:

Fish tissue samples were dried using sodium sulphate and Soxhlet extracted for 6 hours with a hexane/dichloromethane mixture. The co-extracted lipids were removed by alumina column chromatography followed by separation of the PCBs from the chlorinated pesticides using silica column chromatography. Levels were determined by gas chromatography electron capture detection using a 60-meter fused silica capillary column (CP-SIL 8CB, Chrompack); a second column of different polarity was used as confirmation (CP-SIL 19CB, Chrompack).

Quality Assurance:

The quality of the data was assured through the analyses of the appropriate certified reference materials (CRM) with each batch of samples analysed. The results obtained from the analysis of the CRMs are given in Table 1. Analysis of blank samples was also carried out with each batch.

Results and discussion

Mercury

A total of 44 fish muscle samples were analysed for mercury in 1995. Details of the results are given in Table 2. This was comprised of 16 species, which were taken from 5

major Irish ports. Overall, the levels of Hg detected in the edible portion of the fish were low, well within the standard value of $0.5\mu\text{g}\cdot\text{g}^{-1}$ wet weight set by the EU.

The results ranged from 0.03 to $0.28\mu\text{g}\cdot\text{g}^{-1}$ wet tissue weight. The mean result was $0.09\mu\text{g}\cdot\text{g}^{-1}$ and the median was $0.08\mu\text{g}\cdot\text{g}^{-1}$. The highest levels obtained were found in black sole landed at Castletownbere ($0.28\mu\text{g}\cdot\text{g}^{-1}$), megrim at Dunmore East ($0.19\mu\text{g}\cdot\text{g}^{-1}$), cod at Howth ($0.15\mu\text{g}\cdot\text{g}^{-1}$), and monkfish at Rossaveel ($0.15\mu\text{g}\cdot\text{g}^{-1}$).

Heavy Metals

For heavy metal determination, 10 fish samples comprising 5 species were analysed for copper, cadmium, lead, zinc and chromium. Where possible, these fish were chosen as examples of flat, round and oily fish groups

There are no internationally agreed standards or guidelines available for heavy metals in fish for human consumption. Various individual countries have set standard or guidance values and in 1992 the Joint Monitoring Group (JMG) of the Oslo and Paris Conventions for the Prevention of Marine Pollution (OSPAR) produced a compilation of standards and guidance values for contamination in fish (JMG 17/3/10-E). A synopsis of the strictest values used by the Contracting Parties to OSPAR is given in Annex 2. The results of all the analyses undertaken on fish tissue collected during 1995 were within these values. Details are given in Table 3.

Cadmium results were low, all being less than $0.006\mu\text{g}\cdot\text{g}^{-1}$. These results are well below the Dutch 1992 standard of $0.1\mu\text{g}\cdot\text{g}^{-1}$.

Copper concentrations ranged from 0.094 to $0.41\mu\text{g}\cdot\text{g}^{-1}$. The highest value was detected in mackerel landed at Dunmore East. The Norwegian guidance value for copper is $10\mu\text{g}\cdot\text{g}^{-1}$.

The highest concentration of lead found was $0.078\mu\text{g}\cdot\text{g}^{-1}$ in plaice landed at Killybegs. The Dutch standard is $0.5\mu\text{g}\cdot\text{g}^{-1}$ for lead.

Zinc levels ranged from 2.24 to $3.90\mu\text{g}\cdot\text{g}^{-1}$, the highest level was measured in Lemon Sole landed at Howth. The only guideline available for zinc is a 1992 UK level of $50\mu\text{g}\cdot\text{g}^{-1}$.

There is no guideline or standard given for chromium in fish flesh, but the levels found were very low, ranging from 0.015 up to $0.13\mu\text{g}\cdot\text{g}^{-1}$.

Chlorinated hydrocarbons

There are no internationally agreed standards for chlorinated hydrocarbons in fisheries products. The strictest standards and guidance values for these compounds as applied by Contracting Parties to the Oslo and Paris Conventions are given in Annex 3.

Chlorinated hydrocarbon analyses were carried out on 15 tissue samples, comprising 8 species. The results of these analyses are shown in Table 3. They are low when compared with the values given in Annex 3. The oily fish – mackerel and herring – had the highest levels. This is to be expected due to the lipophilic nature of these compounds. Herring landed at Howth gave the highest results for CB101, 153,138 and p,p'DDE. These results are still substantially lower than the strictest standards and guidance values of the OSPAR Contracting Parties.

Conclusion

Based on the analyses of the 1995 samples, mercury concentration in the commercial catch landed at Irish ports is low, which confirms previous studies (O' Sullivan *et al.*, 1991, Nixon *et al.*, 1991, Nixon *et al.*, 1993, Nixon *et al.*, 1994.). All samples tested were within the limits set by the European Commission's Decision of 19 May 1993.

Heavy metal and chlorinated hydrocarbon concentrations are also very low. All results were well below the strictest standards and guidance values of OSPAR Contracting Parties. This is indicative of the unpolluted nature of Irish waters and fisheries products.

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Acknowledgements

The authors wish to thank Dr. Christopher Moriarty for his editorial assistance and the fishermen and fisheries co-ops who provided samples for the programme.

Table 1: Results of the analyses of certified reference materials obtained during the 1995 monitoring programme.

CRM	Certified Value	FRC Value	No. of Analyses
Dogfish muscle DORM-1	$\mu\text{g.g}^{-1}$ dry wt.	$\mu\text{g.g}^{-1}$ dry wt.	
Chromium	3.60 ± 0.40	3.09 ± 0.24	6
Cadmium	0.086 ± 0.012	0.088 ± 0.008	6
Copper	5.22 ± 0.33	5.50 ± 0.38	6
Lead	0.40 ± 0.12	0.46 ± 0.06	4
Mercury	0.798 ± 0.074	0.83 ± 0.03	6
Zinc	21.3 ± 1.0	19.61 ± 0.33	6
Cod Liver Oil CRM 349	$\mu\text{g.kg}^{-1}$ dry wt.	$\mu\text{g.kg}^{-1}$ dry wt.	
CB 28	68 ± 7	67 ± 18	3
CB 52	149 ± 20	142 ± 12	3
CB 101	370 ± 17	346 ± 43	3
CB 118	454 ± 31	433 ± 128	3
CB 153	938 ± 40	939 ± 129	3
CB 180	280 ± 22	273 ± 45	3

Table 2: Mercury concentration ($\mu\text{g}\cdot\text{g}^{-1}$ wet weight) in the edible tissue of fish species landed at selected Irish ports during 1995.

	Species	Sample size	Length range mm	Length mean mm	Water content %	Hg $\mu\text{g}\cdot\text{g}^{-1}$
Castletownbere 16 June	<i>Megrim</i>	10	295 - 340	313	81.7	0.04
	<i>Whiting</i>	10	340 - 450	378	83.4	0.09
	<i>Plaice</i>	10	280 - 415	331	82.5	0.06
	<i>Lemon sole</i>	10	265 - 370	304	82.3	0.08
	<i>Black sole</i>	10	340 - 400	361	82.5	0.28
	<i>Cod nose end</i>	10	510 - 660	560	82.0	0.12
	<i>Cod tail end</i>	10	510 - 660	560	82.5	0.11
	<i>Monk</i>	10	345 - 615	454	83.4	0.10
	<i>Skate</i>	5	550 - 725	637	77.7	0.06
	<i>Haddock</i>	10	345 - 415	388	81.4	0.05
	<i>Hake</i>	10	350 - 455	399	82.5	0.04
	<i>Tuna</i>	5	660 - 730	684	67.3	0.08
Dunmore East 22 June	<i>Prawns</i>	10	NA	NA	79.8	0.10
	<i>Mackerel</i>	10	270 - 310	288	81.2	0.03
	<i>Plaice</i>	10	290 - 365	317	80.0	0.05
	<i>Witch</i>	10	270 - 460	367	82.5	0.05
	<i>Megrim</i>	10	325 - 470	373	79.3	0.19
	<i>Monk</i>	10	410 - 640	490	82.5	0.10
	<i>Haddock</i>	10	350 - 540	432	79.2	0.06
	<i>Cod</i>	10	490 - 670	573	80.2	0.13
	<i>Whiting</i>	10	325 - 470	365	81.0	0.08
Howth 14 June	<i>Lemon sole</i>	10	245 - 310	275	78.6	0.04
	<i>Plaice</i>	10	318 - 376	345	80.2	0.06
	<i>Cod</i>	10	574 - 795	704	81.1	0.15
	<i>Ray</i>	10	476 - 640	560	76.7	0.10
	<i>Haddock</i>	10	350 - 522	451	80.7	0.08
	<i>Whiting</i>	10	272 - 385	339	80.8	0.08
Killybegs 6 June	<i>Megrim</i>	10	375 - 495	434	80.8	0.12
	<i>Herring</i>	10	255 - 295	281	72.6	0.07
	<i>Monk</i>	10	485 - 580	530	83.2	0.13
	<i>Whiting</i>	10	325 - 403	363	83.6	0.13
	<i>Haddock</i>	10	315 - 400	370	82.4	0.06
	<i>Plaice</i>	10	285 - 325	303	83.1	0.09
	<i>Haddock</i>	10	315 - 400	370	82.7	0.07
	<i>Codling</i>	7	360 - 550	426	81.5	0.08
	<i>Hake</i>	10	360 - 470	426	81.4	0.08
Rossaveel 8 June	<i>Haddock</i>	10	345 - 493	410	80.5	0.08
	<i>Megrim</i>	10	277 - 411	314	79.7	0.05
	<i>Cod</i>	10	355 - 452	404	81.3	0.08
	<i>Whiting</i>	10	340 - 450	408	81.5	0.07
	<i>Plaice</i>	25	286 - 327	306	81.6	0.08
	<i>Prawns</i>	10	30 - 43	34	80.8	0.08
<i>Monk</i>	10	312 - 470	385	83.6	0.15	

Table 3a: Heavy metal and chlorinated hydrocarbon concentrations in the edible tissue of fish species landed at selected Irish ports during 1995. (Lengths, water content and sample size are as Table 2.)

	Dunmore East			Howth			Rossaveel	
	22 June			14 June/ 25 Sept.			8 June	
	<i>Mackerel</i>	<i>Plaice</i>	<i>Cod</i>	<i>Plaice</i>	<i>Cod</i>	<i>Herring</i>	<i>Haddock</i>	<i>Megrim</i>
Metals - $\mu\text{g.g}^{-1}$ wet wt.								
Cadmium	0.002	<0.006	<0.006	0.001	<0.006	N.A.	N.A.	N.A.
Copper	0.41	0.14	0.12	0.14	0.12	N.A.	N.A.	N.A.
Lead	<0.004	0.046	0.009	0.006	0.009	N.A.	N.A.	N.A.
Zinc	2.2	3.8	2.9	3.9	3.1	N.A.	N.A.	N.A.
Chromium	0.01	0.1	0.02	0.08	0.03	N.A.	N.A.	N.A.
Chlorinated hydrocarbons - $\mu\text{g.kg}^{-1}$ wet wt.								
CB Congener 28	0.27	0.02	0.02	<0.09	0.02	0.67	<0.06	<0.06
CB Congener 31	0.20	0.02	<0.11	0.03	0.11	0.45	<0.06	<0.06
CB Congener 52	0.37	0.02	0.05	0.04	0.03	1.13	<0.05	<0.05
CB Congener 101	0.77	0.04	0.06	0.04	0.07	2.75	<0.08	0.004
CB Congener 118	0.51	0.06	0.20	0.04	0.13	2.64	<0.05	0.01
CB Congener 153	1.60	0.18	0.57	0.07	0.37	7.17	0.003	0.01
CB Congener 156	0.09	<0.1	0.03	0.01	0.02	0.43	<0.04	<0.04
CB Congener 105	0.19	0.02	0.07	0.03	0.05	1.19	<0.04	<0.04
CB Congener 138	1.35	0.13	0.02	0.11	0.26	6.18	0.003	0.01
CB Congener 180	0.45	0.05	0.24	0.06	0.14	2.23	<0.07	0.01
DDE-p,p'	1.20	0.12	0.12	0.08	0.21	5.94	<0.05	0.004
DDE-o,p'	<0.1	<0.1	<0.1	<0.08	<0.1	0.27	<0.05	<0.05
DDT-p,p'	0.23	0.02	0.02	0.15	0.02	5.12	<0.05	<0.05
DDD-p,p'	0.51	0.02	0.04	0.08	0.07	1.89	<0.05	<0.05
Lindane	1.98	0.07	0.05	0.13	0.05	1.36	<0.05	0.01
Dieldrin	1.56	0.10	0.20	0.21	0.10	5.96	<0.05	0.04
<i>trans</i> -Nonachlor	0.32	0.01	0.04	<0.08	0.05	1.05	<0.05	<0.05
Chlordane, alpha	0.39	0.02	0.02	0.08	0.01	0.73	<0.04	<0.04
Chlordane, gamma	0.05	<0.1	<0.1	<0.09	0.02	0.24	<0.05	<0.05
BHC, alpha	0.49	0.03	0.01	<0.09	0.02	0.55	<0.05	<0.05
HCB	0.73	0.05	0.06	0.11	0.07	1.26	0.01	0.02

N.A = not analysed

Table 3b: Heavy metal and chlorinated hydrocarbon concentrations in the edible tissue of fish species landed at Killybegs during 1995. (Lengths, water content and sample size are as in Table 2.)

	Killybegs							
	6 June							
	<i>Herring</i>	<i>Monkfish</i>	<i>Whiting</i>	<i>Haddock</i>	<i>Plaice</i>	<i>Haddock</i>	<i>Codling</i>	<i>Hake</i>
Metals - $\mu\text{g.g}^{-1}$								
Cadmium	0.002	N.A.	N.A.	N.A.	0.001	N.A.	<0.006	<0.006
Copper	0.43	N.A.	N.A.	N.A.	0.13	N.A.	0.1	0.09
Lead	<0.004	N.A.	N.A.	N.A.	0.078	N.A.	<0.085	<0.085
Zinc	3.3	N.A.	N.A.	N.A.	3.2	N.A.	2.5	2.3
Chromium	0.07	N.A.	N.A.	N.A.	0.03	N.A.	0.02	0.13
Chlorinated hydrocarbons - $\mu\text{g.kg}^{-1}$								
CB Congener 28	0.44	0.03	<0.06	<0.06	0.10	0.01	0.01	N.A.
CB Congener 31	0.35	0.02	<0.06	<0.06	0.07	0.01	<0.08	N.A.
CB Congener 52	0.49	<0.05	<0.05	<0.05	0.02	<0.05	0.03	N.A.
CB Congener 101	0.82	0.01	<0.08	0.003	0.03	0.003	0.06	N.A.
CB Congener 118	0.86	<0.05	<0.05	0.01	0.06	0.01	0.05	N.A.
CB Congener 153	1.08	<0.06	<0.06	0.01	0.05	0.004	0.14	N.A.
CB Congener 156	0.04	<0.04	<0.04	<0.04	0.01	<0.04	0.01	N.A.
CB Congener 105	<0.08	<0.04	<0.04	<0.04	0.04	<0.04	0.04	N.A.
CB Congener 138	0.84	<0.05	<0.05	0.01	0.06	<0.004	0.20	N.A.
CB Congener 180	0.26	<0.07	<0.07	<0.004	0.03	0.003	0.10	N.A.
DDE-p,p'	2.33	0.01	<0.05	0.01	0.05	0.01	0.05	N.A.
DDE-o,p'	<0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.08	N.A.
DDT-p,p'	0.57	<0.05	<0.05	<0.05	0.05	<0.05	0.28	N.A.
DDD-p,p'	0.84	0.02	<0.05	<0.05	<0.05	<0.05	0.21	N.A.
Lindane	1.74	0.02	0.02	0.02	0.03	0.02	0.20	N.A.
Dieldrin	2.12	0.11	0.07	0.06	0.07	<0.05	0.34	N.A.
<i>trans</i> -Nonachlor	1.12	<0.05	<0.05	<0.05	<0.05	<0.05	<0.08	N.A.
Chlordane, alpha	0.70	<0.04	<0.05	<0.04	<0.04	<0.04	0.08	N.A.
Chlordane, gamma	<0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.09	N.A.
BHC, alpha	0.04	<0.05	<0.05	<0.05	<0.05	<0.05	0.08	N.A.
HCB	0.86	0.03	0.01	0.02	0.10	0.03	0.24	N.A.

N.A = not analysed

Annex 1: Selected species, as listed by the European Commission Decision, where the higher acceptable limit of 1.0 µg.g⁻¹ total mercury concentration applies.

Common Name	Species Name
Sharks	all species
Tuna	<i>Thunnus spp.</i>
Little tuna	<i>Euthynnus spp.</i>
Bonito	<i>Sarda spp.</i>
Plain bonito	<i>Orcynopsis unicolor</i>
Swordfish	<i>Xiphias gladius</i>
Sailfish	<i>Istiophorus platypterus</i>
Marlin	<i>Makaira spp.</i>
Eel	<i>Anguilla spp</i>
Bass	<i>Dicentrarchus spp</i>
Sturgeon	<i>Acipenser spp.</i>
Halibut	<i>Hippoglossus hippoglossus</i>
Redfish	<i>Sebastes marinus, S. mentella</i>
Blue ling	<i>Molva dipterygia</i>
Atlantic catfish	<i>Anarhichas lupus</i>
Pike	<i>Esox lucius</i>
Portuguese dogfish	<i>Cantroscymnes coelolepis</i>
Rays	<i>Raja spp.</i>
Scabbardfishes	<i>Lepidopus caudatus, Aphanopus carbo</i>
Anglerfish	<i>Lophius spp.</i>

Annex 2: Heavy metal standard and guidance values for fish tissue - the strictest values applied by Contracting Parties to OSPAR

Contamination	Unit	Qualifiers*	Country
Cadmium	0.1 $\mu\text{g}\cdot\text{g}^{-1}$	W/S	Netherlands
Copper	10 $\mu\text{g}\cdot\text{g}^{-1}$	W/G	Norway
Lead	0.5 $\mu\text{g}\cdot\text{g}^{-1}$	W/S	Netherlands
Mercury	0.3 $\mu\text{g}\cdot\text{g}^{-1}$	W/S	Denmark
Zinc	50 $\mu\text{g}\cdot\text{g}^{-1}$	W/G	U.K.

*W = wet weight; S = standard; G = Guidance value

Annex 3: Chlorinated hydrocarbon standard values for fish - the strictest values applied by Contracting Parties to OSPAR.

Contamination	Unit	Qualifiers*	Country
DDT and its transformation products	500 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	Finland
HCB	50 $\mu\text{g}\cdot\text{kg}^{-1}$	W/G	Norway
$\alpha + \beta$ HCH	50 $\mu\text{g}\cdot\text{kg}^{-1}$	W/G	Norway
γ HCH	100 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	Finland
$\alpha+\beta+\gamma$ HCH	200 $\mu\text{g}\cdot\text{kg}^{-1}$	W/G	Norway/Sweden
PCBs	1000 $\mu\text{g}\cdot\text{kg}^{-1}$	W/G	Norway
CB Congener 28	80 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	FR Germany
CB Congener 52	40 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	Netherlands
CB Congener 101	80 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	FR Germany/Netherlands
CB Congener 118	80 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	Netherlands
CB Congener 138	100 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	FR Germany/Netherlands
CB Congener 153	100 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	FR Germany/Netherlands
CB Congener 180	80 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	FR Germany
Aldrin + dieldrin	100 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	Finland
Lindane	100 $\mu\text{g}\cdot\text{kg}^{-1}$	W/S	Finland

*W = wet weight; S = standard; G = Guidance value

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ISSN 0332-4338