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Further data on heavy metals and organochlorines in marine mammals from German coastal waters.

by

U.Harms [1)]

H.E.Drescher [2)]

and

E.Huschenbeth [3)]

1) Bundesforschungsanstalt für Fischerei, Isotopenlaboratorium
Hamburg, Federal Republic of Germany

2) Neue Universität, Institut für Haustierkunde
Kiel, Federal Republic of Germany

3) Bundesforschungsanstalt für Fischerei, Institut für Küsten- und Binnenfischerei
Hamburg, Federal Rpublic of Germany

Introduction

It is the aim of this study to present further data on the residues of chlorinated hydrocarbons and heavy metals in the organism of seals and whales from the North Sea and the Baltic. Tissues of selected organs of 3 species of seals and 3 species of whales are analysed for their contents of PCB, DDT, Dieldrin, Lindane, Cu, Cd, Zn, Pb and Hg. The marine mammals, resident in the North Sea and the Baltic, in particular the harbour seal Phoca vitulina and the harbour porpoise Phocoena phocoena, are of a major interest in this study. The inclusion of nonresident migrating species in the investigations can contribute to the knowledge of the global distribution of the biocides.

The extent of the contamination of marine ecosystems with biocides is particularly evident in the higher trophic levels. The marine mammals of the North Sea and the Baltic are the final links of the food web in these ecosystems. They are particularly endangered by the accumulating pesticides and heavy metals: effects, for instance, of PCB on the reproduction of seals, have been recorded by HELLE et al. (1976). Marine mammals are important indicator organisms for the marine ecosystem as well as for humans.

Fish is the major food source of the marine mammals investigated in this study. Observations on heavy metals and chlorinated hydrocarbons in fish are used in this article to illustrate the amount of contamination in this trophic level. The data on heavy metal and organochlorine residues in fish from German coastal and offshore waters originate from former basic investigations carried out in 1973-1975 (HUSCHENBETH 1973, HARMS 1975). Further informations on fish from areas off the German North Sea coast are taken from international monitoring studies in the North Sea. Reference is made in this connection to the ICES COOPERATIVE RESEARCH REPORT Nr.58 (1974).

First results on organochlorines and heavy metals in the harbour seal have been published in an earlier report (DRESCHER, HARMS, HUSCHENBETH 1977). Continuing this study, more adult harbour seals have been included. Investigations on the harbour porpoise were carried out according to a resolution of the ICES (C.Res.1976/4:25), formulated at the meeting in Copenhagen in 1976 following a contribution on the decline of this species in the Baltic Sea (OTTERLIND 1976). All harbour porpoises found dead should be investigated for contaminants in their organism.

Material and Methods

All marine mammals investigated in this study have been collected from the North Sea and the Baltic coasts of Schleswig-Holstein (Federal Republic of Germany). The following species are included in the study:

Phoca vitulina: 70 individuals of known age and sex; North Sea.

Phoca hispida: 1 subadult female; North Sea.

Halichoerus grypus: 1 subadult male; North Sea.

Phocoena phocoena: 3 individuals; North Sea (1); Baltic Sea (2).

Hyperoodon ampullatus: 1 individual; North Sea.

Delphinapterus leucas: 1 individual; Baltic Sea.

Investigations on the harbour seals started in 1974. The harbour seals were shot or found dead. The ringed seal died shortly after being found (DRESCHER 1977), and the grey seal was shot. The harbour porpoises and the bottlenose whale stranded on the beach, while the beluga was drowned caught in a fishing net.

Heavy metals

Sample solutions for analyses of the heavy metals zinc, copper, cadmium, lead, and mercury were prepared by wet digestion of the organic material by means of concentrated perchloric and nitric acid as described in a previous publication (HARMS 1975).

Measurements were performed by flame atomic absorption spectrophotometry (Cu and Zn), by flameless atomic absorption with a heated graphite atomizer (Cd and Pb) and by the cold vapour atomic absorption method (Hg).

In order to obtain reliable measurements of extremely small quantities of cadmium (<0.01 µg/g) and lead (<0.1 µg/g) a micro-solvent-extraction procedure with dithizone as chelating reagent and toluene as solvent was developed. The method yielded a recovery of more than 95% as determined by means of radioisotopic tracer techniques. The solvent extraction followed by flameless AAS resulted in detection limits (threefold standard deviation of the value of the blank) of 0.0002 µg/g for cadmium and 0.002 µg/g for lead.

Organochlorines and PCB

The method of the analysis of organochlorines and PCB is identical with that described by HUSCHENBETH(1973). The reliability of the results was affirmed in several international intercalibration excercises (HUSCHENBETH 1977).

Results and discussion

1. Heavy metals

The results on the content of heavy metals in muscle, liver and partially in kidney of whales and in liver of the ringed and grey seal are summarized in Table 1. A comparison of the metal contents in muscle and liver tissue of fish and the harbour seals is given in figure 1.

The concentrations of Cu and Zn in muscle and liver tissue do not alter markedly from fish to the higher level of marine mammals.

The elements Cu and Zn contribute vital functions to the metabolism of fish, whales and seals and there is evidence that the animals can regulate the metal levels in their organs and tissues. The values of different year classes are probably log-normally distributed with a prevalence of values lower than the mean. However there was no reliable indication of elevated Cu and Zn contents with increased age in either of the species analysed.

The analytical results of Cd and Pb provide also no convincing data of an increase in the concentration of both elements at the higher trophic level of marine mammals. Compared with the muscle tissue the liver shows increased levels probably due to its higher metabolic turnover.

A certain net increase in liver tissue element concentration in older seals could be detected. However, due to the considerable high variability of data within the different year classes, a significant relation between age and Cd and Pb contents could not be ascertained.

The cadmium data of seal kidney provide a far better impression of an age dependent accumulation.

Juvenile seals, on an average, revealed cadmium values of 0.1 µg/g, while adult seals of 6-7 years showed Cd contents upto 1 µg per g.

The level of confidence of lead and cadmium data is certainly lower than that of the other metals mentioned above.

For both elements, data are often reported to be near or below the level of detection in the methods used by the workers.

During the analytical procedure in this study a method sufficiently sensitive to detect cadmium at a level of 0.00X µg/g was used. The same applies to the detection of lead, where levels of 0.0X µg/g were found.

This may give the reason why values of Cd and Pb published in this paper are lower than those reported by other workers (ROBERTS et al. 1976) who used methods with higher detection limits.

It has been found that fish from the North Sea, off the German coasts, contain an average of 0.06 µg/g mercury in their muscle tissue. Fish from onshore fishing grounds frequently contain values up to 0.13 µg/g.

There is no obvious indication of higher mercury residues in the liver of fish. In contrast to copper, zinc, cadmium and lead mercury levels in the liver of fish tend to be the same or slightly lower than in the muscle tissue.

In general terms it appeared that mercury was mainly accumulated in the liver of the investigated marine mammals. In the present study the highest total mercury level up to 160 µg/g was found in some of the oldest seals.

Mercury levels in other tissues of seals examined were substantially lower, ranging 1.6 - 12.5 µg/g in the kidney, 1-10 µg/g in the muscle tissue and 0.1-1.4 µg/g in the brain.

A simular gradation between the mercury content in the muscle and liver tissue could also be recognized in harbour porpoises. The mercury content in the liver tissue increased with the size of the animals. This may indicate an age dependent relationship.

An examination of the seal data of different age classes implied that a relationship existed between the mercury concentration in liver tissue and age of the animals.

In a recently published paper on the "determination of heavy metals in tissues of the common seal" by ROBERTS et al.(1976) this hypothesis was strongly supported.

The results of these workers are reproduced in figure 2, showing three regression curves (marked with an asterisk) of age accumulation of mercury in the liver tissue of the common seals from the coast off the Netherlands, East Anglia and West Scotland.

The regression equation for age accumulation in the liver tissue of seals from the German North Sea coast can be expressed by a double logarithmical function, lg concentration = a + b · lg age (concentration in $\mu g/g$, age in years), which correspond to the plot of ROBERTS et al. mentioned above.

On the basis of this diagram one can deduce that mercury accumulation in the liver of adult seals from the German North Sea coast is higher ($p < 0.01$) than in the liver of seals off the British east coast and the Scottish west coast but lower than in the liver of animals from the coast off the Netherlands.

Mercury in marine fish from the North Atlantic is present almost entirely as methylmercury (WESTÖÖ 1967, JÖRISSEN 1974, WESTÖÖ 1975).

As the diet of seals and marine mammals under study consists mainly of fish one would expect a similarly appreciable high percentage of organically bound mercury in these animals.

However in the harbour porpoises analysed in this study the amount of methylmercury in liver tissue, expressed as percentage of total mercury, was low (about 20%) and in the seals the values ranged from 8-65%. The percentage of methylmercury was lowest in seal specimens with highest total mercury contents, i.e. in the older animals. The fraction of methylmercury was higher in juvenile animals that exhibited lower total mercury contents. Similar figures were published by GASKIN et al. (1972, 1973) for harbour seal (<u>Phoca vitulina</u>) and harbour porpoises (<u>Phocoena phocoena</u>)

from the Bay of Funday region, by BUHLER et al. (1975) for California sea lions (<u>Zalophus californianus californianus</u>) and by KOEMAN et al. (1975) as well as by ROBERTS et al. (1976) for seals from the North Sea off the coast of the Netherlands and the UK, respectively.

All these data give strong support to the hypothesis, as expressed by BUHLER (1975), that a demethylation process of ingested methylmercury occurs in the liver of marine mammals, followed by a retention of inorganic mercury in this organ.

2. PCB and organochlorines

The results of PCB and organochlorine content in the fat and liver of the whales and the ringed seal analysed in this study are summarized in Table 2.

In the toothed whales, the PCB content in the blubber samples ranged from 6.2 μg/g in the white whale to 140 μg/g in one of the harbour porpoises.

For comparison the results of TARUSKI et al. (1975) are cited, that revealed a range of 0.7 μg/g to 147 μg/g for blubber samples of toothed whales of the east and west coasts of North America.

The concentrations of total DDT in whale blubber were lower than those of the PCBs, ranging from 2.4-45.8 μg/g. In this connection reference is made to a publication of GASKIN et al. (1971), who found total DDT values up to 520 μg/g in the depot fat of harbour porpoises of the east coast of Canada.

In general in warm-blooded animals, where the metabolism of organochlorines is accelerated, the DDE value is significantly higher as compared to the values of TDE and DDT. (Table 2)

As has previously been shown for harbour seals, the pesticides Lindane and Dieldrin were also low in the whales analysed, with one exception of a higher Dieldrin value (4.48 μg/g) in the blubber of a harbour porpoise. In general it appeared from the data obtained that the contamination levels of PCB and total DDT were of similar magnitude in harbour seal and harbour porpoise.

Because of their lipophylic nature, the persistent environmental contaminants DDT and PCB tend to accumulate in tissues with high lipid contents so that the highest tissue residues are found in body fat. In figure 3 the prevailing total DDT and PCB levels in fish are plotted in contrast to those in seal. The pesticide burden of the various tissues of the species analysed is almost certainly a reflection of their lipid content. As reported in the earlier paper (DRESCHER et al. (1977) high contaminations of PCB and total DDT were already present in very young seals, and no specific relation to age could be found. One can conclude that organochlorine concentrations in fat tissue of these animals are probably not a function of exposure over time, and that high levels are correlated with feeding behaviour rather than with long individual life span.

Summary

Studies on heavy metals and organochlorines in harbour seals from the Waddensea of Northern Germany were continued. The investigations were also extended to other marine mammals found on the German North Sea and Baltic coasts: grey seal (1), ringed seal (2), harbour porpoise (3), beluga (1), bottlenose whale (1).

No significant differences seem to occur in the copper, zinc, cadmium and leads contents of whales as compared to seals. And the level of contamination of these elements in muscle and liver tissue do not altermarkedly from fish to the higher trophic level of marine mammals. There is a distinctly higher accumulation of mercury in the liver of the marine mammals analysed as compared to fish. High levels in seals could be correlated with long life span of the animals. In contrast to fish a high proportion of the total mercury in the liver of harbour seals and harbaour porpoises was present as inorganic mercury.

The contamination levels of PCB and total DDT were of similar magnitude in harbour seal and toothed whales.

Because of their lipophylic nature, the persistent organochlorines tend to accumulate in tissues with high lipid contents so that the highest tissue residues are found in body fat (blubber).

A specific relation of PCB and total DDT levels in blubber to age (size) could not be foùnd, and high values are probably correlated with feeding behaviour rather than with long individual life span.

References

BUHLER, D.R., R.R.CLAEYS and B.R.MATE, 1975: Heavy metal and chlorinated hydrocarbon residues in california sea lions (Zalophus californianus californianus). J.Fisheries Research Board of Canada 32:2391-2397

DRESCHER, H.E., 1977: Über den Fund einer Kegelrobbe, Phoca hispida, an der Nordseeküste von Schleswig-Holstein Zoologischer Anzeiger (Jena), in press.

DRESCHER, H.E., U.HARMS and E.HUSCHENBETH, 1977: Organochlorines and heavy metals in the harbour seal (Phoca vitulina) from the German North Sea coast. Marine Biology 41:99-106

GASKIN, D.E., M.HOLDRINET and R.FRANK, 1971: Organochlorine pesticide residues in harbour porpoises from the Bay of Fundy Region. Nature Vol. 233:499-500

GASKIN, D.E., K.ISHIDA and R.FRANK, 1972: Mercury in harbour porpoises (Phocoena phocoena) from the Bay of Fundy Region. J.Fisheries Research Board of Canada 29:1644-1646

GASKIN, D.E., R.FRANK, M.HOLDRINET, K.ISHIDA, C.J.WALTON and M.SMITH, 1973: Mercury, DDT and PCB in harbour seals (Phoca vitulina) from the Bay of Fundy and Gulf of Maine. J.Fisheries Research Board of Canada 30:471-475

HARMS, U, 1975: The levels of heavy metals (Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Hg) in fish from onshore and offshore waters of the German Bight. Z.Lebensmittelunters.-u.Forsch.157:125-132

HELLE, E., M.OLSSON and S.JENSEN, 1976: PCB levels correlated with pathological changes in seal uteri. Ambio 5:261-263

HUSCHENBETH, E., 1973: Zur Speicherung von chlorierten Kohlenwasserstoffen in Fisch. Arch.Fisch.Wiss.24:105-116

HUSCHENBETH, E., 1977: Fortführung der Untersuchungen zur Speicherung von chlorierten Kohlenwasserstoffen in Fischen in den Jahren 1973-1976. Arch.Fisch.Wiss., in press

ICES COOPERATIVE RESEARCH REPORT Nr.58, 1974: The ICES coordinated monitoring programme in the North Sea.

JÜRISSEN, U., 1974: Analytik und Vorkommen des Gesamt- und Methyl-Quecksilbers in Lebensmitteln.
Inaugural-Dissertation Westf. Wilhelms-Universität Münster

KOEMAN, J.H., W.S.M.van de VEN, J.J.M.de GEIJ, P.S.TJIOE and J.L.van HAAFTEN, 1975: Mercury and Selenium in marine mammals and Birds.
The Science of the Total Environment 3:279-287

OTTERLIND, G., 1976: The harbour porpoise (Phocoena phocoena) endangered in Swedish waters.
ICES C.M.1976/N:16
Marine Mammals Committee

ROBERTS, T.M., P.B.HEPPLESTON and R.D.ROBERTS, 1976: Distribution of heavy metals in tissues of the common seal (Phoca vitulina).
Marine Pollution Bulletin 7:194-196

TARUSKI, A.G., C.E.OLNEY and H.E.WINN, 1975: Chlorinated hydrocarbons in cetaceans.
J.Fish.Res.Board Can.32:2205-2209

WESTÖÖ, G., 1967: Determination of methyl Hg compounds in foodstuffs.
Acta Chem.Scand.21:1790-1800

WESTÖÖ, G. and B.OHLIN, 1975: Methylmercury levels in fish and shellfisch, February 1971-July 1974.
Var föda 27, Suppl.Nr.1

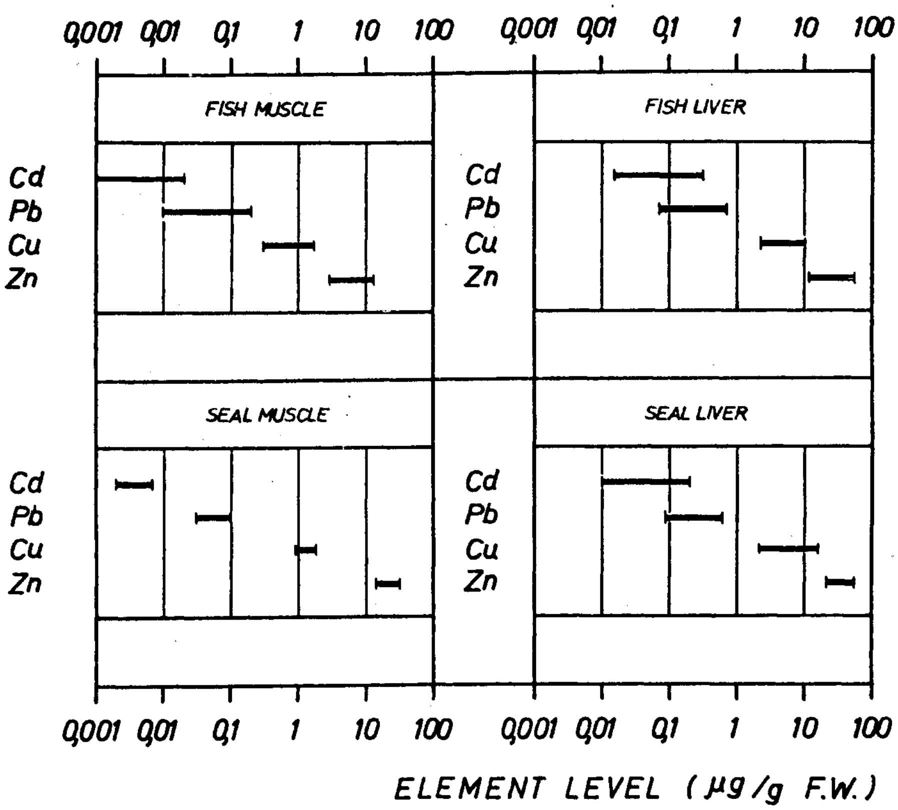

Figure 1: Prevailing levels of heavy metals copper, zinc, cadmium and lead in liver and muscle tissue of fish (cod, plaice, flounder, herring) and harbour seal.

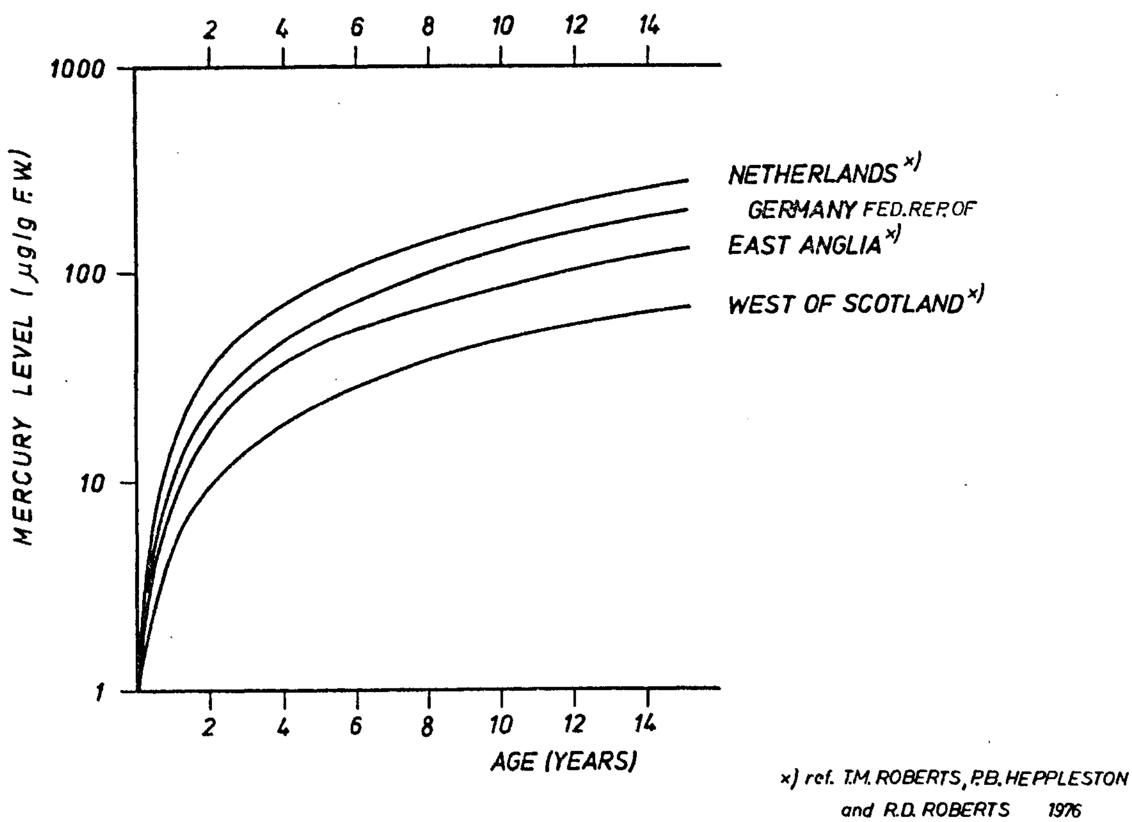

Figure 2: Age accumulation of mercury in liver tissue of the harbour seal.

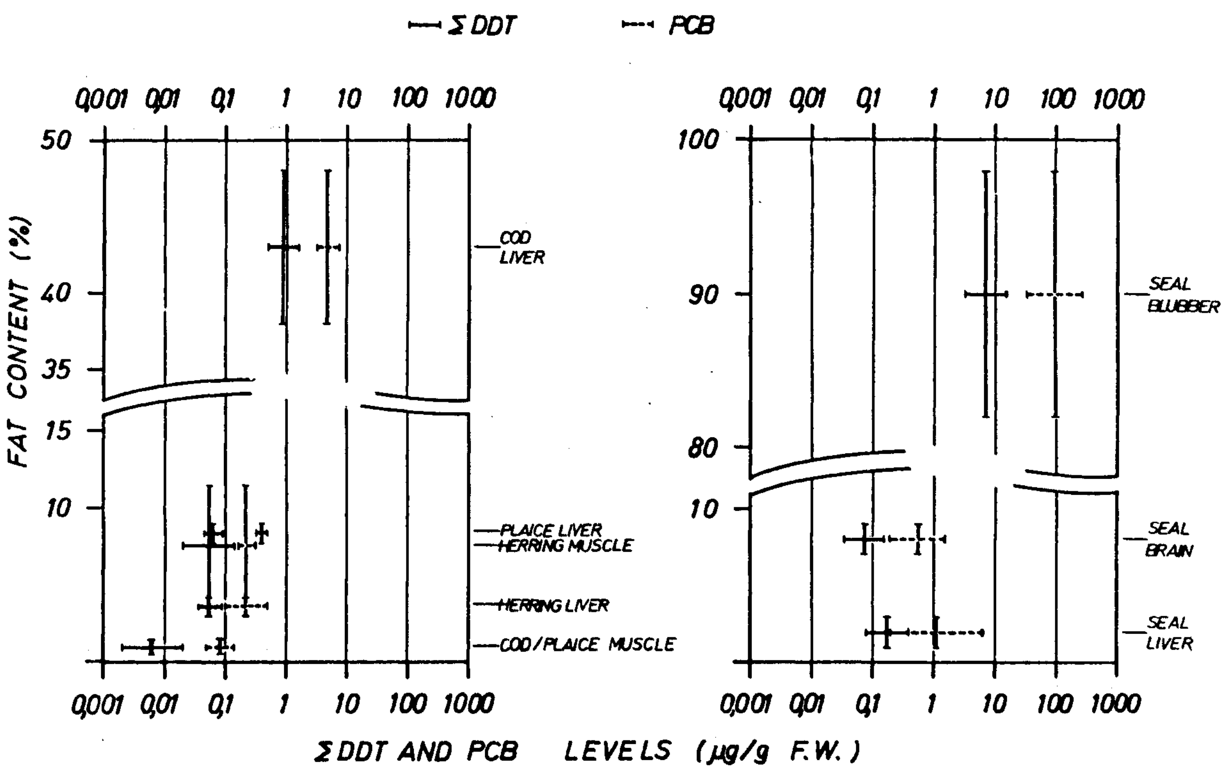

Figure 3: Prevailing levels of total DDT and PCB in relation to fat content in tissues of fish and harbour seal.

Table 1: Heavy metals in marine mammals from German coastal waters.

Data relate to fresh weight. (abbreviations: f = female, m = male)

Characterization of species analysed	Cu (µg/g) muscle	Cu liver	Cu kidney	Zn (µg/g) muscle	Zn liver	Zn kidney	Cd (µg/g) muscle	Cd liver	Cd kidney	Pb (µg/g) muscle	Pb liver	Pb kidney	Total Hg (µg/g) muscle	Total Hg liver
HARBOUR PORPOISE (Phocoena phocoena)														
1:length 80 cm, f. Baltic, 0.7.76.	2.7	15.0		21.0	50.0		0.002	0.023		0.03	0.17		0.15	0.70
2:length 126 cm, m. Baltic, 12.76	1.8	4.0	3.1	12.4	34.0	20.0	0.002	0.025	0.077	0.07	0.43	0.15	0.92	2.5
3:length 153 cm, f. North Sea, 01.77.	2.1	6.0	3.2	14.4	49.0	24.0	0.006	0.19	0.95	0.05	0.35	0.17	3.3	26.0
BOTTLENOSE WHALE (Hyperoodon ampullatus) length 570 cm, m. North Sea, 03.76.	0.55	2.8		13.5	23.0		0.040	5.6		0.03	0.18		0.33	0.38
BELUGA WHALE (Delphinapterus leucas) length 271 cm, m. Baltic, 12.76	1.1	20.4	3.1	20.0	32.0	29.5	0.007	0.90	1.9	0.08	0.36	0.13	1.6	4.4
RINGED SEAL (Phoca hispida) length 84 cm, f. North Sea, 08.75.		2.1			40.0			0.31			0.24			0.64
GREY SEAL Halichoerus gryphus) age 24 months, m. North Sea, 11.75		20.9			61.0			0.021			0.31			19.5

Table 2: Organochlorine and PCB residues in marine mammals from German coastal waters.

Data relate to fresh weight. (abbreviations: f = female, m = male, bl. = blubber, liv. = liver)

Characterization of species analysed	Hexane-extractable fat (%)		PCB (µg/g)		DDT (µg/g)		TDE (µg/g)		DDE (µg/g)		Σ DDT (µg/g)		Lindane (µg/g)		Dieldrin (µg/g)	
	bl.	liv.	bl.	liv.	bl.	liv.	bl.	liv.	bl.	liv.	bl.	liv.	bl.	liv.	bl.	liv.
HARBOUR PORPOISE (Phocoena phocoena)																
1: length 80 cm, f. Baltic, 0.7.76.	87.9	4.0	140.0	10.0	9.2	0.14	13.5	0.73	23.2	0.94	45.9	1.8	1.1	0.029	4.5	0.076
2: length 126 cm, m. Baltic, 12.76	91.8	2.7	88.6	2.4	8.0	0.040	8.1	0.19	13.2	0.14	29.3	0.37	0.47	0.012	1.9	0.050
3: length 153 cm, f. North Sea, 0.1.77.	90.2	2.2	15.2	0.4	0.69	0.008	0.68	0.033	1.0	0.013	2.4	0.054	0.16	0.005	0.61	0.015
BOTTLENOSE WHALE (Hyperoodon ampullatus) length 570 cm, m. North Sea, 0.3.76	94.9		37.1		3.9		2.2		8.1		14.2		0.18		0.36	
BELUGA WHALE (Delphinapterus leucas) length 271 cm, m. Baltic, 12.76	94.7	2.7	6.2	0.34	3.0	0.008	2.8	0.040	2.7	0.043	8.5	0.091	0.36	0.008	1.1	0.091
RINGED SEAL (Phoca hispida) length 84 cm, f. North Sea, 0.8.75	82.0		15.0		2.3		2.3		2.4		7.0		0.24		0.24	