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Metals and Organochlorines in Sperm Whales (*Physeter macrocephalus*) Stranded around the North Sea during the 1994/1995 Winter

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During the winter of 1994/1995, some 21 sperm whales (*Physeter macrocephalus*) were stranded around the North Sea, on the coasts of the United Kingdom, Germany, Belgium and The Netherlands. This is an abnormally high number of strandings to occur on North Sea coasts. In both 1988 and 1990 32 sperm whales were stranded, but these were generally on the Atlantic coasts of the British Isles and Norway, rather than North Sea coasts (Berrow *et al.*, 1993). Evans (1992) has recorded a clear increase both in strandings of sperm whales on British and Irish coasts this century, and in sightings of groups of animals (rather than lone individuals) to the west of the British Isles. Both sightings and strandings of sperm whales between 1967 and 1990 were concentrated around Shetland, Orkney and the outer Hebrides, suggesting that their main approach to the land mass is from the north-west (Sheldrick *et al.*, 1991). Sperm whales are oceanic animals which rarely enter shallow or semi-enclosed areas of the sea, and are thought to approach close to shore only when sick (Martin, 1990). Females and immature animals remain in low latitudes, and only mature males venture into latitudes higher than about 40–45° in both hemispheres. In most areas, sperm whales feed almost exclusively on cephalopods (squid and octopus), although in a few areas, fish form an important component of their diet. For instance, close to the coast of Iceland, sperm whales were found to have been feeding primarily on deep-sea fish such as lumpsuckers, angler fish and red-fish which are found to depths of 500 m or more (Martin & Clarke, 1986). Prey are usually taken in midwater at depths greater than 400 m, although some bottom feeding also occurs. In the North Atlantic, sperm whales feed on the Grand Banks off Newfoundland, as well as on the continental slope to the west of the British Isles, and north towards Iceland (Evans, 1987; Martin, 1990). Male sperm whales may not find it easy to feed successfully in the shallow waters of the North Sea, which in the central and southern areas are less than 100 m in depth (A. R. Martin, pers. comm.).

Immediately after death, samples of blubber were collected from seven of the sperm whales stranded around the North Sea during the winter of 1994/1995, and a liver sample was also collected from one individual. As the internal temperature of sperm whales rises rapidly after death to the detriment of the internal organs, this represented an unusual opportunity to determine trace metal concentrations in sperm whale liver sampled in good condition. The samples were obtained through the Greenpeace Exeter Research Laboratory with appropriate CITES certification. Details of the dates and locations of strandings and biological information for each animal are given in Table 1 along with reference numbers which identify individual animals.

Blubber samples were analysed for organochlorine pesticides and metabolites, and a range of chlorobiphenyl (CB) congeners, using established methodology based upon analysis by gas chromatography with electron capture detection (Allchin *et al.*, 1989). This method was modified in the light of recommendations which followed the intercomparison programme organized under the auspices of the International Council for the Exploration of the Sea (de Boer *et al.*, 1992, 1994; de Boer & van der Meer, in press). Chlorobiphenyl congeners in all samples were also qualitatively confirmed by GC/MS analysis. Trace metals, arsenic and selenium were analysed in the liver sample using recently established methodology based upon acid digestion with microwave heating, followed (except for mercury) by analysis using inductively coupled plasma/mass spectrometry. Mercury was analysed using atomic fluorescence detection, following reduction with tin(II) chloride (Jones & Laslett, 1994). All analyses were conducted under an analytical quality protocol requiring the analysis of blanks and reference materials alongside each batch of samples. Further details of method performance are given elsewhere (Law *et al.*, 1991; Law, 1994).

Table 2 presents the concentrations of trace metals, As and Se in the liver sample. Concentrations of Cr and Ni were low at 0.79 and 0.39 mg kg^{-1} wet wt, respectively. Few data have been reported for these elements in marine mammalian liver, the maximum values to date being 2.0 mg kg^{-1} wet wt for Cr and 2.1 mg kg^{-1} wet wt for Ni. There is insufficient information at present to assess the significance of such concentrations, as the metal speciation in both prey and predator is unknown (Law, in press). The concentrations of Cu and Zn are believed to be homeostatically controlled in marine mammals and those seen in the sperm whale (2.3 mg kg^{-1} wet wt for Cu and 34 mg kg^{-1} wet wt for Zn) are towards the lower end of the ranges tentatively assigned (Law *et al.*, 1991; Law, in press). Arsenic has previously been determined in only a few species of marine mammals (harbour seals, common dolphins and pilot whales), the overall range of concentrations reported being 0.01–2.9 mg kg^{-1} wet wt (Law, in

TABLE 1
Locations, dates of stranding, and biological data for the sperm whales sampled.

Ref. no.	Date found	Location	Position	Age (years)	Length (m)	Blubber thickness (behind dorsal fin; mm)
UK4026	7/12/94	Sanday, Orkney Islands, UK	59°16′N 2°22′W	20+	12.3	130
UK4029	7/12/94	Sanday, Orkney Islands, UK	59°16′N 2°22′W	25+	13.2	115
UK4031	7/12/94	Sanday, Orkney Islands, UK	59°16′N 2°22′W	23+	13.4	100
MI4059	4/11/94	Baltrum Island, Wadden Sea	53°45′N 7°25′E	NK	13.9	110
MI5004	12/1/95	Kijkduin, Scheveningen, The Netherlands	52°08′N 4°15′E	NK	14.1	NK
MI5005	12/1/95	Kijkduin, Scheveningen, The Netherlands	52°08′N 4°15′E	NK	14.7	140*
MI5006	12/1/95	Kijkduin, Scheveningen, The Netherlands	52°08′N 4°15′E	NK	15.0	NK

NK: Not known.
*Blubber thickness measured laterally; no dorsal measurement taken.

TABLE 2
Concentrations of seven trace metals, arsenic and selenium in the liver of sperm whale MI5005 (mg kg^{-1} wet wt).

TS%	Cr	Ni	Cu	Zn	As	Se	Cd	Hg	Pb
31.4	0.79	0.39	2.3	34	0.71	11	30	34	0.11

TS%: Percentage dry matter.

press). Marine fish and invertebrates can contain quite high concentrations of As (up to 100 mg kg^{-1}), although the majority is present as organoarsenical compounds and is of relatively low toxicity. The concentration of As in the sperm whale liver was 0.71 mg kg^{-1} wet wt, i.e. within the previously reported range. The concentrations of Hg and Se were 34 and 11 mg kg^{-1} wet wt respectively, a Hg:Se molar ratio of 1.22. A molar ratio close to 1 results from the process by which marine mammals demethylate methylmercury and immobilize it as mercuric selenide, thereby detoxifying potentially toxic organomercurials ingested from their diet (Law, in press). No determination of methylmercury was conducted on this occasion.

The concentration of Cd was high at 30 mg kg^{-1} wet wt. High concentrations of Cd have previously been reported in the livers and (especially) kidneys of marine mammals which inhabit areas remote from pollution sources, but which consume prey species which are themselves relatively rich in Cd. These include pilot whales from the Faroe Islands and Ross seals from Antarctica which prey upon cephalopods, as high concentrations of Cd accumulate in the livers and gonads of cephalopods (Law, in press). Pilot whales around the Faroe Islands feed primarily upon squid taken mostly at depths of 100–500 m. Seasonal movements of pilot whales towards the coast have also been related to inshore movements of squid (Desportes & Mouritsen, 1993). The Cd concentration found in the sperm whale is within a tentative threshold area of effect of 20–200 mg kg^{-1} wet wt, set by extrapolation from humans (Law, in press). As for Hg, marine mammals have developed mechanisms to limit the toxicity of dietary metals such as Cd and the degree of metal binding to proteins is, therefore, an important factor in the interpretation of concentration data. The concentration of lead in the liver analysed was low at 0.11 mg kg^{-1} wet wt. Concentrations up to approximately 2 mg kg^{-1} wet wt have been reported previously in the livers of both grey seals from north-west England and harbour seals from Alaska (Law, in press).

Tables 3–5 show the concentrations of organochlorine pesticides and their metabolites, and individual CB congeners and the sums of CB congeners (ΣICES 7 and the sum of the 25 congeners determined), in blubber samples. The CB congeners of the ICES primary list are CBs 28, 52, 101, 118, 138, 153 and 180. α-, β- and γ-HCH, HCB and dieldrin were detected in all samples. The concentrations were lower than those found in bycaught harbour porpoises (*Phocoena phocoena*) from the Shetland Islands (Law, 1994), but of the same order as those found in a sperm whale stranded in Cornwall, England in 1990 (MAFF, 1992). Residues of *cis*- and *trans*-chlordane and *trans*-nonachlor, derived from the use of technical chlordane, were also detected in all samples; in this case, no comparable data are known to exist. Both the *o,p′*- and *p,p′*-isomers of DDD, DDE and DDT were detected in all samples. The *o,p′*-isomers were all found at lower concentrations than the corresponding *p,p′*-isomers, reflecting the historic usage of technical DDT, with the bulk of the DDT group residues present as the persistent metabolite *p,p′*-DDE. Concentrations were broadly similar to those found in harbour porpoises from the Shetland Islands, and of the same order as those seen in the single sperm whale analysed previously (MAFF, 1992; Law, 1994).

These data demonstrate the accumulation of organochlorine pesticides and metabolites from oceanic food webs, following their long-range transport from terrestrial sources. Ballschmiter *et al.* (1989) observed that global equilibrium has not yet been reached for PCBs and that environmental inputs are continuing. The atmospheric transport of organochlorines and PCBs to remote regions is facilitated by their long environmental half-lives and physical behaviour (Oehme & Mano, 1984; Oehme, 1991), and it has been suggested that the continuing use of large quantities of persistent organochlorines in the tropics leads to volatilization and subsequent condensation at lower temperatures in high latitudes (Tanabe *et al.*, 1994). The increasing contamination of Arctic biota by such compounds is believed to result from this process (Wania & Mackay, 1993).

TABLE 3

Concentrations of other organochlorine compounds in sperm whale blubber (mg kg^{-1} wet wt).

Ref. no.	α-HCH	β-HCH	γ-HCH	HCB	Dieldrin	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-DDD	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	*trans*-Chlordane	*cis*-Chlordane	*trans*-Nonachlor
UK4026	0.012	0.008	0.06	0.13	0.2	0.054	3.6	0.053	0.3	0.46	1.1	0.085	0.17	0.42
UK4029	0.012	0.008	0.05	0.16	0.27	0.063	4.6	0.055	0.39	0.68	1.3	0.12	0.21	0.53
UK4031	0.012	0.008	0.046	0.18	0.3	0.07	4.4	0.075	0.49	0.85	1.5	0.12	0.25	0.63
MI4059	0.006	0.009	0.13	0.3	0.33	0.014	3.9	0.048	0.44	0.95	1.8	0.17	0.34	0.89
MI5004	0.004	0.008	0.09	0.18	0.23	0.067	3	0.062	0.39	0.63	1.1	0.11	0.23	0.58
MI5005	0.01	0.009	0.1	0.31	0.45	0.12	5.2	0.11	0.65	1.1	1.9	0.2	0.38	0.98
MI5006	0.007	0.005	0.085	0.25	0.36	0.09	4.1	0.092	0.54	0.94	1.5	0.17	0.32	0.78

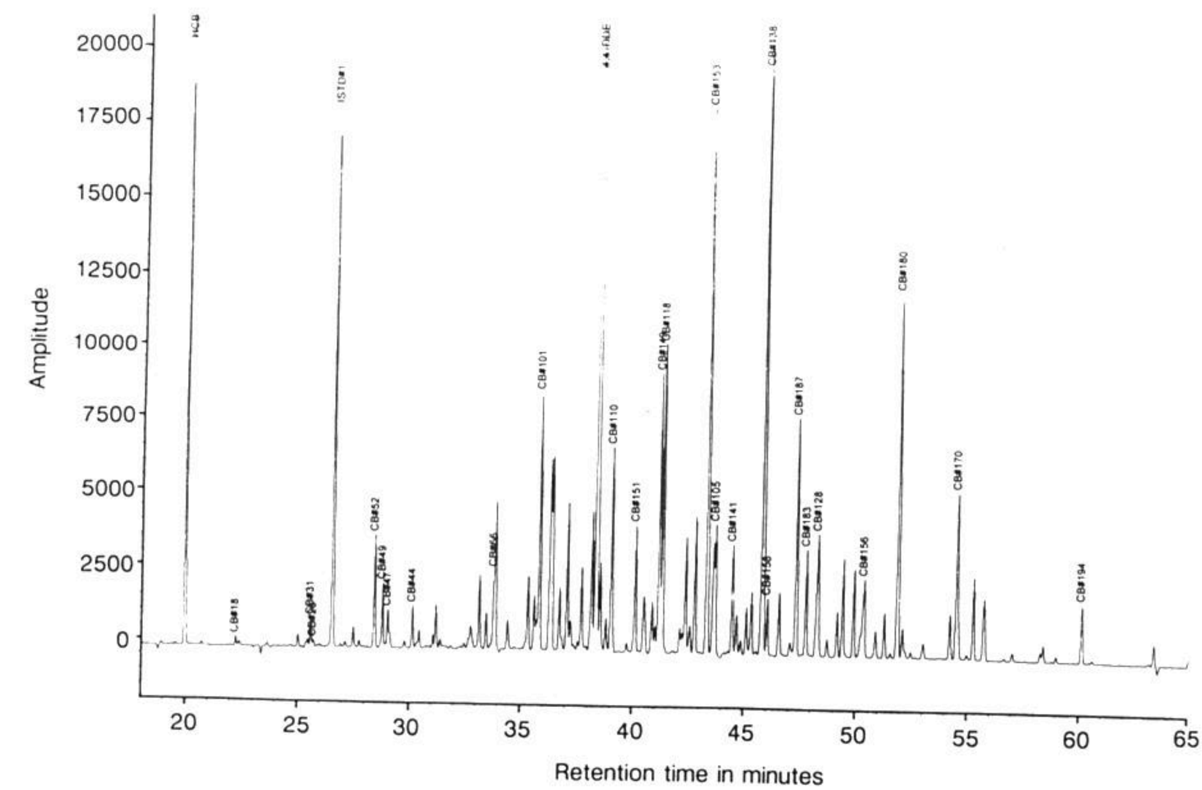
TABLE 4

Concentrations of 25 individual CB congeners in sperm whale blubber in order of elution on an HP-5 column (mg kg^{-1} wet wt).

Ref. no.	%HEL	CB18	CB31	CB28	CB52	CB49	CB47	CB44	CB66	CB101	CB110	CB151	CB149	CB118	CB153	CB105	CB141	CB138	CB158	CB187	CB183	CB128	CB156	CB180	CB170	CB194
UK4026	69	<0.01	0.012	<0.01	0.056	0.019	<0.005	0.008	0.096	0.19	0.21	0.057	0.16	0.25	0.47	0.085	0.048	0.43	0.058	0.18	0.044	0.056	0.041	0.24	0.08	0.018
UK4029	51	<0.01	0.013	<0.01	0.091	0.048	<0.005	0.006	0.14	0.3	0.31	0.092	0.27	0.35	0.6	0.11	0.082	0.56	0.074	0.24	0.069	0.064	0.057	0.31	0.11	0.023
UK4031	64	<0.01	0.017	<0.01	0.11	0.048	<0.005	0.016	0.15	0.32	0.34	0.11	0.3	0.37	0.69	0.12	0.091	0.63	0.074	0.26	0.083	0.08	0.064	0.36	0.13	0.028
MI4059	74	<0.01	0.039	<0.01	0.17	0.06	0.005	0.04	0.21	0.36	0.41	0.13	0.35	0.47	0.78	0.15	0.09	0.74	0.09	0.26	0.08	0.1	0.07	0.35	0.13	0.023
MI5004	48	<0.01	0.02	<0.01	0.1	0.036	0.008	0.026	0.12	0.22	0.23	0.077	0.21	0.26	0.45	0.088	0.054	0.41	0.047	0.16	0.054	0.064	0.043	0.21	0.08	0.015
MI5005	55	<0.01	0.034	<0.01	0.2	0.077	0.027	0.043	0.21	0.39	0.42	0.16	0.41	0.49	0.83	0.16	0.11	0.8	0.079	0.3	0.11	0.11	0.078	0.39	0.16	0.029
MI5006	47	<0.01	0.03	<0.01	0.17	0.06	0.023	0.042	0.17	0.31	0.35	0.13	0.33	0.37	0.65	0.12	0.085	0.6	0.06	0.24	0.088	0.091	0.063	0.31	0.13	0.023

%HEL: Percentage of hexane-extractable lipid. CB congeners numbered according to IUPAC nomenclature.

(a)



(b)

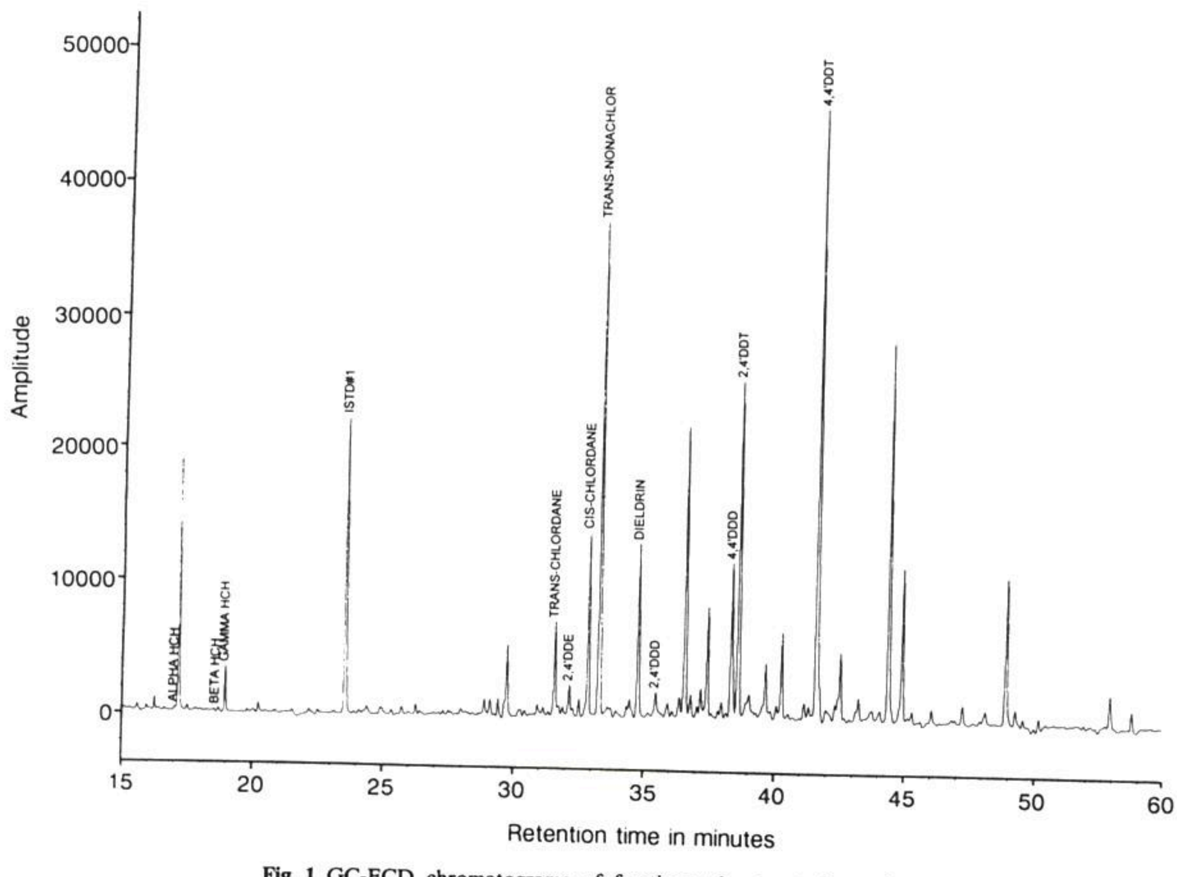


Fig. 1 GC-ECD chromatograms of fractionated extracts from the blubber of sperm whale MI5006 on an HP-5 (5% phenylmethyl siloxane) stationary phase. (a) Fraction 1 containing HCB, *p,p'*-DDE and chlorobiphenyls; (b) fraction 2 containing the remaining organochlorine pesticides and metabolites.

TABLE 5
Concentrations of summed CB congeners (mg kg^{-1} wet wt).

Ref. no.	%HEL	ΣICES7	Σ25CBs
UK4026	69	1.64	2.37
UK4029	51	2.21	3.36
UK4031	64	2.48	3.73
MI4059	74	2.87	4.43
MI5004	48	1.65	2.57
MI5005	55	3.10	4.85
MI5006	47	2.41	3.83

ΣICES7: Sum of the seven CB congeners of the ICES primary list.
Σ25CBs: Sum of the 25 CB congeners determined.

The concentrations of CBs in these samples were relatively low (ΣICES 7 concentrations were 1.6–3.1 mg kg^{-1} wet wt, or 2.4–5.6 mg kg^{-1} on a lipid basis) compared to those seen both in small cetaceans from UK waters and in two long-finned pilot whales (*Globicephala melas*) stranded on UK coasts (Law, 1994), despite the similarity in diet between pilot and sperm whales (Martin, 1990; Desportes & Mouritsen, 1993). Similarly, low concentrations of CBs were found in the blubber of two sperm whales stranded on the Isle of Mull (west Scotland) and in Cornwall during 1990 (ΣICES 7 concentrations of 0.3 and 1.7 mg kg^{-1} wet wt, respectively; MAFF, 1992; Wells & Echarri, 1992). The predominant congener found here was CB153; the other major congeners present (CBs 101, 110, 149, 138, 180 and 187) are all known to be persistent in cetaceans (Tanabe *et al.*, 1988; Boon *et al.*, 1992, 1994). The CB concentrations in the blubber of some small cetaceans (common and bottlenose dolphins; harbour porpoises) mostly feeding in coastal waters are often an order of magnitude higher than those found in the sperm whales studied here (Law, 1994), but the toxicological significance of such concentrations cannot be fully evaluated.

Examples of chromatograms of the CB and pesticide fractions for one of the sperm whales are shown in Fig. 1. The CB profiles for the individual animals were very similar, but the concentration range was also smaller than that seen in small cetaceans living close to the coast. This is perhaps unsurprising, as sperm whales live and feed offshore remote from the sources of organochlorine compounds, and probably exploit a more homogeneous diet.

Positive correlations were found between body length and concentration for all organic contaminants except α- and β-HCH. The negative correlation between length and α-HCH was significant at the 95% level. Positive correlations with body length were significant at the 95% level for the following analytes: HCB, dieldrin, *p,p'*-DDD, *o,p'*-DDT, *cis*- and *trans*-chlordane, *trans*-nonachlor and CB congener numbers 44, 47, 49, 52 and 151. Age-related accumulation of organochlorine residues in male cetaceans has been reported previously (Aguilar, 1987), and occurs because the input from the diet exceeds the ability of the animals to excrete or metabolize these comounds. It would be instructive to compare the concentrations found in female sperm whales feeding solely in low latitudes prior to their first pregnancy (when their accumulation should parallel that of males) to those reported here. The use of persistent organochlorine pesticides in tropical regions has lagged behind that in the developed countries of the northern hemisphere, and for some classes of compounds may still be increasing (Tanabe *et al.*, 1994), although reliable information on usage is difficult to obtain (Voldner & Li, 1995).

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Aguilar, A. (1987). Using organochlorine pollutants to discriminate marine mammal populations: a review and critique of methods. *Mar. Mamm. Sci.* **3**, 242–262.
Allchin, C. R. Kelly, C. A. & Portmann, J. E. (1989). Methods of Analysis for Chlorinated Hydrocarbons in Marine and other Samples. Aquatic Environment Protection: Analytical Method, MAFF Directorate of Fisheries Research, Lowestoft, 6, 25 pp.
Ballschmiter, K.-H., Rappe, C. & Buser, H. R. (1989). Chemical properties, analytical methods and environmental levels of PCBs, PCTs, PCNs and PBBs. In *Halogenated Biphenyls, Terphenyls, Naphthalene, Dibenzodioxins and Related Products*, 2nd Edn (R. D. Kimbrough & A. A. Jensen, eds), pp. 47–69. Elsevier, Amsterdam.
Berrow, S. D., Evans, P. G. H. & Sheldrick, M. C. (1993). An analysis of sperm whale *Physeter macrocephalus* L. stranding and sighting records from Britain and Ireland. *J. Zool. Lond.* **230**, 333–337.
Boon, J. P., van Arnhem, E., Jansen, S., Kannan, N., Petrick, G., Schulz, D., Duinker, J. C., Reijnders, P. J. H. & Goksøyr, A. (1992). The toxicokinetics of PCBs in marine mammals with special reference to possible interactions of individual congeners with the cytochrome P450-dependent monooxygenase system: an overview. In *Persistent Pollutants in Marine Ecosystems* (C. H. Walker & D. R. Livingstone, eds), pp. 119–159. Pergamon Press, Oxford.
Boon, J. P., Oostingh, I., van der Meer, J. & Hillebrand, M. Th. J. (1994). A model for the bioaccumulation of chlorobiphenyl congeners in marine mammals. *European J. Pharmacol., Environ. Toxicol. Pharmacol. Section* **270**, 237–251.
de Boer, J. & van der Meer, J. (In press). Report on the Results of the ICES/IOC/OSPARCOM Intercomparison exercise on the Determination of Chlorobiphenyl Congeners in Marine Media Steps 3 and 4. ICES Cooperative Resarch Report. International Council for the Exploration of the Sea, Copenhagen, Denmark.
de Boer, J., Duinker, J. C., Calder, J. A. & van der Meer, J. (1992). Interlaboratory study on the analysis of chlorobiphenyl congeners. *J. Assoc. Off. Anal. Chem.* **75**, 1054–1062.
de Boer, J., van der Meer, J., Reutergårdh, L. & Calder, J. A. (1994). Interlaboratory study on the analysis of chlorobiphenyls in cleaned-up seal blubber and marine sediment extracts. *J. Assoc. Off. Analyt. Chem.* **77**, 1411–1422.
Desportes, G. & Mouritsen, R. (1993). Preliminary results on the diet of long-finned pilot whales off the Faroe Islands. In *Biology of Northern Hemisphere Pilot Whales* (G. P. Donovan, C. H. Lockyer & A. R. Martin, eds), pp. 305–324. International Whaling Commission, Special Issue 14, Cambridge.
Evans, P. G. H. (1987). *The Natural History of Whales and Dolphins.* Christopher Helm Ltd, Bromley, UK.
Evans, P. G. H. (1992). *Status Review of Cetaceans in British and Irish Waters.* UK Mammal Cetacean Society, Oxford.
Jones, B. R. & Laslett, R. E. (1994). Methods for the Analysis of Trace Metals in Marine and other Samples. Aquatic Environment Protection: Analytical Method, MAFF Directorate of Fisheries Research, Lowestoft, 11, 29 pp.
Law, R. J. (1994). Collaborative UK Marine Mammal Project: Summary of Data Produced 1988–1992. Fisheries Research Technical Report, MAFF Directorate of Fisheries Research, Lowestoft, 97, 42 pp.
Law, R. J. (In press). Metals in marine mammals. In *Interpreting Environmental Contaminants in Wildlife Tissues* (N. Beyer, G. Heinz & A. W. Redmon, eds). Lewis Publishers, Inc., Chelsea, Michigan.
Law, R. J., Fileman, C. F., Hopkins, A. D., Baker, J. R., Harwood, J., Jackson, D. B., Kennedy, S., Martin, A. R. & Morris, R. J. (1991). Concentrations of trace metals in the livers of marine mammals (seals, porpoises and dolphins) from waters around the British Isles. *Mar. Pollut. Bull.* **22**, 183–191.

MAFF (1992). Monitoring and Surveillance of Non-radioactive Contaminants in the Aquatic Environment and Activities Regulating the Disposal of Wastes at Sea, 1990. Aquatic Environment Monitoring Report, MAFF Directorate of Fisheries Research, Lowestoft, 30, 66 pp.

Martin, A. R. (1990). *Whales and Dolphins*. Salamander Books Ltd, London.

Martin, A. R. & Clarke, M. R. (1986). The diet of sperm whales (*Physeter macrocephalus*) captured between Iceland and Greenland. *J. Mar. Biol. Assoc. UK* **66**, 779–790.

Oehme, M. (1991). Dispersion and transport paths of toxic persistent organochlorines to the Arctic—levels and consequences. *Sci. Tot. Environ.* **106**, 45–53.

Oehne, M. & Mano, S. (1984). The long range transport of organic pollutants to the Arctic. *Fresenius Z. Analyt. Chem.* **319**, 141–146.

Sheldrick, M. C., George, J. D., Chimonides, P. J. & Phillips, S. (1991). An Analysis of Cetacean Strandings Around the British Isles Between 1967 and 1990. A Report for the UK Department of the Environment. The Natural History Museum, London, 175 pp.

Tanabe, S., Watanabe, S., Kan, H. & Tatsukawa, R. (1988). Capacity and mode of PCB metabolism in small cetaceans. *Mar. Mamm. Sci.* **4**, 103–124.

Tanabe, S., Iwata, H. & Tatsukawa, R. (1994). Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. *Sci. Tot. Environ.* **154**, 163–177.

Voldner, E. C. & Li, Y.-F. (1995). Global usage of selected persistent organochlorines. *Sci. Tot. Environ.* **160/161**, 201–210.

Wania, F. & Mackay, D. (1993). Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. *Ambio* **22**, 10–18.

Wells, D. E. & Echarri, I. (1992). Determination of individual chlorobiphenyls (CBs) including non-*ortho* and mono-*ortho* chlorosubstituted CBs in marine mammals from Scottish waters. *Intern. J. Environ. Analyt. Chem.* **47**, 75–97.