A Review of Heavy Metal Levels in Marine Vertebrates and some Studies of Mercury in Seabirds

David Richard Thompson

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CANDIDATE'S DECLARATION

I declare that the work recorded in this thesis is entirely my own, unless otherwise stated, and that it is of my own composition. No part of this work has been submitted for any other degree.

David Thompson

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CONTENTS

ABSTRACT

A review of the levels, accumulation patterns and geographical variations of heavy metals (As, Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, Zn) in marine vertebrates (marine fish, seabirds and marine mammals) was made.

A method was developed to allow organic mercury to be extracted from feather samples, and total and organic mercury levels measured in feathers and internal tissues of a range of seabirds species. The relative proportions of inorganic and organic mercury in internal tissues were investigated for a range of seabirds and related to variations in frequency of feather moult and longevity.

The effects of age, reproduction and feather moult upon mercury levels and dynamics were investigated in great skuas of known age, and common guillemots collected at specific points during the breeding season.

The form of mercury in seabird feathers was determined and historical changes in mercury burdens of a range of British seabirds were assessed by incorporating the organic mercury extraction technique to overcome museum contamination problems and analysing mercury concentrations in feather samples from preserved and contemporary specimens.

The mercury levels of Scottish golden and white-tailed eagles were measured and related to trends in reproductive success and dietary variation.

The use of mercury concentration conversion ratios was assessed and their validity briefly considered.

CHAPTER 1

General introduction

The monitoring of the levels and effects of environmental contaminants has increased markedly over recent decades with the manifestation of severe toxicological phenomena directly associated with anthropogenic emissions of pollutants to the environment. Perhaps the best known of such incidents were those involving halogenated hydrocarbon compounds, such as DDT, lindane, the cyclodiene group compounds such as dieldrin or HEOD, aldrin or HHDN, heptaclor and, more recently, polychlorinated biphenyls or PCBs. Being powerful pesticides, compounds such as DDT were widely used as early as 1939 and throughout the 1939-1945 world war to control malarial parasites and typhus-bearing lice. Their use controlling both insect-borne diseases and agricultural pests resulted in increased food production, and undoubtedly saved many lives. However, the accumulation of organochlorine compounds up food chains with the resultant death and breeding failure of many seed-eating birds and their predators, following widespread agricultural application, aroused many concerns about the deleterious effects they could cause.

The pioneering work of Ratcliffe (1967, 1970) revealed that elevated organochlorine levels in raptors, resulting from feeding upon contaminated prey, effected reproductive success by reducing eggshell thickness and embryo fertility. The breeding success, adult survival and consequently overall population size, of many birds of prey dropped markedly through contamination with organochlorines.

Although now no longer used in many countries, so widespread was their use that such compounds can be detected in biota from every environment on the planet, indicating global transport and assimilation far from the source of contamination.

Being man-made and extremely stable, the effects of organochlorines were profound since, unlike most heavy metals, they have no biological function and animals had no adaptive detoxification processes in response to elevated levels.

There are, therefore, clear distinctions between the novel hydrocarbon compounds and the naturally-occurring heavy metals. Since many, if not all, heavy metals exhibit cycles through the biological, chemical and geological environments there would have been, in evolutionary terms, sufficient time for biota to adapt in some way to natural levels of exposure to a whole range of metals. Many heavy metals are essential for life with well-defined biological functions, often in enzyme systems or other large proteins. This is not to suggest that the raising of natural metal levels through anthropogenic emissions would be harmless, since all essential metals become toxic in excess.

Mercury, lead and cadmium can be considered non-essential, all having no known biological function, and are the three heavy metals most likely to cause pollution problems in marine ecosystems (Bryan, 1984). Lantzy & Mackenzie (1979) reported that after lead, mercury had the highest value for the ratio of anthropogenic/natural inputs to the environment and it has been this highly toxic metal which has probably received most attention. The well-documented poisoning incidents in Japan (Kurland et al., 1960), Iraq (Bakir et al., 1973) and Sweden (Borg et al., 1969; Johnels & Westermark, 1969), in which mercury of industrial and agricultural origin caused profound toxicological problems and, in Japan and Iraq, human fatalities, highlighted the potential problem of mercury as an environmental contaminant.

Bryan (1979) indicated that methyl mercury, a lipid-soluble and highly toxic form of mercury, was the only metal or metal ligand for which evidence existed for widespread bioamplification up food chains. It was this form of mercury which was the cause of the problems in Japan and Iraq, and methyl mercury and related members of the alkyl group which caused death and breeding failure in seed-eating birds and their predators in Sweden. Such accumulation, resulting in relatively high mercury concentrations in top predators, particularly in marine systems, has focused much attention upon seabirds as indicators of mercury contamination of their environment (for example, Delbeke et al., 1984; Gochfeld, 1980; Hutton, 1981; Norheim, 1987; Renzoni et al., 1986).

Although some pelagic fish and marine mammals have been shown to accumulate mercury to relatively high levels (for example, Beckett & Freeman, 1974; Honda et al., 1983; Mackay et al., 1975; Shomura & Craig, 1974), they have several disadvantages as marine monitoring organisms for mercury. Geographical comparisons are hindered by the vast areas such species cover and large samples of fresh specimens are difficult to obtain. The choice of organ or tissue to be analysed tends to be restricted to internal tissues, notably liver, kidney and muscle with the unavoidable consequence of killing animals sampled. Seabirds, however, tend to be confined to relatively well-defined locations during the breeding season, allowing geographical variations within species or groups of species to be assessed. They can be sampled relatively easily and efficiently, but it is the choice of target organ with respect to mercury monitoring which gives birds a distinct advantage over other vertebrate groups. The egg has been used by several workers to monitor mercury levels in both marine and terrestrial systems (for example, Barrett et al., 1985; Becker et al., 1985; Focardi et al., 1988; Gilman et al., 1977; Newton et al., 1989; Ohlendorf & Harrison, 1986). However, it has been the use of feathers to monitor mercury levels in birds which has provided a means by which large numbers of individuals can readily be assessed in a manner which avoids killing the specimens. Mercury is deposited into the growing feather following moult and is bound strongly to disulphide linkages within the keratin molecule (Crewther et al., 1965). Levels of mercury in feathers are unaffected by various vigorous treatments (Appelquist et al., 1984). Hence, once fully grown, feathers are both chemically stable and effectively isolated from processes occurring within the bird. The use of feathers to measure mercury in birds, and seabirds in particular, has revealed pronounced inter-species variations due in part to differences in the exposure to mercury via the diet, but other factors, including stage of the moulting process, feather type(s) analysed, adaptive detoxification processes and bird age could all be influential in determining the mercury level measured.

Despite feathers being a relatively convenient means of monitoring mercury in birds, the way in which feather mercury levels relate to those of internal tissues, how feather mercury levels reflect seasonal fluctuations in mercury concentrations of other tissues and the use of feathers to assess historical changes in mercury exposure of particular species are all areas of mercury monitoring requiring further assessment. Furthermore, the patterns of mercury accumulation with age and the ability to biotransform organic (methyl) mercury into an inorganic storage form have been little studied in birds, in contrast to the relatively large body of work undertaken on these subjects in other marine vertebrates.

The aims of this study were to shed some more light onto these aspects of mercury accumulation, storage and dynamics in seabirds, using both feather and internal tissue samples from a wide variety of species and locations. It was hoped to investigate the relative proportions of inorganic and organic mercury in south Atlantic seabirds, to determine the effects of age upon mercury accumulation in tissues of ringed great skuas *Catharacta skua*, to assess the seasonal fluctuations in mercury burdens of common guillemots *Uria aalge*, to make use of museum study skins to investigate any historical trends in mercury exposure in a range of seabirds, to comment upon the validity of inter-tissue mercury concentration conversion factors and to assess the possible deleterious effects of mercury upon the breeding success of Scottish golden eagles *Aquila chrysaetos* and white-tailed eagles *Haliaeetus albicilla*. Although not usually thought of as seabirds, many golden eagles in the west of Scotland feed to a large extent upon gulls *Larus* sp. and fulmars *Fulmarus glacialis* in the absence or scarcity of live, terrestrial prey and, thus, can be thought of as occupying a place at the top of a marine food chain.

The reader's attention is drawn to the particular format of the thesis, in which each chapter has been treated as a separate section, with its own introduction, discussion and reference list. The inclusion of the latter will obviously result in some works being cited repeatedly, but many are relevant only to the chapter in which they appear, and as such are more appropriately placed than if part of one large reference list at the end of the work. Furthermore, the manner in which works are referred to in Chapter 2 differs from that in other chapters; this is due to this particular chapter having been written as part of a volume to be published in the United States of America where the use of superscripted numbers, each representing a particular work, was preferred.

At submission of this thesis (November, 1989), the status of each chapter was as follows:-

Chapter 1. Introduction in thesis only.

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Chapter 9. In thesis only.

Chapter 10. Discussion in thesis only.

1.1 REFERENCES

Appelquist, H., Asbirk, S. & Drabaek, I. (1984). Mercury monitoring: mercury stability in bird feathers. Mar. Pollut. Bull. 15, 22-24.

Bakir, F., Damluji, S.F., Amin-Zaki, L., Murtadha, M., Khalidi, A., Al-Rawi, N.Y., Tikriti, S., Dhahir, H.I., Clarkson, T.W., Smith, J.C. & Doherty, R.A. (1973). Methylmercury poisoning in Iraq. Science 181, 230-241.

Barrett, R.T., Skaare, J.U., Norheim, G., Vader, W. & Froslie, A. (1985). Persistent organochlorines and mercury in eggs of Norwegian seabirds 1983. Environ. Pollut. (A) 39, 79-93.

Becker, P.H., Ternes, W. & Russel, H.A. (1985). Schadstoffe in Gelegen von Brutvogeln der deutschen Nordseekuste. II. Quecksilber. J. Orn. 126, 253-262. (English summary).

Beckett, J.S. & Freeman, H.C. (1974). Mercury in swordfish and other pelagic species from the western Atlantic. Spec. Scient. Rep. Natn. Oceanic Atmos. Adm. U.S. (Fisheries) 675, 154-159.

Borg, K., Wanntorp, H., Erne, K. & Hanko, E. (1969). Alkyl mercury poisoning in Swedish wildlife. Viltrevy 6, 301-379.

Bryan, G.W. (1979). Bioaccumulation of marine pollutants. Phil. Trans. R. Soc. Lond. B 286, 483-505.

Bryan, G.W. (1984). Pollution due to heavy metals and their compounds. In, Marine Ecology. Kinne, O. (ed.). Wiley, Chichester. pp. 1289-1431.

Crewther, W.G., Fraser, R.D.B., Lennox, F.G. & Lindley, H. (1965). The chemistry of keratins. Adv. Prot. Chem. 20, 191-346.

Delbeke, K., Joiris, C. & Decadt, G. (1984). Mercury contamination of the Belgian avifauna 1970-1981. Environ. Pollut. (B) 7, 205-221.

Focardi, S., Fossi, C., Lambertini, M., Leonzio, C. & Massi, A. (1988). Long term monitoring of pollutants in eggs of yellow-legged herring gull from Capraia Island (Tuscan Archipelago). Environ. Monit. Assess. 10, 45-50.

Gilman, A.P., Fox, G.A., Peakall, D.B., Teeple, S.M., Carroll, T.R. & Haymes, G.T. (1977). Reproductive parameters and egg contaminant levels of Great Lakes herring gulls. J. Wildl. Manage. 41, 458-468.

Gochfeld, M. (1980). Mercury levels in some seabirds of the Humboldt Current, Peru. Environ. Pollut. (A) 22, 197-205.

Honda, K., Tatsukawa, R., Itano, K., Miyazaki, N. & Fujiyama, T. (1983). Heavy metal concentrations in muscle, liver and kidney tissue of striped dolphin, Stenella coeruleoalba, and their variations with body length, weight, age and sex. Agric. Biol. Chem. 47, 1219-1228.

Hutton, M. (1981). Accumulation of heavy metals and selenium in three seabird species from the United Kingdom. Environ. Pollut. (A) , 26, 129-145.

Johnels, A.G. & Westermark, T. (1969). Mercury contamination of the environment in Sweden. In, Chemical Fallout. Current Research on Pesticides. Millar, M.W. & Berg, G.G. (eds.). Thomas, Springfield. pp. 221-239.

Kurland, L.T., Faro, S.N. & Seidler, H. (1960). Minamata disease. The outbreak of a neurological disorder in Minamata, Japan and its relationship to the ingestion of sea food contaminated by mercuric compounds. Wld. Neurol. 1, 370-395.

Lantzy, R.J. & Mackenzie, F.T. (1979). Atmospheric trace metals: global cycles and assessment of man's impact. Geochim. Cosmochim. Acta 43, 511-525.

Mackay, N.J., Kazacos, M.N., Williams, R.J. & Leedow, M.I. (1975). Selenium and heavy metals in black marlin. Mar. Pollut. Bull. 6, 57-61.

Newton, I., Bogan, J.A. & Haas, M.B. (1989). Organochlorines and mercury in the eggs of British peregrines Falco peregrinus. Ibis 131, 355-376.

Norheim, G. (1987). Levels and interactions of heavy metals in seabirds from Svalbard and the Antarctic. Environ. Pollut. 47, 83-94.

Ohlendorf, H.M. & Harrison, C.S. (1986). Mercury, selenium, cadmium and organochlorines in eggs of three species of Hawaiian seabird species. Environ. Pollut. (B) 11, 169-191.

Ratcliffe, D.A. (1967). Decrease in eggshell weight in certain birds of prey. Nature 215, 208-210.

Ratcliffe, D.A. (1970). Changes attributable to pesticides in egg breakage frequency and eggshell thickness in some British birds. J. appl. Ecol. 7, 67-107.

Renzoni, A., Focardi, S., Fossi, C., Leonzio, C. & Mayol, J. (1986). Comparison between concentrations of mercury and other contaminants in eggs and tissues of Cory's shearwater Calonectris diomedea collected on Atlantic and Mediterranean islands. Environ. Pollut. (A) 40, 17-35.

Shomura, R.S. & Craig, W.L. (1974). Mercury in several species of billfishes taken off Hawaii and southern California. Spec. Scient. Rep. Natn. Oceanic Atmos. Admin. U.S. (Fisheries) 675, 160-163.

CHAPTER 2

Metal levels in marine vertebrates

2.1 INTRODUCTION

Following the documentation of anthropogenic mercury contamination of aquatic and terrestrial food webs in Japan, Sweden and Iraq, [8,16,60,99] together with cadmium poisoning, also in Japan, [59] the distribution of these and other heavy metals within the marine environment has been increasingly studied in recent years. The potential risks to human health have prompted many investigations with respect to the more toxic metals cadmium, lead and mercury. Of these metals, lead and mercury, in that order, are thought to show the highest values for the ratio anthropogenic/natural input [109] and are likely, therefore, to pose the most serious pollution threat. Furthermore, Bryan [22] states that mercury, and more specifically, methyl-mercury, is the only metal for which evidence exists for bioamplification up marine food chains.

The heavy metals can be divided into non-essential elements (lead, mercury and probably cadmium) and essential elements with relatively well-defined roles and functions (copper, iron, selenium and zinc). For other heavy metals few data on levels in marine vertebrates exist, although a short summary of levels of arsenic, chromium, manganese and nickel is given in section 2.8.

Account should be taken of the limitations of data reported on metal levels in marine vertebrates. Seasonal variation in metal concentrations in seabirds with respect to moult cycles, for example, can be considerable (see chapter by Walsh in this volume). Seabirds sampled at the start of moult will contain relatively high concentrations of mercury in liver tissues, for example, but as the 'body pool' of this metal diminishes with the formation of new feathers, birds sampled at a later stage of the moult cycle will contain relatively less mercury in liver tissues. This variation has been clearly demonstrated in the black-eared kite _Milvus migrans lineatus_, as reported by Honda _et al._ [88] and is likely to be common to all seabirds exposed to mercury. Similar variations in metal levels may exist in other marine groups and should be considered in any interpretation of data. The sources of many samples used for metal analysis pose other limitations. Biases may be introduced by the use of seabirds 'found dead' or by the use of beached or stranded marine mammals, although the collection of fresh samples of this latter group is both difficult and restricted by the scarcity of many species. Furthermore, with the enhancement and refinement of analytical techniques over the last ten years, it is clear that the results from early investigations into metal levels in marine vertebrates are less reliable than those from recent studies.

In this review, the marine vertebrates have been, for convenience, treated in the following sub-groups:- marine fish, both Chondrichthyes and Osteichthyes; seabirds, excluding sea ducks and divers (loons); marine mammals (which have been further sub-divided into the Pinnipedia, the Cetacea and the Sirenia with other marine mammal groups). The metal concentration data which have been presented in the various tables are not intended to be a complete record of all work on each respective group for a particular metal; the data included in the tables are a representative selection of work, used here to illustrate particular trends or differences, other work being referred to in the text. Unless otherwise stated, the data presented in the various tables refer to samples made up of both male and female individuals, and age/length data are included only when accumulation effects of a particular metal are likely to be a factor.

2.2 CADMIUM

2.2.1 Introduction

In vertebrates, cadmium is usually located in a low molecular weight metalloprotein, metallothionein, but is believed to have little or no biological function.

2.2.2 Cadmium in marine fish

Cadmium levels in fish are low, often below instrumental detection limits with values rarely exceeding 0.2 µg g^{-1} wet weight in muscle tissue.[3,10,36,49,70,71,74,75,85,91,112,118,132-135,151-153,168,176,179,186-188] Values tend to be higher in liver and kidney tissues,[15,70,74,133,135,151,168,186-188] Mackay et al.,[118] for example, reporting cadmium concentrations in liver tissues of black marlin *Makaira indica* ranging from 0.2-83.0 µg g^{-1} wet weight with a mean value of 9.2 µg g^{-1} wet weight.

Changes in cadmium concentration with increasing fish age/size have not been studied to any great extent; several studies report no correlation with increasing size/weight/length of fish[85,91,118] whilst, in others, cadmium has been shown to increase with increasing fish weight/length[7,36] which would seem appropriate for this metal, given its tendency to increase in concentration with increasing age/size in other groups of marine vertebrates. Relatively high cadmium levels have been attributed to high incidence of Crustacea in the diet[82] and possible pollution effects.[83] Positive correlations between cadmium and zinc concentrations in marine fish have been shown to exist.[91,118] A summary of references to cadmium levels in marine fish is presented in Table 2.1.

TABLE 2.1: Summary of the references to heavy metals in marine fish.

Class	Chondrichthyes	28 29 40 49 55 57 71 74 76 77 108 115 116 127 132-135 154 168 175 179 183 184 187
	Osteichthyes	3 7 10 11 14 15 28 31 34 36 40 48 49 57 58 70 73-79 82 83 85 91 101 105 108 110 112 113 118 122 127 132-135 151-154 158 160 163 164 166 173 175 186-188
Location	European Coastal	3 7 48 70 82 83 85 91 112 113 132-135 151 153 154 168 176 179 186 188
	Australian Coastal	10 29 31 40 49 71 115 116 118 122 152 175 183
	West Atlantic Ocean	11 14 34 57 58 74-77 187
	East Atlantic Ocean	73
	Pacific Ocean	15 36 55 73 78 79 105 110 127 158 160 163 164 166 173
	Indian Ocean	73 101 108 184
Metal	Cadmium	3 7 10 15 36 49 70 71 74 75 82 83 85 91 112 118 132-135 151-154 168 176 179 186-188
	Copper	3 10 15 34 49 70 71 74 75 83 91 112 118 132-135 151-154 168 176 179 186-188
	Iron	34 83 152 179
	Lead	3 7 10 15 40 70 71 74 75 82 83 112 118 132-135 152-154 168 176 179 186
	Mercury	10 11 28 29 31 34 40 48 55 57 58 70 73-79 83 101 105 108 112 113 115 116 118 127 132-135 151 153 154 158 163 164 166 173 175 183 184 186 187
	Selenium	10 28 58 71 101 113 116 118 122 164
	Zinc	3 7 10 15 34 36 49 71 74 75 82 83 91 112 118 132-135 151-154 168 176 179 186-188
	Others	10 14 15 34 49 70 71 74 75 83 91 110 112 118 132-135 152-154 160 179 187 188

2.2.3 Cadmium in seabirds

Cadmium levels in seabird tissues tend to decrease in the order kidney > liver > muscle with very low or undetectable levels in feathers and eggs.[2,13,21,25,90,92-94,130,138,140,141,145,149,155,157,167,177] The extremely high cadmium concentrations in eggs of sooty terns *Sterna fuscata* from Hawaii reported by Stoneburner and Harrison[170] (mean concentration 75.04 $\mu g\ g^{-1}$ wet weight) would appear to be anomalous and are in total contrast to cadmium levels in eggs of the same species, also from Hawaii, reported by Ohlendorf and Harrison[146] which failed to exceed the limit of detection (0.1 $\mu g\ g^{-1}$ wet weight). Similarly, the relatively high cadmium concentrations (up to 27 $\mu g\ g^{-1}$ wet weight) in feathers of Hawaiian seabirds reported by Cheng *et al.*[30] are difficult to explain. Representative data from northern and southern hemisphere studies are presented in Table 2.2. The variations in kidney cadmium levels in seabirds are likely to reflect both dietary differences and, although not studied extensively, age accumulation effects. Cadmium concentration in the kidney has been shown to correlate positively with age in the great skua *Catharacta skua skua*[61] and also increases with age in laughing gulls *Larus atricilla*,[155] royal terns *Sterna maxima* and sandwich terns *Sterna sandvicensis*.[120]

Those seabirds which feed predominantly on pelagic cephalopods, in particular, and large Euphausid crustaceans which accumulate cadmium to relatively high levels, tend to exhibit relatively elevated cadmium concentrations.[90,130,141,149] There is, however, some evidence to suggest that cadmium is regulated to some extent in seabirds. Muirhead and Furness[130] noted that the distributions of cadmium levels in a

TABLE 2.2: Cadmium concentrations (μg g^{-1} wet weight) in liver and kidney tissue of seabirds from the Antarctic (A), Gough Island (G) and Spitsbergen (S).

Species	Number Sampled	Liver Mean	Liver Range	Kidney Mean	Kidney Range	Locality	Ref.
Adelie penguin *Pygoscelis adeliae*	10	4	1- 8	51	24- 93	A	90
Chinstrap penguin *Pygoscelis antarctica*	13	2	1- 4	19	9- 39	A	141
Rockhopper penguin *Eudyptes crestatus*	12	14	4-26	72	32-122	G	130
Macaroni penguin *Eudyptes chrysolophus*	9	9	4-34	49	18-166	A	141
Wandering albatross *Diomedea exulans*	2	32	24-41	137	127-148	G	130
Yellow-nosed albatross *Diomedea chlororhynchos*	9	9	3-17	25	15- 46	G	130
Sooty albatross *Phoebetria fusca*	8	26	22-33	76	58- 92	G	130
Southern fulmar *Fulmarus glacialoides*	6	5	2-10	38	16- 75	A	141
Northern fulmar *Fulmarus glacialis*	10	17	6-32	55	22-114	S	141
Atlantic petrel *Pterodroma incerta*	13	19	9-40	61	42-102	G	130
Kerguelen petrel *Pterodroma brevirostris*	14	15	10-21	45	22- 68	G	130
Soft-plumaged petrel *Pterodroma mollis*	18	15	8-41	48	32- 90	G	130
Broad-billed prion *Pachyptila vittata*	31	16	9-26	33	19- 72	G	130
Great shearwater *Puffinus gravis*	12	15	6-27	74	38- 99	G	130
Little shearwater *Puffinus assimilis*	13	14	9-21	43	23- 71	G	130
Grey-backed storm petrel *Garrodia nereis*	8	12	8-18	23	18- 36	G	130
White-faced storm petrel *Pelagodroma marina*	7	8	6-12	33	25- 55	G	130
White-bellied storm petrel *Fregetta grallaria*	8	11	9-15	21	18- 26	G	130
Common diving petrel *Pelecanoides urinatrix*	17	7	3-14	32	17- 74	G	130
Tristan skua *Catharacta skua hamiltoni*	13	3	1- 5	26	13- 45	G	130
Brown skua *Catharacta skua lonnbergi*	8	5	4- 7	33	25- 42	A	141
South polar skua *Catharacta maccormicki*	8	5	<1- 7	25	4- 36	A	141
Glaucous gull *Larus hyperboreus*	11	4	<1- 9	23	4- 58	S	141
Little auk *Alle alle*	9	4	2- 6	21	6- 34	S	141
Brunnich's guillemot *Uria lomvia*	9	4	2-11	16	7- 38	S	141

range of seabird species from Gough Island did not differ significantly from Gaussian. This trend was also found for the essential metals copper and zinc, although the intraspecific variation of cadmium was higher than for these latter metals. From the data in Tables 2.2-2.4 it can be seen that cadmium concentrations in seabird kidney tissues range from 4-166 $\mu g\ g^{-1}$ wet weight. The range of concentrations in seal kidney tissues is 0.1-146.2 $\mu g\ g^{-1}$ wet weight whilst in whales and dolphins a range of <0.1-205.4 $\mu g\ g^{-1}$ wet weight is seen. Hence, in seabirds the range of cadmium values in kidney tissues tends to be of an order of magnitude less than that in both seals and whales and dolphins. Therefore, although cadmium shows age-related concentration increases, seabirds would appear to show some weak regulation of cadmium levels. Evidence of kidney damage was noted by Nicholson and Osborn [139] in north east Atlantic seabirds, this being attributed largely to naturally-occurring, high cadmium concentrations and existing despite the presence of metallothionein. The latter is thought to offer some protection against cadmium toxicity, especially in kidney tissue, cadmium binding strongly to this protein. Zinc is also bound by metallothioneins. Hence, zinc and cadmium concentrations have been shown to be positively correlated in kidney tissue of many seabirds. [94,129,130,138,141,157]

2.2.4 Cadmium in marine mammals

2.2.4.1. Pinnipeds

Seals show the same general pattern of cadmium distribution as seabirds in that levels tend to decrease in the order kidney > liver > muscle. [1,23,27,43,45,80,81,98,117,119,123,159,161,167,180,189] Cadmium concentrations in a range of species are given in Table 2.3. Comparisons between and within species are

TABLE 2.3: Cadmium concentrations ($\mu g\ g^{-1}$ wet (w) or dry (d) weight) in liver (L), kidney (K) and muscle (M) tissue of Pinnipeds.

Species	No. Sampled	Tis.	Mean	Range	Locality	Age[a]	Ref.
California sea lion	10	L	15.1	5.7- 90.0[d]	California	10-14	123
Zalophus californianus	10	K	115.0	85.0-569.0[d]	(females)	10-14	
Steller sea lion	19	L	0.7	0.1- 1.3[w]	Hokkaido,	<1- 8.8	80
Eumetopias jubata	21	K	4.2	0.8- 10.0[w]	Japan	<1- 8.8	
	15	M	<0.1	<0.1- 0.2[w]		<1- 8.8	
Northern fur seal	9	L	1.8	0.6- 4.6[w]	Washington	1-20	1
Callorhinus ursinus	9	K	5.8	0.2- 15.6[w]	coast, USA	1-20	
Harbour seal	31	L	----	<0.1- 0.2[w]	German North	<1- 8	45
Phoca vitulina	16	K	----	<0.1- 0.4[w]	Sea coast	<1- 8	
Ringed seal	29	L	7.3	2.7- 14.9[w]	West	----	98
Phoca hispida	29	K	37.4	9.0-146.2[w]	Greenland	----	
	29	M	<0.1	<0.1- 0.4[w]		----	
Harp seal	57	L	12.0[w]	----------	Gulf of St.	6+	161
Phoca groenlandica	56	K	38.8[w]	----------	Lawrence	6+	
	56	M	0.1[w]	----------	(females)	6+	
Ribbon seal	2	L	2.6	2.1- 3.1[w]	Okhotsk Sea	3- 5	81
Histriophoca fasciata	16	M	----	<0.1- 0.3[w]		1-16	
Grey seal	66	L	0.8	<0.1- 8.5[w]	East coast,	1- 9	119
Halichoerus grypus	70	K	2.1	0.1- 15.1[w]	Scotland	1- 9	
Leopard seal	15	L	5.1	0.8- 29.0[w]	Antarctic	----	180
Hydrurga leptonyx	15	M	<0.1	----------		----	
Weddell seal	2	L	1.1	1.0- 1.3[w]	Antarctic	Ad.[b]	189
Leptonychotes weddellii	2	K	6.4	2.9- 9.9[w]		Ad.	
	2	M	0.2	<0.1- 0.3[w]		Ad.	
Crabeater seal	5	L	38.8[d]	----------	Antarctic	----	167
Lobodon carcinophagus	5	K	102.1[d]	----------		----	
	5	M	0.4[d]	----------		----	
Ross seal	20	L	103.9	33.0-422.0[d]	Antarctic	----	117
Ommatophoca rossi							
Elephant seal	1	M	0.4[w]	----------	Antarctic	----	43
Mirounga leonina							

a- age in years; b- adults

hindered by presentation of data by different authors either on wet or dry weight bases, often without appropriate conversion factors, and further complicated by age-accumulation effects for this element. Cadmium concentration has been shown to increase with age (size) in several species.[45,81,123,159,161] Diet would appear to play an important role in determining cadmium levels in seals; those species feeding on cephalopods and crustaceans, for example, Ross seals Ommatophoca rossi, showing high levels[117] whilst predominantly fish-eating species, for example, harbour seals Phoca vitulina and grey seals Halichoerus grypus show lower cadmium levels.[27,45,46,84,86,159] Cadmium levels may correlate with liver selenium levels[123 161] suggesting a degree of protection by selenium to cadmium toxicity,[121] although the role of metallothionein, especially in kidney tissue, is important.[111]

2.2.4.2 Cetaceans

In common with seabirds and seals, the whales and dolphins show the same general body distribution pattern of cadmium in that organ concentrations decrease in the order kidney > liver > muscle.[26,41,50,51,84,89,104,169,182] Representative data are presented in Table 2.4. Comparisons are, again, hindered by age accumulation effects, although there is general agreement between the data presented in Table 2.4 and those from other studies.[51,169] Cadmium concentrations have been shown to be positively correlated with body length[50,89] and similarly to body weight and age.[89]

A positive correlation between zinc and cadmium levels has been demonstrated in the liver and kidney tissues of striped dolphin Stenella coeruleoalba.[89] Dietary sources are likely to be important since high cadmium levels are known to be found in

TABLE 2.4: Cadmium concentrations ($\mu g\ g^{-1}$ wet weight) in liver (L), kidney (K) and muscle (M) tissue of Cetaceans.

Species	No. Sampled	Tis.	Mean	Range	Locality	Leng.[a]	Ref.
Beluga	1	L	0.9	---------	Baltic Sea	2.7	84
Delphinapterus leucas	1	K	1.9	---------		2.7	
	1	M	<0.1	---------		2.7	
Narwhal	37	L	32.0	1.3-130.8	Pond Inlet,	3.7	182
Monodon monoceros	54	K	63.5	1.0-205.4	Canada	3.8	
	58	M	0.2	<0.1- 1.1		4.3	
Striped dolphin	57	L	6.3	<0.1- 11.1	East coast,	---	89
Stenella coeruleoalba	54	K	24.8	<0.1- 69.6	Japan	---	
	58	M	0.1	<0.1- 0.3		---	
Short-finned pilot whale	1	L	69.4	---------	North	---	41
Globicephala macrorhynchus	1	K	121.5	---------	Queensland	---	
	1	M	0.4	---------		---	
Harbour porpoise	17	L	0.2	<0.1- 0.9	East coast,	---	50
Phocoena phocoena	17	K	1.1	0.2- 2.9	Scotland (males)	---	
Goose-beaked whale	2	L	50.5	37.0- 64.0	Bermuda	---	104
Ziphius cavirostris	2	K	47.5	33.0- 62.0		---	
	4	M	0.2	---------		---	
Bottlenose whale	1	L	5.6	---------	North Sea	5.7	84
Hyperoodon ampullatus	1	M	<0.1	---------		5.7	
Bowhead whale	1	L	1.5	---------	Alaska	10.0	26
Balaena mysticetus	2	K	1.4	<0.1- 2.8		9.4	
	2	M	<0.1	---------		9.4	

a- mean length in metres

cephalopods [124] whilst fish tend to exhibit lower cadmium concentrations. The low cadmium levels in harbour porpoise Phocoena phocoena, [50,84] for example, may reflect low cadmium levels in fish which predominate in the diet of this cetacean.

2.2.4.3 Sirenians and other groups

The dugong Dugong dugon shows the same pattern of cadmium distribution as found in other marine mammals and seabirds [42] with the kidney exhibiting the highest concentrations (ranging from <0.04-59 $\mu g\ g^{-1}$ wet weight). The two studies of cadmium in dugong muscle are in general agreement [42,128] with levels in the range <0.02-0.12 µg g^{-1} wet weight. A positive correlation between cadmium concentration and age and with zinc in both liver and kidney tissue has been demonstrated by Denton et al. [42] The correlation between metals may simply be a reflection of the tendency for both to increase with age. Cadmium levels in polar bear *Ursus maritimus* liver have been shown to correlate positively with age by Norstrom et al. [144] but the levels are generally low (< 1 µg g^{-1} wet weight) reflecting the tendency for polar bears to eat seal skin and blubber which contain relatively low levels of cadmium. Cadmium concentrations in polar bears were found to be higher in the west Arctic compared to the east Arctic. [144] Cadmium concentrations in otters *Lutra lutra* from the Orkney Islands have been found to be generally low with liver levels ranging from 'not detected' to 0.39 µg g^{-1} wet weight. Kidney concentrations were slightly higher, falling between 0.08 and 0.56 µg g^{-1} wet weight. [126]

2.2.5 Conclusions

Highest levels of cadmium reported in marine vertebrates have been found in kidney tissue of Ross seals (422 µg g^{-1} dry weight), [117] narwhals *Monodon monoceros* (205 µg g^{-1} wet weight), [182] and macaroni penguins *Eudyptes chrysolophus* (166 µg g^{-1} wet weight). [141] Generally, cadmium tends to accumulate to a greater extent and to relatively high concentrations in kidney tissue of higher marine vertebrates. This pattern is less well defined in marine fish, although this may reflect the comparatively low levels found in fish and the difficulty in measuring accurately small increases or fluctuations. Being non-essential and so not metabolically regulated but accumulated and stored in a nontoxic situation in most marine vertebrates, cadmium shows age-related concentration increases, especially in marine mammals,[45,50,80,89,123,161,159] this often in association with similar and correlated increases in zinc concentrations.

There is some evidence to suggest that cadmium levels can be better regulated by seabirds than by marine mammals,[130] and that age accumulation is more pronounced in mammals. It would seem likely that, along with mercury and, to a lesser extent lead, cadmium is potentially a pollution threat, although clear-cut examples of anthropogenic influence causing environmental damage by cadmium are few. Long-lived seabirds and marine mammals feeding on cephalopods appear to accumulate cadmium to the greatest extent[117,130,141] and may be most vulnerable to cadmium pollution.

2.3 COPPER

2.3.1 Introduction

Copper is an essential element in vertebrates, being associated with numerous metalloenzymes and metalloproteins.

2.3.2 Copper in marine fish

Copper concentrations in fish tissues show little variation with location or species and would appear to be under close physiological regulation. Generally, muscle copper levels have means of around 0.3-0.8 $\mu g\ g^{-1}$ wet weight with few values less than 0.2 $\mu g\ g^{-1}$ or greater than 2.5 $\mu g\ g^{-1}$.[3,10,34,70,83,118,132-135,151-153,187] Copper concentrations tend to be higher in liver and kidney tissues relative to muscle.[70,118,151,168,179,187] From studies of copper concentrations in cartilaginous fish,[71,168,179,187] there would appear to be little difference in copper levels between sharks and their allies and the bony fish.

Copper concentration shows little or no tendency to increase or decrease with increasing fish length which is not unexpected for an essential element. [34,71,91,118] A summary of references to copper levels in marine fish is presented in Table 2.1.

2.3.3 Copper in seabirds

Copper concentrations in seabird tissues exhibit low variation on both inter-species and geographical bases, again suggesting close metabolic regulation of this metal. Mean copper concentrations in liver tissue tend to be around 6 $\mu g\ g^{-1}$ wet weight with few values greater than 10 $\mu g\ g^{-1}$. In general, kidney copper concentrations tend to be lower than liver concentrations with levels in muscle lower still. Representative copper concentration data from studies of a range of species from the southern and northern hemispheres are presented in Table 2.5. Other studies have yielded similar results to those presented. Data for birds from the Antarctic [2,90,141,167] are in close agreement with those in Table 2.5, although the high muscle copper concentrations in three species of petrel presented by Anderlini *et al.* [2] are difficult to explain. Studies of metal levels in crested terns *Sterna bergii* [92] and fairy prions *Pachyptila turtur* [21] from Australia, brown pelicans from the U.S. [13] and kelp gulls *Larus dominicanus* and silver gulls *Larus novaehollandiae* from estuarine regions of New Zealand [177] have produced comparable copper concentrations to those above. In a study of Antarctic and northern hemisphere birds, [141] those birds from Spitsbergen showed significantly higher copper levels relative to Antarctic species. However, the difference was not great.

TABLE 2.5: Copper concentrations (µg g^{-1} wet weight) in liver and kidney tissue of seabirds from the Antarctic (A), Gough Island (G) and Spitsbergen (S).

Species	Number Sampled	Liver Mean	Liver Range	Kidney Mean	Kidney Range	Locality	Ref.
Adelie penguin *Pygoscelis adeliae*	10	4.7	3.3- 6.1	3.6	2.9- 4.5	A	90
Chinstrap penguin *Pygoscelis antarctica*	13	4.5	3.6- 6.0	3.6	2.8- 5.7	A	141
Rockhopper penguin *Eudyptes crestatus*	12	4.1	2.8- 5.8	3.8	2.7- 6.1	G	130
Macaroni penguin *Eudyptes chrysolophus*	9	4.0	2.4- 5.3	3.2	2.6- 3.7	A	141
Wandering albatross *Diomedea exulans*	2	6.6	4.9- 8.4	5.2	4.7- 5.6	G	130
Yellow-nosed albatross *Diomedea chlororhynchos*	9	5.0	3.5- 7.0	3.3	2.8- 4.9	G	130
Sooty albatross *Phoebetria fusca*	8	6.3	4.1- 8.5	4.6	4.2- 5.3	G	130
Southern fulmar *Fulmarus glacialoides*	6	4.1	3.4- 4.8	4.5	3.3- 6.3	A	141
Northern fulmar *Fulmarus glacialis*	10	6.2	5.6- 6.7	4.1	3.3- 4.7	S	141
Atlantic petrel *Pterodroma incerta*	13	4.9	3.6-13.0	6.1	4.5- 9.3	G	130
Kerguelen petrel *Pterodroma brevirostris*	14	6.4	3.4-17.0	4.9	3.8- 8.4	G	130
Soft-plumaged petrel *Pterodroma mollis*	18	5.2	3.5-12.0	5.9	4.1- 8.0	G	130
Broad-billed prion *Pachyptila vittata*	31	6.4	3.6- 8.4	4.4	3.2- 6.0	G	130
Great shearwater *Puffinus gravis*	12	5.9	5.1- 8.4	6.1	4.7-11.0	G	130
Little shearwater *Puffinus assimilis*	13	7.9	5.5-13.0	5.8	2.8-24.0	G	130
Grey-backed storm petrel *Garrodia nereis*	8	7.6	4.9-15.0	6.5	4.5- 8.3	G	130
White-faced storm petrel *Pelagodroma marina*	7	8.5	5.7-11.0	7.0	6.2- 8.4	G	130
White-bellied storm petrel *Fregetta grallaria*	8	6.3	3.4- 8.1	6.4	5.2- 7.5	G	130
Common diving petrel *Pelecanoides urinatrix*	17	6.9	5.3-10.0	5.5	2.8- 8.0	G	130
Tristan skua *Catharacta skua hamiltoni*	13	4.2	3.1- 5.4	4.6	3.3- 6.6	G	130
Brown skua *Catharacta skua lonnbergi*	8	4.6	3.7- 5.6	4.5	3.6- 5.7	A	141
South polar skua *Catharacta maccormicki*	8	5.8	4.5- 7.0	4.6	3.3- 6.1	A	141
Glaucous gull *Larus hyperboreus*	11	7.3	5.5-10.0	5.2	4.1- 6.8	S	141
Little auk *Alle alle*	9	8.4	6.8- 9.4	6.4	5.3- 9.7	S	141
Brunnich's guillemot *Uria lomvia*	9	8.2	6.4- 9.4	6.9	4.1-11.2	S	141

2.3.4 Copper in marine mammals

2.3.4.1 Pinnipeds

Copper concentrations in a selection of seal species are presented in Table 2.6. From these and other data, copper levels tend to decrease from liver > kidney > muscle. [45,46,51,84,98,123,161,167,180,189] Within a given species there is variation in tissue copper concentration. However, this variation is not thought to represent accumulation of copper with increasing size/age of animal. [45,117,161] Martin *et al.* [123] found significantly higher copper concentrations in liver and kidney tissue of female California sea lions *Zalophus californianus* with premature pups when compared to females with normal term pups. In this case, the balance of other elements, particularly mercury, selenium and bromine was reported to be important. Geographical variation of copper levels as expressed by this group is unclear. Harbour seals from areas of the North and Wadden Seas [45,46,84] might be expected to have elevated copper levels in view of the relatively polluted nature of such locations. This does not seem to be the case (Table 2.6). Furthermore, within a study of copper levels in the harp seal *Phoca groenlandica* from several locations, no clear geographical trend could be deduced. [161] Diet has been cited as playing an important role in determining the copper burden of seals, in that high levels of copper observed in Ross seals are thought to be natural and reflect the relatively high levels of this metal in squid, the main prey of this species. [117]

2.3.4.2 Cetaceans

Copper levels in various whale species are presented in Table 2.7. As with the data for seal tissue copper

TABLE 2.6: Copper concentrations (µg g^{-1} wet (w) or dry (d) weight) in liver (L), kidney (K) and muscle (M) tissue of Pinnipeds.

Species	No. Sampled	Tis.	Mean	Range	Locality	Ref.
California sea lion	10	L	86.0	61.0-285.0^d	California	123
Zalophus californianus	10	K	22.4	21.2- 52.3^d	(females)	
Harbour seal	58	L	----	2.6- 17.0^w	German North	45
Phoca vitulina	16	K	----	2.3- 4.0^w	Sea coast	
Ringed seal	29	L	11.6	4.5- 22.3^w	West	98
Phoca hispida	29	K	10.6	5.0- 21.8^w	Greenland	
	29	M	1.3	1.0- 1.6^w		
Harp seal	57	L	24.3^w	----------	Gulf of St.	161
Phoca groenlandica	56	K	6.7^w	----------	Lawrence	
	50	M	1.8^w	----------	(females)	
Grey seal	38	L	28.9	6.2- 75.0^w	Farne Islands,	27
Halichoerus grypus	37	K	3.0	1.6- 5.0^w	N.E. England	
					(females)	
Leopard seal	15	L	44.6	16.5- 68.2^w	Antarctic	180
Hydrurga leptonyx	15	M	0.7	0.4- 1.2^w		
Weddell seal	2	L	20.4	15.0- 25.8^w	Antarctic	189
Leptonychotes weddellii	2	K	8.1	5.1- 11.0^w		
	2	M	0.9	0.9- 1.0^w		
Crabeater seal	5	L	74.0^d	----------	Antarctic	167
Lobodon carcinophagus	5	K	33.3^d	----------		
	5	M	5.0^d	----------		
Ross seal	20	L	83.0	16.0-255.0^d	Antarctic	117
Ommatophoca rossi						
Elephant seal	1	M	4.1^d	----------	Antarctic	43
Mirounga leonina						

concentrations, the levels in cetaceans generally decrease in the order liver > kidney > muscle. The values reported in Table 2.7 are in close agreement with each other, despite large geographical variation in the origins of species analysed. Close regulation of copper levels is not unexpected given that it is an essential element. Wagemann _et al._ [182] reported a negative correlation of copper concentration with length in the narwhal,

TABLE 2.7: Copper concentrations ($\mu g\ g^{-1}$ wet weight) in liver (L), kidney (K) and muscle (M) tissue of Cetaceans.

Species	No. Sampled	Tis.	Mean	Range	Locality	Ref.
Beluga	1	L	20.4	--------	Baltic Sea	84
Delphinapterus leucas	1	K	3.1	--------		
	1	M	1.1	--------		
Narwhal	37	L	5.3	2.0-20.3	Pond Inlet,	182
Monodon monoceros	54	K	2.3	1.8- 3.5	Canada	
	58	M	0.7	0.5- 1.2		
White-beaked dolphin	1	L	6.4	--------	Kolding Fjord,	4
Lagenorchynchus albirostris	1	M	1.4	--------	Denmark	
Striped dolphin	57	L	8.1	3.6-15.2	East coast,	89
Stenella coeruleoalba	30	K	3.1	1.5- 6.1	Japan	
	59	M	2.0	1.3- 3.4		
Short-finned pilot whale	1	L	6.4	--------	North	41
Globicephala macrorhynchus	1	K	3.7	--------	Queensland	
	1	M	0.7	--------		
Harbour porpoise	17	L	7.3	2.7-12.8	East coast,	50
Phocoena phocoena	17	K	3.8	2.6- 4.8	Scotland (males)	
Goose-beaked whale	2	L	5.2	3.2- 7.1	Bermuda	104
Ziphius cavirostris	2	K	5.6	3.8- 7.3		
	4	M	0.5	--------		
Bottlenose whale	1	L	2.8	--------	North Sea	84
Hyperoodon ampullatus	1	M	0.6	--------		
Bowhead whale	1	L	3.1	--------	Alaska	26
Balaena mysticetus	2	K	0.6	0.3- 0.9		
	2	M	0.2	--------		

a trend supported by Honda _et al._ [89] in the striped dolphin with respect to length and weight in kidney tissue and age in both liver and kidney tissue. The latter study noted a marked decrease in copper concentration in 0 to 1 year-old dolphins, the levels then remaining relatively stable in immature and mature animals. Overall, copper concentration decrease was correlated more strongly both with body length and body weight increase which Honda _et al._ [89] attributed to greater importance of metabolic turnover which itself is correlated with body size, as opposed to age or exposure time, in determining copper levels. With only one study of copper levels in a baleen whale [26] it is difficult to make comparisons with the toothed whales.

2.3.4.3 Sirenians and other groups

Copper concentrations in the dugong have been reported by Denton et al. [42] and by Miyazaki et al. [128] Levels in liver tissue ranged from 2-160 $\mu g\ g^{-1}$ wet weight [42] which, at the upper extreme, represent the highest values in any marine mammal studied. Kidney values are in the same range (0.5-3.2 $\mu g\ g^{-1}$ wet weight) as other marine mammals, as are values for muscle (0.1-1.0 $\mu g\ g^{-1}$ wet weight) which are also in close agreement between the two studies. [42,128] Denton et al. [42] noted that copper levels in both liver and kidney show a negative correlation with age, although the highest liver copper concentration occurred in a male of at least 33 years of age. Unlike the findings of Honda et al., [89] the copper levels decreased consistently with age, these decreased concentrations being linked to depigmentation in certain individuals. Dietary levels of copper are considered by the authors to be relatively low in dugongs, although hepatic copper was negatively correlated with increasing concentrations of zinc, cadmium and iron. Norstrom et al. [144] reported relatively high levels of copper in liver tissue of polar bear, concentrations of this element being correlated with zinc levels. Copper concentrations were not found to be correlated with age in the polar bear. [144]

2.3.5 Conclusions

Within each respective sub-group of marine vertebrates covered by this review, there is marked agreement with respect to copper levels regardless of species or geographical location. Highest copper levels in marine vertebrates have been reported in liver tissue of California sea lions (285 µg g^{-1} dry weight),[123] kidney tissue of little shearwater _Puffinus assimilis_ (24 µg g^{-1} wet weight),[130] liver tissue of black marlin (22 µg g^{-1} wet weight),[118] and liver tissue of beluga _Delphinapterus leucas_ (20.4 µg g^{-1} wet weight).[84] It would seem that concentrations of this essential metal are relatively closely regulated, and it is unlikely to show any substantial age-related concentration increase, although its role when at low dietary concentrations, in the absorption of other metals, could be relatively important.[42]

2.4 IRON

2.4.1 Introduction

In vertebrates, iron is found most notably as an essential component of several metalloproteins, including haemoglobin and myoglobin and also a number of metalloenzymes.

2.4.2 Iron in marine fish

There are few data on iron levels in marine fish. As an essential element, iron is fairly uniform in its concentration between the few studies which have investigated this metal. Muscle concentrations range from <1 to about 14 µg g^{-1} wet weight with mean concentrations around 7 µg g^{-1} wet weight and less.[34,83,152,179] Liver and kidney concentrations would appear to be somewhat higher; Vas[179] found iron levels up to 12 and 15 µg g^{-1} wet weight in kidney and liver tissues, respectively, for tope _Galeorhinus galeus_ from Liverpool Bay, north west England. A summary of the references to iron levels in marine fish is presented in Table 2.1.

2.4.3 Iron in seabirds

Again, few data exist on the iron levels in seabirds. This metal is unlikely to show marked accumulation effects and is thought to be less of a potential toxic threat when compared to other essential metals. Honda *et al.* [90] reported very high liver iron concentrations in Adelie penguins *Pygoscelis adeliae* (range 233-1670 µg g^{-1} wet weight) with lower levels in kidney tissue and lower still in muscle tissue. The mean breast feather iron level ranged from 6-66 µg g^{-1} wet weight. Male Adelie penguins show a redistribution of iron from muscle to liver during a period of starvation after mating resulting in significantly higher hepatic iron concentrations compared to females. Studies on terns [35,92] have reported iron levels lower than those for Adelie penguins with liver concentrations less than 300 µg g^{-1} wet weight in crested terns [92] and less than 200 µg g^{-1} in common tern *Sterna hirundo* [35] chicks.

2.4.4 Iron in marine mammals

2.4.4.1 Pinnipeds

Data for iron levels in seals are presented in Table 2.8. Comparisons between species are hindered by data presentation either on a dry weight basis [117,123] or on a wet weight basis, [46,189] although liver iron concentrations are higher when compared to kidney and muscle tissues (Table 2.8). The extremely high iron concentrations in some seal species (Table 2.8) may reflect increased levels of myoglobin associated with deep-diving. No age-accumulation trends have been reported and there is no evidence to suggest that this metal is a pollutant in seals.

TABLE 2.8: Iron concentrations (µg g^{-1} wet (w) or dry (d) weight) in liver (L), kidney (K) and muscle (M) tissue of Pinnipeds.

Species	No. Sampled	Tis.	Mean	Range	Locality	Ref.
California sea lion	10	L	2000	730-5590^{d}	California	123
Zalophus californianus	10	K	448	349- 618^{d}	(females)	
Harbour seal	8	L	----	28-2340^{w}	Dutch	46
Phoca vitulina	2	K	----	31- 66^{w}	Wadden Sea	
Weddell seal	2	L	665	389- 940^{w}	Antarctic	189
Leptonychotes weddellii	2	K	389	159- 618^{w}		
	2	M	252	237- 267^{w}		
Ross seal	20	L	519	231- 961^{d}	Antarctic	117
Ommatophoca rossi						
Elephant seal	1	M	147^{w}	--------	Antarctic	43
Mirounga leonina						

2.4.4.2 Cetaceans

Data for iron levels in whales and dolphins are presented in Table 2.9. As in seals and seabirds, the liver would appear to concentrate iron to the highest level, presumably due to its high blood content, although the few, relatively high, concentrations reported in seals have not been reported for whales and dolphins. Honda *et al.* [89] described an increase in iron concentration with age in striped dolphin, up to about 8 years, the iron level remaining roughly constant thereafter.

2.4.4.3 Sirenians and other groups

Denton *et al.* [42] reported extremely high liver iron concentrations (up to 21674 µg g^{-1} wet weight) in dugongs from North Queensland. Levels in kidney were somewhat lower, (up to 588 µg g^{-1} wet weight) whilst maximum muscle levels reached 82 µg g^{-1} wet weight and are generally of the same order as values reported by Miyazaki *et al.* [128] Iron concentration was shown to be positively correlated with age in liver and muscle tissue. [42]

TABLE 2.9: Iron concentrations (µg g^{-1} wet weight) in liver (L), kidney (K) and muscle (M) tissue of Cetaceans.

Species	No. Sampled	Tis.	Mean	Range	Locality	Ref.
Striped dolphin	57	L	215	------	East coast,	89
Stenella coeruleoalba	30	K	143	40-267	Japan	
	59	M	159	47-222		
Short-finned pilot whale	1	L	557	------	North	41
Globicephala macrorhynchus	1	K	202	------	Queensland	
	1	M	218	------		
Goose-beaked whale	2	L	500	472-528	Bermuda	104
Ziphius cavirostris	2	K	181	180-182		
	4	M	106	------		

These high iron concentrations in the liver of the dugong were related to high dietary iron levels and much of the iron was found to be stored as haemosiderin. Iron concentration in liver tissue of polar bears was found to average 130 µg g^{-1} wet weight and as such is lower than values reported for seals and whales (Tables 2.8 & 2.9). No age effects were noted.[144]

2.4.5 Conclusions

Overall, there are relatively few data on iron levels in marine vertebrate groups, although the exceptionally high values reported by Denton *et al.*[42] of over 21000 µg g^{-1} wet weight in liver tissue of dugongs are notable. As an essential element, it is unlikely that iron will have any real pollution-derived effects, except in severe and localised cases, and levels will tend to be closely regulated. The levels of iron in deep-diving marine mammals may prove to be of interest. The relationship between iron metabolism, iron flux dynamics and myoglobin storage, for example, may be worthy of further investigation.

2.5 LEAD

2.5.1 Introduction

Lead has no known biological function or requirement and can be classified as non-essential. Environmental lead derived from anthropogenic sources is likely to have increased markedly in recent decades with the addition of alkyl lead to petrol as an 'anti-knock' agent.

2.5.2 Lead in marine fish

Marine fish tend to have low muscle lead levels, generally within the range from limits of detection to 1 $\mu g\ g^{-1}$ wet weight with values rarely exceeding 2 $\mu g\ g^{-1}$ wet weight.[10,70,71,74,75,83,112,118,132-135,151-154,168,176,179,186] Where evaluated, liver and kidney lead levels tend to be higher than muscle lead levels.[70,74,118,151,186]

As a non-essential element, one might expect lead to show some accumulation effects with age or size of fish. In black marlin, Mackay _et al._[118] reported no such increase in lead concentration with increasing weight, length or girth in both muscle and liver tissue. In relatively more polluted, coastal and estuarine systems both elevated lead levels and age/size accumulation effects have been reported. Badsha & Sainsbury[7] noted an increase in lead concentration with increasing weight and length of whiting _Merlangius merlangus_ from the Severn estuary, south west England whilst Hardisty _et al._[82] reported somewhat higher lead concentrations than generally found in other studies in whole fish samples from the same locality with mean lead concentrations of 24 $\mu g\ g^{-1}$ dry weight in whiting. Generally, only in coastal areas do lead levels show any increase above values which can best be described as low. This increase may reflect anthropogenic inputs of this metal. A summary of the references to lead in marine fish is presented in Table 2.1.

2.5.3 Lead in seabirds

Seabirds, in a similar way to marine fish, exhibit generally low levels of lead, rarely exceeding 1 µg g^{-1} wet weight in any tissue, [13,21,90,92,120,140,141,145,155,157] although bone has been shown to concentrate lead compared to other tissues [90,93,94,120,145,155,177] and Bull et al. [24] found relatively high liver lead levels (1-10 µg g^{-1} wet weight) in gulls (Larus sp.) found dead on the Mersey estuary, north west England. The dead gulls showed evidence consistent with poisoning in experimental gulls dosed with lead in the laboratory. [148] Similarly high lead levels have been reported in laughing gulls from Galveston Bay, Texas by Hulse et al., [93] liver tissue values averaging 5.3 µg g^{-1} wet weight with a maximum value of 13.8 µg g^{-1} wet weight. These levels agree closely with the earlier findings of Munoz et al. [131] but Reid and Hacker [155] noted a significant decrease in lead levels between 1977 and 1980 in this species. The decline was attributed to the reduction in lead emissions to the local environment.[155] The pattern of lead distribution within the bird is less-well defined than for most other metals, the distinct gradient of concentrations between organs being less clear-cut, except for high levels found in bone.

In studies which include data on seabird bone lead concentrations, the majority give values which fail to approach bone lead levels in feral pigeons in a highly lead-polluted environment of London. Those fall in the range 108-669 µg g^{-1} dry weight. [95] Turner et al. [177] reported bone lead levels of over 1900 µg g^{-1} expressed as 'bone ash' in the silver gull from estuarine regions of New Zealand which are notable, if not directly comparable to other studies, and may be the result of ingestion of lead shot. However, Hutton, [94] reported higher bone lead levels in the herring gull *Larus argentatus* (mean 37.7 µg g^{-1} dry weight) compared to the great skua (mean 4.5 µg g^{-1} dry weight). This difference was attributed to the coastal distribution of the former which would be likely to result in this species being exposed to relatively higher lead concentrations, and the relatively oceanic distribution of the latter, far from any anthropogenic lead sources, although atmospheric transport of this metal is known to be important. Generally, it would appear that avian lead levels tend to be low in oceanic environments whilst there is some evidence of increased lead concentration in some seabirds with coastal distributions.

2.5.4 Lead in marine mammals

2.5.4.1 Pinnipeds

Data on lead concentrations in various seal tissues are presented in Table 2.10. It can be seen that levels are generally low and concentrations rarely exceed 1 µg g^{-1} wet weight in any tissue, [1,19,27,45,46,51,84,86,98,117,159,161] although bone and teeth tend to accumulate higher concentrations than do the soft organs. [19] Elevated lead levels tend to be found in seals inhabiting relatively industrialised, coastal regions. Lead concentrations of up to 17 µg g^{-1} wet weight in liver tissue of grey seals from the east coast of Scotland were reported by Holden, [86] although McKie *et al.* [119] noted lead levels consistently below the limit of detection (<0.5 µg g^{-1} wet weight) for the same species from the same

TABLE 2.10: Lead concentrations ($\mu g\ g^{-1}$ wet (w) or dry (d) weight) in liver (L), kidney (K) and muscle (M) tissue of Pinnipeds.

Species	No. Sampled	Tis.	Mean	Range	Locality	Ref.
California sea lion	6	L	1.30^{d}	---------	California	19
<u>Zalophus californianus</u>	6	K^{a}	2.00^{d}	---------		
	6	M	1.10^{d}	---------		
Northern fur seal	9	L	0.50	$0.20-0.80^{w}$	Washington	1
<u>Callorhinus ursinus</u>	9	K	1.00	$0.80-1.80^{w}$	coast, USA	
Harbour seal	31	L	----	$0.10-0.55^{w}$	German North	45
<u>Phoca vitulina</u>	16	K	----	$0.14-0.55^{w}$	Sea coast	
Ringed seal	29	L	----	$<0.01-0.03^{w}$	West	98
<u>Phoca hispida</u>	29	K	----	$<0.01-0.48^{w}$	Greenland	
	29	M	0.04	$0.02-0.10^{w}$		
Harp seal	57	L	0.13^{w}	---------	Gulf of St.	161
<u>Phoca groenlandica</u>	56	K	0.04^{w}	---------	Lawrence	
	56	M	0.03^{w}	---------	(females)	
Grey seal	9	L	7.00	$<3.0-17.00^{w}$	East Scotland	86
<u>Halichoerus grypus</u>						
Ross seal	20	L	0.01	$0.00-0.08^{d}$	Antarctic	117
<u>Ommatophoca rossi</u>						
Elephant seal	1	M	7.11^{w}	---------	Antarctic	43
<u>Mirounga leonina</u>						

a- kidney medulla

area, a similar trend being noted by Caines [27] in grey seals from the Farne Islands, north east England. Harbour seals which are found relatively close inshore, tend to show higher lead levels than other more pelagic species which may reflect anthropogenic effects with respect to lead. Holden [86] reported lead values from 3 $\mu g\ g^{-1}$ wet weight up to 12 $\mu g\ g^{-1}$ wet weight in liver tissue of harbour seals from the east coast of Scotland and England. However, even the lower end of this range is never reached in studies of the same species from similar European coastal sites [45,46,159] which throws Holden's data into doubt. In contrast, Ross seals from the Antarctic exhibit very low lead levels (0-0.08 $\mu g\ g^{-1}$ dry weight), this reflecting the remoteness from any industrialisation of the Antarctic.[117] The relatively high lead level in muscle tissue of an elephant seal _Mirounga leonina_ (7.11 $\mu g\ g^{-1}$ wet weight), also from the Antarctic,[43] is difficult to explain whilst the maximum concentration of 99.2 $\mu g\ g^{-1}$ wet weight in the muscle tissues of ringed seals _Phoca hispida_ from east Arctic Canada, as reported by Fallis,[51] would appear to be erroneous. Ronald _et al._[161] reported no bioaccumulation of lead by harp seals whilst a similar finding is noted by Roberts _et al._[159] for the harbour seal.

2.5.4.2 Cetaceans

Representative data on lead concentrations in whale and dolphin tissues are presented in Table 2.11. Lead concentrations are consistently low (< 1 $\mu g\ g^{-1}$ wet weight) in all studies [26,41,51,84,89,104,182] with levels generally higher in liver tissue > kidney > muscle. This distribution pattern is less well defined for lead than for other metals. Higher lead concentrations have been reported in the harbour porpoise and white-beaked dolphin _Lagenorchynchus albirostris_ from the Danish coast when compared to other species.[4] A positive correlation between lead concentration and age, length and weight in liver and muscle tissue was found by Honda _et al._[89] in striped dolphins, the relationship with age being strongest. Lead concentration increased with age up to 1 year then remained fairly constant up to 18 years whereafter a steady increase in lead concentration was noted. The rapid increase in concentration up to 1 year was attributed to lead transfer from the mother via the milk, the 'levelling off' of lead

TABLE 2.11: Lead concentrations (µg g^{-1} wet weight) in liver (L), kidney (K) and muscle (M) tissue of Cetaceans.

Species	No. Sampled	Tis.	Mean	Range	Locality	Ref.
Beluga	1	L	0.36	--------	Baltic Sea	84
Delphinapterus leucas	1	K	0.13	--------		
	1	M	0.08	--------		
Narwhal	37	L	0.03	0.01-0.06	Pond Inlet,	182
Monodon monoceros	54	K	0.02	<0.01-0.08	Canada	
	58	M	0.01	<0.01-0.04		
White-beaked dolphin	1	L	4.50	---------	Kolding Fjord,	4
Lagenorchynchus albirostris	1	M	2.20	---------	Denmark	
Striped dolphin	57	L	0.22	0.03-0.64	East coast,	89
Stenella coeruleoalba	30	K	0.17	0.01-0.71	Japan	
	59	M	0.18	0.04-0.26		
Short-finned pilot whale	1	L	<0.12	---------	North	41
Globicephala macrorhynchus	1	K	<0.12	---------	Queensland	
	1	M	<0.09	---------		
Harbour porpoise	4	L	3.50	1.90-5.30	Danish	4
Phocoena phocoena	4	M	3.30	1.60-4.70	coast	
Goose-beaked whale	2	L	<0.50	---------	Bermuda	104
Ziphius cavirostris	2	K	<0.50	---------		
	4	M	<0.50	---------		
Bottlenose whale	1	L	0.18	---------	North Sea	84
Hyperoodon ampullatus	1	M	0.03	---------		
Bowhead whale	1	L	0.12	---------	Alaska	26
Balaena mysticetus	2	K	0.78	0.71-0.85		
	2	M	0.22	0.10-0.34		

concentration with age between 1-18 years was the result of a 'dilution effect' of increasing body size and the gradual increase of lead concentration with increasing age above 18 years coincided with the termination of increase in body weight. 89

2.5.4.3 Sirenians and other groups

Lead levels in dugongs were found to be consistently low with values < 0.09 µg g^{-1} wet weight in liver and kidney tissue

[42] whilst slightly higher in muscle tissue (maximum value 0.25 μg g^{-1} wet weight).[42,128] These low levels probably simply reflect the unpolluted nature of the sampling sites. Otters from northern Scotland were found to have lead levels of up to 3.65 and 3.80 μg g^{-1} wet weight in liver and kidney tissue respectively with up to 10 μg g^{-1} wet weight in hair.[126] These values are comparable to the highest values reported for dolphins (Table 2.11) and may reflect anthropogenic influences.

2.5.5 Conclusions

If lead levels in marine vertebrates were to exhibit any sign of being the direct result of pollution, the coastal environment would be the most likely area in which such trends would be manifest. Anthropogenic sources of this metal would tend to enter the marine environment along coastal and estuarine systems, although atmospheric transport of lead offers an alternative route to the sea.

Lead has no biological function and is likely, therefore, to exhibit age-related accumulation trends similar to those of cadmium and mercury. The levels measured in marine vertebrates, however, tend to be low, often at the limits of detection, although there is evidence to suggest that, especially in coastal environments, lead levels show some degree of elevation and that this lead is of industrial origin. Both Hardisty *et al.* [82] and Badsha and Sainsbury [7] reported relatively high lead concentrations (>20 μg g^{-1} dry weight) in whole fish samples of whiting from the Severn estuary, south west England whilst Murray and Portmann [135] noted a maximum lead concentration of 4.2 μg g^{-1} wet weight in muscle tissues of thornback rays *Raja clavata* from the Irish Sea. Bull *et al.* [24] noted relatively high lead levels (up to 10 $\mu g\ g^{-1}$ wet weight) in liver tissue of gulls found dead from the Mersey estuary, north west England. Harbour porpoises from the Danish coast have been found to contain lead at a maximum concentration of 5.3 $\mu g\ g^{-1}$ wet weight in liver tissues. [4] Hard tissues, such as bone and teeth, tend to exhibit the highest lead concentrations; Hutton [94] noted a maximum lead concentration of 78 $\mu g\ g^{-1}$ dry weight in bone tissue of herring gulls from the Isle of May, Scotland.

2.6 MERCURY

2.6.1 Introduction

Mercury has no known biological function and as such can be classified as non-essential. Within the marine biosphere, mercury has been found to exist in both inorganic and organic forms, the relative proportion of these two forms varying in different marine groups.

2.6.2 Mercury in marine fish

In contrast to other heavy metals, mercury shows well-defined age/size accumulation trends in larger and longer-lived species of pelagic fish. Such fish were the subject of confiscation following the establishment by the U.S. Food and Drug Administration of a maximum permissible level of 5 $\mu g\ g^{-1}$ wet weight of mercury in fish. This move followed mercury measurements in swordfish and tuna which revealed concentrations above this level and which were initially suggested to be the result of widespread, anthropogenic mercury emission to the marine environment. It is more likely, however, that mercury levels measured are natural and are a consequence of accumulation and storage without metabolic regulation of tissue levels.

Many studies on a wide range of marine fish have reported positive correlations between mercury concentration and a measure of age, weight or length of fish.[11,29,34,40,48,73,77-79,101,115,116,118,127,158,163,164,175,183,184] This relationship is especially noteworthy when one compares the small number of corresponding relationships reported for the other, non-essential metals cadmium and lead. This may, however, reflect the increased interest in mercury as a potential threat to human health. Despite this tendency for mercury to increase in concentration with increasing size/age of some fish, muscle mercury levels tend to be less than 1 µg g^{-1} wet weight with kidney and liver levels slightly higher (liver > kidney > muscle).[10,31,34,55,57,70,73-79,83,101,105,108,115,116,127,132-135,151,153,154,158,166,175,186] Considerably higher mercury values have been reported in groups such as marlin, swordfish, tuna and various shark species.[11,28,29,40,58,118,158,163,164,184] Evidence of slightly elevated mercury levels in fish from inshore, polluted areas is given by Harms[83] and Murray and Norton,[134] although a general trend of decline in mercury levels is noted by the latter study of fish caught around the British Isles and is supported by the findings of Murray and Portmann.[135]

Mercury in fish muscle would appear to be predominantly in the organic form (>80% of total mercury),[10,28,31,101,116,158,173,175,183] although this relationship is different in some large, pelagic species which have muscle organic mercury levels of only 40 % or less of the muscle total mercury level.[158,164] This percentage decreases further in liver and kidney tissue.[158,164] The relationship between organic and inorganic mercury in fish tissues is worthy of further investigation in view of the possible biotransformations of this element, from the organic form to the inorganic form which are thought to take place in top predators. A summary of the references to mercury levels in marine fish is presented in Table 2.1.

2.6.3 Mercury in seabirds

Total mercury levels in some seabirds from both southern and northern hemisphere studies are presented in Table 2.12. From this selection of data, it can be seen that total mercury levels vary enormously both within and between species. This general trend is true for all studies and is in contrast to the relatively limited variations in concentration of the essential metals copper and zinc. In addition to increased variation in mercury levels compared to variation in essential metals, the distribution of mercury concentrations within samples from seabird populations tend to be skewed with several high mercury values and, therefore, differ markedly from Gaussian. Muirhead and Furness [130] noted that mercury levels showed the greatest deviation from a Gaussian distribution in a range of seabirds from Gough Island relative to the essential metals copper and zinc and the non-essential metal cadmium. This finding is consistent with mercury accumulation rather than metabolic regulation.

Liver mercury levels tend to be greater than kidney levels which in turn exceed muscle and egg levels. [2,13,32,90,94,129,130,138,140,145,149] The levels of mercury in livers of wandering albatrosses _Diomedea exulans_ and sooty albatrosses _Phoebetria fusca_ are by far the highest yet reported in any seabird [130] (Table 2.12). This raises important questions as to what constitutes anthropogenic mercury and what are natural levels; since the above birds were obtained from Gough Island in the

TABLE 2.12: Total mercury concentrations (µg g^{-1} wet weight) in liver tissue of seabirds from the Antarctic (A), Gough Island (G) and Spitsbergen (S).

Species	Number Sampled	Mean	Range	Locality	Ref.
Adelie penguin *Pygoscelis adeliae*	10	<0.1	<0.1- 0.2	A	90
Chinstrap penguin *Pygoscelis antarctica*	13	0.5	0.2- 0.8	A	141
Rockhopper penguin *Eudyptes crestatus*	12	2.3	1.0- 3.7	G	130
Macaroni penguin *Eudyptes chrysolophus*	9	0.9	0.4- 1.5	A	141
Wandering albatross *Diomedea exulans*	2	268.0	266.0-271.0	G	130
Yellow-nosed albatross *Diomedea chlororhynchos*	9	7.7	4.8- 20.0	G	130
Sooty albatross *Phoebetria fusca*	8	141.0	80.0-227.0	G	130
Southern fulmar *Fulmarus glacialoides*	6	2.9	0.8- 6.2	A	141
Northern fulmar *Fulmarus glacialis*	10	2.1	0.6- 4.2	S	141
Cape petrel *Daption capense*	7	1.3	---------	A	143
Snow petrel *Pagodroma nivea*	7	0.7	---------	A	143
Atlantic petrel *Pterodroma incerta*	13	28.0	14.0- 53.0	G	130
Kerguelen petrel *Pterodroma brevirostris*	14	4.6	1.9- 6.8	G	130
Soft-plumaged petrel *Pterodroma mollis*	18	21.0	4.0-103.0	G	130
Broad-billed prion *Pachyptila vittata*	31	0.4	0.1- 1.1	G	130
Great shearwater *Puffinus gravis*	12	2.0	0.8- 6.5	G	130
Little shearwater *Puffinus assimilis*	13	1.2	0.6- 1.6	G	130
Common diving petrel *Pelecanoides urinatrix*	17	0.5	0.2- 1.5	G	130
Tristan skua *Catharacta skua hamiltoni*	13	7.4	0.9- 17.0	G	130
Brown skua *Catharacta skua lonnbergi*	8	7.5	1.0- 12.0	A	141
South polar skua *Catharacta maccormicki*	8	2.7	1.7- 6.6	A	141
Glaucous gull *Larus hyperboreus*	11	1.6	0.8- 2.3	S	141
Little auk *Alle alle*	9	0.5	0.4- 0.7	S	141
Brunnich's guillemot *Uria lomvia*	9	0.6	0.3- 0.9	S	141

south Atlantic Ocean, far from any industrial source of mercury, it can be expected that they represent natural levels, although global transport of this metal cannot be ignored.

Maximum liver mercury concentrations from other studies rarely exceed 20 µg g^{-1} even on a dry weight basis, and are usually less than 10 µg g^{-1}.[2,20,32,39,61,87,90,94,138,140-143,145,149,177] Feathers have been used to monitor mercury levels in birds to a greater extent than for any other metal e.g.[44,62,72,185] since mercury bonds strongly to disulphide linkages[33] and mercury levels in feathers are not affected by various vigorous treatments.[5] The results obtained from such studies are difficult to compare, largely due to variation caused by the specific type of feathers analysed and the stage of moult of the bird at the time feathers were taken.[63] For these reasons, feather mercury values have been reported which both exceed corresponding liver and kidney concentrations[2,61,90,94,145,149,177] and which are less than corresponding liver and kidney concentrations.[61,149] Mercury levels in eggs tend to be low, rarely exceeding 0.5 µg g^{-1} wet weight,[2,9,13,47,53,97,140,146] although elevated levels have been reported in royal tern eggs from the Texas coast[103] and in gannet _Sula bassana_ eggsfrom Norway.[53,54] The extremely high mercury levels reported by Stoneburner _et al._[171] in sooty terns from Florida (mean 7.93 µg g^{-1} wet weight) are somewhat anomalous and may be erroneous, in that they are about twice as high as levels in common tern eggs thought to be associated with toxic effects and reduced reproductive success.[52]

The form of mercury in seabird tissues has received little attention. Osborn _et al._[149] reported mercury being predominantly organic in liver and kidney tissue of three species of seabirds from the north east Atlantic whilst Norheim *et al.*[143] found the proportion of organic mercury in liver tissue of the south polar skua *Catharacta maccormicki* from the Antarctic to vary from almost 100% to about 20% of the total mercury level. The negative correlation between percentage organic mercury and total mercury in this latter study was found to be statistically significant. Recent work on the relative proportion of organic and inorganic mercury in liver tissue of seabirds from Gough Island has revealed that, in some species, the organic fraction can be as little as 3% of the total mercury level. It would appear that, in such species, eliminatory mechanisms and detoxifying processes may be important in determining the mercury level of internal organs.[174] Age-accumulation trends of mercury are poorly documented, largely due to lack of birds of known age for which metal levels have been determined. Furness and Hutton[61] found a positive, but weak, correlation between liver mercury levels and age in the great skua.

2.6.4 Mercury in marine mammals

2.6.4.1 Pinnipeds

Data on the levels of total mercury in seal tissues are presented in Table 2.13. There is extensive variation in mercury concentrations both inter-specifically and intra-specifically, a trend which is otherwise only seen to any extent in cadmium. Generally, liver tissue exhibits the highest total mercury concentration, followed by kidney and muscle tissues, in that order.[1,17,27,45,51,56,66,86,98,100,102,119,123,159,161,162,165,178,180,189] It is not possible within the context of this review, to compare all studies of mercury levels in seals; this would prove difficult when the limitation of data presentation

TABLE 2.13: Total mercury concentrations ($\mu g\ g^{-1}$ wet (w) or dry (d) weight) in liver (L), kidney (K) and muscle (M) tissue of Pinnipeds.

Species	No. Sampled	Tis.	Mean	Range	Locality	Age[a]	Ref.
California sea lion	10	L	747.0	284.0-1026.0[d]	California	10-14	123
<u>Zalophus californianus</u>	10	K	28.4	12.1- 43.2[d]	(females)	10-14	
Northern fur seal	29	L	----	3.0- 19.0[w]	Pribilof	2- 3	1
<u>Callorhinus ursinus</u>	29	M	----	0.1- 0.4[w]	Is., Alaska (males)	2- 3	
Walrus	46	L	1.8	0.1- 7.3[w]	Thule Dist.,	1-26	17
<u>Odobenus rosmarus</u>	58	M	<0.1	<0.1- 0.1[w]	Greenland	1-26	
Harbour seal	31	L	----	1.6- 160.0[w]	German North	<1- 8	45
<u>Phoca vitulina</u>	16	K	----	1.6- 12.5[w]	Sea coast	<1- 8	
Ringed seal	83	L	27.5[w]	----------	West Arctic	12.8[b]	165
<u>Phoca hispida</u>	83	M	0.7[w]	----------	Canada	12.8[b]	
Harp seal	57	L	12.7[w]	----------	Gulf of St.	6+	161
<u>Phoca groenlandica</u>	56	K	1.0[w]	----------	Lawrence	6+	
	56	M	0.3[w]	----------	(females)	6+	
Grey seal	70	L	27.8	0.2- 125.9[w]	East coast,	1- 9	119
<u>Halichoerus grypus</u>	68	K	2.7	0.8- 6.7[w]	Scotland	1- 9	
Bearded seal	56	L	26.2[w]	----------	East Hudson	4.9[b]	165
<u>Erignathus barbatus</u>	55	M	<0.1[w]	----------	Bay	4.9[b]	
Leopard seal	15	L	4.5	0.7- 12.2[w]	Antarctic	----	180
<u>Hydrurga leptonyx</u>	15	M	0.1	<0.1- 0.5[w]		----	
Weddell seal	2	L	5.8	3.1- 8.5[w]	Antarctic	Ad.[c]	189
<u>Leptonychotes weddellii</u>	2	K	0.7	0.4- 1.0[w]		Ad.	
	2	M	0.1	0.1- 0.2[w]		Ad.	
Ross seal <u>Ommatophoca rossi</u>	20	L	3.4	0.7- 19.1[d]	Antarctic	----	117
Hooded seal	10	L	16.7	2.8- 44.4[w]	West	----	98
<u>Cystophora cristata</u>	10	M	0.3	0.2- 0.5[w]	Greenland	----	

a- age in years; b- mean age in years; c- adults

either on wet weight basis or dry weight basis is taken into account. Mercury concentrations in seal tissues are likely to be a reflection of both dietary mercury levels within differing prey types and age accumulation processes. Hence, species such as the walrus <u>Odobenus rosmarus</u> which feeds to a large extent on benthic invertebrates, tends to have relatively low mercury levels.[17] Conversely, fish-eating species, such as harbour seals, ringed seals and grey seals, tend to exhibit relatively high mercury concentrations.[1,27,45,56,66,84,86,98,102,119,156,159,162,165,178] These inter-species differences are complicated by the tendency for mercury concentration to increase with age in seal tissue.[1,18,45,86,106,123,156,159,161,162,165]

Martin _et al._[123] found high mercury levels in California sea lions and noted a strong correlation between this metal and selenium (see seaction 2.6.5) and bromine in mothers with normal term pups. This balance broke down with respect to bromine in (younger) mothers with premature pups, suggesting that the balance of these elements is important. The levels of bromine were investigated by Reijnders[156] in harbour seals, although no correlation with age was found for this element and no conclusions were drawn with respect to the role of bromine and mercury toxicity.

The form of mercury in seal tissue has been investigated in several studies. Generally, liver mercury tends to be predominantly in the inorganic form[17,23,56,66,98,102,156,165] whilst organic mercury predominates in muscle tissue.[23,98,102,165] This contrasts with mercury form in marine fish tissue where mercury tends to be organic (see section 2.6.2). This reduction in the proportion of organic mercury in seal liver has been cited as evidence for a biotransformation of the toxic, organic form into the less-toxic, inorganic storage form. The subsequent storage of inorganic mercury would explain the accumulation of mercury in seal tissues with age.

2.6.4.2 Cetaceans

Total mercury data for some whales and dolphins are presented in Table 2.14 (Odontoceti) and Table 2.15 (Mysticeti). Both inter-species and intra-species variation in mercury levels is large for this group, in keeping with similar trends for mercury in other marine vertebrate groups. As with mercury concentrations in seals, this variation is likely to reflect both inter-species dietary differences with corresponding differing mercury levels, and age-accumulation trends. The general difference between mercury levels in toothed whales (Table 2.14) and baleen whales (Table 2.15) is, however, striking. Reported mercury values for the latter group never exceed 0.4 $\mu g\ g^{-1}$ wet weight in liver tissue whilst the striped dolphin, for example, has been found to contain up to 485 μg mercury g^{-1} wet weight in liver tissue.[89] Toothed whales, in general, exhibit liver mercury concentrations in excess of 0.4 $\mu g\ g^{-1}$ wet weight (Table 2.14, for example). This marked dichotomy is likely to be the result of clear-cut dietary differences, baleen whales feeding on prey which are generally lower down the marine food chain and which tend to have relatively low mercury concentrations.

The distribution pattern of mercury within the body is similar to that for seabirds and seals. Liver tissue tends to accumulate the highest mercury concentrations with kidney tissue > muscle tissue.[4,12,50,51,67-69,84,89,98,169,182,190] This pattern is less clear in the case of baleen whales with internal organs having fairly uniform, low mercury concentrations.[26,98,136]

The tendency for mercury to show a strong positive correlation with age/length of whale[6,50,67,69,89,136] complicates the overall mercury picture and makes direct comparisons between studies difficult. Honda *et al.*[89] noted a

TABLE 2.14: Total mercury concentrations ($\mu g\ g^{-1}$ wet weight)in liver (L), kidney (K) and muscle (M) tissue of Cetaceans (Odontoceti).

Species	No. Sampled	Tis.	Mean	Range	Locality	Len.[a]	Ref.
Beluga	7	L	6.3	2.5- 12.1	West Arctic,	3.6	114
<u>Delphinapterus leucas</u>	7	M	0.7	0.6- 1.0	Canada	3.6	
Narwhal	37	L	6.1	0.6- 13.1	Pond Inlet,	3.7	182
<u>Monodon monoceros</u>	54	K	1.7	0.4- 5.7	Canada	3.8	
	58	M	0.9	0.2- 1.6		4.3	
Risso's dolphin	1	L	1.2	---------	West coast,	2.1	190
<u>Grampus griseus</u>	1	K	0.6	---------	Scotland	2.1	
White-beaked dolphin	1	L	19.0	---------	Kolding Fjord,	2.4	4
<u>Lagenorchynchus albirostris</u>	1	M	2.0	---------	Denmark	2.4	
White-dotted dolphin	1	M	1.7	---------	Ogasawara,	1.7	6
<u>Stenella attenuata</u>					Japan		
Striped dolphin	45	L	205.0	1.7-485.0	East coast,	---	89
<u>Stenella coeruleoalba</u>	20	K	8.7	0.9- 17.6	Japan	---	
	51	M	7.0	0.5- 15.7		---	
Long-snouted dolphin	2	L	9.5	6.0- 13.0	St. Lucia,	1.9	68
<u>Stenella longirostris</u>	2	K	2.5	2.3- 2.7	Lesser	1.9	
	2	M	1.1	0.9- 1.3	Antilles	1.9	
Gill's bottle-nosed dolphin	1	M	51.8	---------	Shizouka,	3.1	6
<u>Tursiops gilli</u>					Japan		
Short-finned pilot whale	5	L	88.7	19.2-157.0	St. Lucia,	4.3	68
<u>Globicephala macrorhynchus</u>	4	K	10.0	6.0- 14.0	Lesser	4.3	
	5	M	4.0	2.8- 5.4	Antilles	4.3	
Long-finned pilot whale	12	M	4.2	3.0- 5.2	Wakayama,	3.4	6
<u>Globicephala melaena</u>					Japan		
Finless black porpoise	1	M	0.2 (foetus)	---------	Kanagawa,	0.7	6
<u>Neophocaena phocaenoides</u>					Japan		
Harbour porpoise	41	L	11.2	---------	Deer Island,	1.3	69
<u>Phocoena phocoena</u>	23	K	1.8	---------	east Canada	1.3	
	60	M	0.9	---------	(males)	1.3	
Bottlenose whale	1	L	0.4	---------	North Sea	5.7	84
<u>Hyperoodon ampullatus</u>	1	M	0.3	---------		5.7	
Sperm whale	7	M	1.3	1.1- 1.6	North	11.4	136
<u>Physeter catodon</u>					Pacific		

a- mean length in metres

strong positive correlation between mercury concentration and age in liver tissue of striped dolphins, but a levelling-off of mercury concentration in kidney and muscle tissue after about 18 years. The correlation of mercury concentration with age in liver, kidney and muscle tissues was stronger than those with both length and weight. Gaskin et al. [69] found that in harbour porpoises, liver mercury levels correlated well with age, length and weight whereas, in other tissues, the correlations with weight and length were not so strong as that with age.

As with seals, the form of mercury in whale tissue has been investigated in several studies. Generally, in liver tissue, the majority of mercury is in the inorganic form. [50,67-69,96,98,190] Muscle tissue tends to have a relatively greater proportion of organic mercury compared to inorganic mercury than does liver tissue. [6,67-69,96,98,136] Although the data for mercury form within the various prey organisms of whales are not comprehensive, it is generally thought that the vast majority is in the organic, methyl form. This observed reduction in organic mercury relative to total mercury, especially in liver tissue, is believed to be evidence of a biotransformation of the metal into the less-toxic, inorganic form, although the gradual accumulation of small quantities of the latter cannot be ruled out as an alternative mechanism.

2.6.4.3 Sireniens and other groups

Denton and Breck [40] determined total mercury levels in two dugongs from North Queensland. Concentrations were found to be low with maximum values of 0.05 $\mu g\ g^{-1}$ wet weight in both liver and kidney tissue. Mercury levels in liver tissue of polar bears from various areas of the Canadian Arctic were found to average from about 17 to 53 $\mu g\ g^{-1}$ wet weight with maximum values over

TABLE 2.15: Total mercury concentrations ($\mu g\ g^{-1}$ wet weight) in liver (L), kidney (K) and muscle (M) tissue of Cetaceans (Mysticeti).

Species	No. Sampled	Tis.	Mean	Range	Locality	Leng.[a]	Ref.
Minke whale	6	L	0.18	0.07-0.41	West	----	98
<u>Balaenoptera acutorostrata</u>	6	M	0.15	0.09-0.25	Greenland	----	
Sei whale	9	M	0.03	0.02-0.07	South	14.3	136
<u>Balaenoptera borealis</u>					Pacific		
Fin whale	8	M	0.02	0.01-0.03	South	20.2	136
<u>Balaenoptera physalus</u>					Pacific		
Bowhead whale	1	L	<0.01	---------	Alaska	9.4	26
<u>Balaena mysticetus</u>	2	K	<0.01	---------		9.4	
	2	M	<0.01	---------		9.4	

a- mean length in metres

90 $\mu g\ g^{-1}$ wet weight. The inter-area differences in liver mercury concentrations were significant in some cases, and a positive correlation between mercury levels and bear age was also noted. [144]

Otters from the Orkney Islands were found to contain up to 20.3 $\mu g\ g^{-1}$ wet weight total mercury in liver tissue with a mean value of 4.7 $\mu g\ g^{-1}$ wet weight. Kidney levels were lower with a maximum of only 3 $\mu g\ g^{-1}$ wet weight. Hair values were found to range from 9.5 to 29.5 $\mu g\ g^{-1}$ wet weight. [126]

2.6.5 <u>Selenium levels and interactions with mercury in marine vertebrates</u>

The role that selenium plays in mediating the toxicity and determining the accumulation patterns of mercury (and also cadmium) has received much attention since the observations of Parizek and Ostadalova [150] on the prevention by selenium of the deleterious effects of Hg^{2+} on the kidneys and intestine. A complete appraisal of this important topic is not practicable within the context of this review, (see Magos and Webb [121]),

TABLE 2.16: Selenium concentrations ($\mu g\ g^{-1}$ wet (w) or dry (d) weight) in liver (L), kidney (K) and egg (E) tissue of seabirds.

Species	No. Sampled	Tissue	Mean	Range	Locality	Ref.
Chinstrap penguin *Pygoscelis antarctica*	13	L	5.4	3.2- 7.2^{w}	Antarctic	141
Macaroni penguin *Eudyptes chrysolophus*	9	L	22.0	14.0-28.0^{w}	Antarctic	141
Southern fulmar *Fulmarus glacialoides*	6	L	13.0	11.0-16.0^{w}	Antarctic	141
Northern fulmar *Fulmarus glacialis*	10	L	3.0	1.4- 6.4^{w}	Spitsbergen	141
Wedge-tailed shearwater *Puffinus pacificus*	25	E	1.2^{w}	--------	Hawaii	146
Brown pelican	10	L	6.8^{w}	--------	Gulf of	145
Pelecanus occidentalis	10	K	3.5^{w}	--------	California	145
	18	E	0.3	0.2- 0.4^{w}	W. coast, U.S.A.	13
Red-footed booby *Sula sula*	25	E	0.8^{w}	--------	Hawaii	146
Great skua	10	L	19.7	6.7-34.6^{d}	Foula	61
Catharacta skua skua	9	K	32.8	13.3-89.1^{d}		
Brown skua *Catharacta skua lonnbergi*	8	L	24.0	3.6-34.0^{w}	Antarctic	141
South polar skua *Catharacta maccormicki*	8	L	18.0	2.9-39.0^{w}	Antarctic	141
Herring gull	9	L	7.9	6.9- 9.3^{d}	Isle of May	94
Larus argentatus	7	K	14.1	8.6-19.4^{d}		
Kelp gull *Larus dominicanus*	34	K	2.0^{w}	--------	New Zealand	177
Glaucous gull *Larus hyperboreus*	11	L	2.2	1.3- 3.8^{w}	Spitsbergen	141
Silver gull *Larus novaehollandiae*	29	K	2.2^{w}	--------	New Zealand	177
Sooty tern *Sterna fuscata*	23	E	1.3^{w}	--------	Hawaii	146
Royal tern *Sterna maxima*	30	E	1.0	0.4- 2.1^{w}	Texas	103
Little auk *Alle alle*	9	L	2.6	1.5- 4.5^{w}	Spitsbergen	141
Brunnich's guillemot *Uria lomvia*	9	L	1.9	1.1- 2.6^{w}	Spitsbergen	141

although the general trends within the marine vertebrates are presented.

A summary of the references to selenium and other heavy metals, in marine fish is presented in Table 2.1. Selenium has been shown to accumulate with age/length in several studies of marine fish.[113,116,118,164] Furthermore, a positive correlation between selenium and mercury has been demonstrated in several species [58,101,116,118,164] while Leonzio et al. [113] reported a strong, positive correlation between age and the sum of the selenium and mercury concentrations (nmoles g^{-1}) in muscle tissue of striped mullet Mullus barbatus.

Selenium levels in various seabird tissues are presented in Table 2.16. Positive, but weak, correlations between selenium levels and age have been found in kidney and, to a lesser extent, liver tissues of great skuas. [61] Significant correlations between selenium and mercury levels have been found by Furness and Hutton [61] in great skuas, by Hutton [94] in herring gulls and by Norheim [141] in a range of seabird species from both northern and southern hemisphere locations.

Data on selenium levels in seals are presented in Table 2.17. There is great variation both within and between species. Selenium has been shown to correlate positively with age in several studies. [107,156,161,165] As with marine fish and seabirds, positive correlations between selenium and mercury levels have been found in seal tissues, most notably, liver tissue. [102,106,107,123,156,161,165,178] A similar pattern emerges for whales and dolphins, data for this group being presented in Table 2.18. Itano et al. [96] noted a general increase in selenium concentration with age in liver and muscle tissue of striped dolphins. Positive correlations between selenium concentration and mercury concentration have been noted in liver and muscle tissues. [6,96,106,107,169] Studies on polar bears from the Canadian Arctic also show that selenium concentration increased with age and that selenium and mercury levels are highly correlated with each other. [144]

In general, the consistent finding that mercury and

TABLE 2.17: Selenium concentrations ($\mu g\ g^{-1}$ wet (w) or dry (d) weight) in liver (L), kidney (K) and muscle (M) tissue of Pinnipeds.

Species	No. Sampled	Tis.	Mean	Range	Locality	Age[a]	Ref.
California sea lion	10	L	260.0	92.0-352.0[d]	California	10-14	123
<u>Zalophus californianus</u>	10	K	22.0	9.2- 33.8[d]	(females)	10-14	
Harbour seal	8	L	109.0	3.9-350.0[w]	Dutch	Ad.[b]	156
<u>Phoca vitulina</u>	4	K	7.1	2.3- 10.0[w]	Wadden Sea	Ad.	
Ringed seal	42	L	15.2	---------	West Arctic	12.8[c]	165
<u>Phoca hispida</u>					Canada		
Harp seal	16	L	5.8[w]	---------	Gulf of St.	6+	161
<u>Phoca groenlandica</u>	12	K	2.9[w]	---------	Lawrence	6+	
	13	M	0.6[w]	---------	(females)	6+	
Grey seal	10	L	38.1	8.6- 88.0[w]	Great	----	178
<u>Halichoerus grypus</u>					Britain		
Bearded seal	10	L	20.8[w]	---------	East Hudson	4.9[c]	165
<u>Erignathus barbatus</u>					Bay		
Leopard seal	15	L	3.3	2.6- 4.9[w]	Antarctic	----	180
<u>Hydrurga leptonyx</u>	15	M	0.6	0.4- 0.7[w]		----	
Weddell seal	1	L	1.0[w]	---------	Antarctic	----	180
<u>Leptonychotes weddellii</u>	1	M	0.3[w]	---------		----	

a- age in years; b- adults; c- mean age in years

selenium levels tend to be significantly and positively correlated with each other has been suggested as being indicative of some form of protection by selenium against mercury toxicity. This has been supported by evidence of a molar ratio for mercury:selenium of approximately 1:1 in several studies.[65,106,107,123,165,169,178,182] Conversely, however, some studies, predominantly of marine fish, have reported mercury:selenium molar ratios which show an excess of selenium[28,58,61,101,164] or an excess of mercury.[6,102]

How selenium acts in affording protection against mercury toxicity is debateable, although, in feeding experiments using quail <u>Coturnix</u> sp.[64] and minnows <u>Phoxinus phoxinus</u>,[37] it has

TABLE 2.18: Selenium concentrations (µg g^{-1} wet weight) in liver (L), kidney (K) and muscle (M) tissue of Cetaceans.

Species	No. Sampled	Tis.	Mean	Range	Locality	Leng.[a]	Ref.
Narwhal	37	L	4.1	0.6- 8.0	Pond Inlet,	3.7	182
Monodon monoceros	54	K	3.2	1.7- 4.9	Canada	3.8	
	58	M	0.4	0.3- 0.9		4.3	
White-dotted dolphin	1	M	0.7	--------	Ogasawara,	1.7	6
Stenella attenuata					Japan		
Striped dolphin	15	L	48.6	--------	East coast,	---	96
Stenella coeruleoalba	14	K	5.6	--------	Japan	---	
	26	M	2.8	--------		---	
Gill's bottle-nosed dolphin	1	M	13.9	--------	Shizouka,	3.1	6
Tursiops gilli					Japan		
Short-finned pilot whale	4	L	44.2	22.8-61.6	Cumberland	3.7	169
Globicephala macrorhynchus	4	K	7.2	3.0-10.0	Island, USA	3.7	
Long-finned pilot whale	12	M	0.9	0.6- 1.3	Wakayama,	3.4	6
Globicephala melaena					Japan		
Finless black porpoise	1	M	0.2 (foetus)	--------	Kanagawa,	0.7	6
Neophocaena phocaenoides					Japan		
Bowhead whale	2	L	0.1	<0.1- 0.1	Alaska	9.4	26
Balaena mysticetus	2	K	---	<0.1- 0.1		9.4	
	2	M	0.1	<0.1- 0.2		9.4	

a- mean length in metres

been clearly shown to do so. Sumino _et al._ [172] suggested that selenite releases methyl mercury from its linkages with proteins and, thus, influences its tissue distribution. In experimental studies of seal liver tissue, van de Ven _et al._, [178] found no evidence of any effect of selenium on the demethylation process of mercury whilst Martoja and Viale [125] located mercuric selenide storage granules in the liver tissue of the goose-beaked whale _Ziphius cavirostris_. Stoneburner [169] has suggested that the breakdown of the 1:1 mercury:selenium molar relationship may be associated with strandings of whales; a similar breakdown of the relative proportions of elements in

California sea lions has been linked with premature births.[123] In this case, the mercury:selenium ratio was near unity for mothers of both full-term and premature pups, but the levels of bromine were severely depressed from the 1:1:1 (mercury:selenium:bromine) ratio in mothers with premature pups.

2.6.6 Conclusions

Of all the heavy metals covered in this review, mercury exhibits the most pronounced age-related concentration changes and variation both within and between species and also between different marine groups. Its high toxicity and relatively long biological half-life combine to make this metal the most serious pollution threat from the group of metals covered in this review. Generally, the liver tissue of marine vertebrates accumulates mercury to the highest concentration. The highest reported mercury concentrations in liver tissues of the respective marine groups covered are up to 1026 $\mu g\ g^{-1}$ dry weight in California sea lions,[123] up to 485 $\mu g\ g^{-1}$ wet weight in striped dolphins,[89] up to 271 $\mu g\ g^{-1}$ wet weight in wandering albatrosses[130] and up to 63 $\mu g\ g^{-1}$ wet weight in black marlin.[118]

The relationship between inorganic and organic mercury within respective marine groups is of note. The fact that much of the mercury in some marine mammal tissues is largely inorganic whereas that in their prey is thought to be predominantly organic, has been suggested as evidence for a detoxification mechanism for mercury in these long-lived, top predators. It could well be, therefore, that relatively high mercury levels in some species are natural and that some marine animals have become adapted, over an evolutionary time-span, to dietary mercury. Whether this is the case for all marine vertebrates is open to speculation, but those species unlikely to encounter large amounts of mercury, via their respective diets, for example, would be especially susceptible to unusual, anthropogenic sources of mercury.

Although much work has been carried out on the levels of mercury and its relationships with other metals, there are still many aspects of its fluxes within the marine biosphere which remain unclear. Direct relationships between prey/predator mercury levels, mercury retention processes, mercury eliminatory pathways and their relative importance in different species and meaningful data on harmful and deleterious effects of mercury in wild populations are a few of the many areas where further work should be done.

2.7 ZINC

2.7.1 Introduction

Zinc can be classified as an essential element since it is a requirement of several metalloproteins, particularly metalloenzymes.

2.7.2 Zinc in marine fish

Zinc concentrations in marine fish tend to be fairly uniform, regardless of species and location. As with copper, this is to be expected of an essential element and levels are likely to be closely regulated. Generally, mean muscle concentrations of zinc are less than 10 µg g^{-1} wet weight,[10, 15,34,36,49,71,74,75,83,112,118,132-135,137,151-154,168,176,179, 187] although values in excess of this level have been reported, but some of these include 'whole fish' samples.[3,7,49,82,135, 137,186,188]

There are few data on the distribution of zinc within marine fish. It would appear, however, that levels are higher in liver and kidney relative to muscle. [74,118,133,135,151,168,179,186-188] Zinc shows little or no tendency to increase or decrease in concentration with increasing age/length of fish. Positive correlations between zinc and cadmium concentration in marine fish have been noted for black marlin and striped mullet by Mackay _et al._ [118] and Hornung and Ramelow [91] respectively.

2.7.3 _Zinc in seabirds_

Zinc levels in liver and kidney tissue of some seabirds from northern and southern hemisphere studies are presented in Table 2.19. These data show general agreement between species with little variation which one would expect for an essential element. Comparison between studies is hindered by data presentation on either a wet weight basis or a dry weight basis. Where expressed on a dry weight basis, liver zinc levels tend to be below 200 µg g^{-1}, [2,32,35,138,145,157] although higher zinc concentrations have been noted by Hutton [94] in the great skua (range 61-497 µg g^{-1} dry weight) and by Osborn _et al._ [149] in the northern fulmar _Fulmarus glacialis_ (range 225-688 µg g^{-1} dry weight). Liver zinc levels have been found to be generally less than 100 µg g^{-1} on a wet weight basis. [21,90,92,130,141]

Kidney zinc levels are comparable to those of liver tissue, although high kidney concentrations have been noted in association with high kidney cadmium concentrations, this positive correlation being statistically significant in several studies. [94,129,130,138,141,157] This relationship between zinc and cadmium is thought to involve zinc binding by metallothionein which, by binding cadmium, offers protection against cadmium toxicity. [147] Muscle zinc levels in seabirds

TABLE 2.19: Zinc concentrations ($\mu g\ g^{-1}$ wet weight) in liver and kidney tissue of seabirds from the Antarctic (A), Gough Island (G) and Spitsbergen (S).

Species	Number Sampled	Liver Mean	Liver Range	Kidney Mean	Kidney Range	Locality	Ref.
Adelie penguin <u>Pygoscelis adeliae</u>	10	48	32-73	49	30-71	A	90
Chinstrap penguin <u>Pygoscelis antarctica</u>	13	36	29-46	31	25-38	A	141
Rockhopper penguin <u>Eudyptes crestatus</u>	12	40	27-61	63	41-86	G	130
Macaroni penguin <u>Eudyptes chrysolophus</u>	9	41	31-62	46	34-84	A	141
Wandering albatross <u>Diomedea exulans</u>	2	53	49-57	48	45-52	G	130
Yellow-nosed albatross <u>Diomedea chlororhynchos</u>	9	48	29-59	35	31-42	G	130
Sooty albatross <u>Phoebetria fusca</u>	8	67	47-86	56	42-65	G	130
Southern fulmar <u>Fulmarus glacialoides</u>	6	42	36-54	47	39-69	A	141
Northern fulmar <u>Fulmarus glacialis</u>	10	73	50-95	50	32-96	S	141
Atlantic petrel <u>Pterodroma incerta</u>	13	45	33-64	62	50-71	G	130
Kerguelen petrel <u>Ptreodroma brevirostris</u>	14	44	29-81	45	35-54	G	130
Soft-plumaged petrel <u>Pterodroma mollis</u>	18	43	30-56	50	36-78	G	130
Broad-billed prion <u>Pachyptila vittata</u>	31	44	30-75	36	29-47	G	130
Great shearwater <u>Puffinus gravis</u>	12	38	33-45	46	27-88	G	130
Little shearwater <u>Puffinus assimilis</u>	13	40	28-54	50	34-66	G	130
Grey-backed storm petrel <u>Garrodia nereis</u>	8	42	29-77	28	15-49	G	130
White-faced storm petrel <u>Pelagodroma marina</u>	7	34	20-44	39	30-46	G	130
White-bellied storm petrel <u>Fregetta grallaria</u>	8	38	28-46	38	35-48	G	130
Common diving petrel <u>Pelecanoides urinatrix</u>	17	38	28-51	46	33-78	G	130
Tristan skua <u>Catharacta skua hamiltoni</u>	13	22	18-32	37	28-53	G	130
Brown skua <u>Catharacta skua lonnbergi</u>	8	32	22-51	42	31-51	A	141
South polar skua <u>Catharacta maccormicki</u>	8	35	21-46	40	22-48	A	141
Glaucous gull <u>Larus hyperboreus</u>	11	32	26-47	46	37-57	S	141
Little auk <u>Alle alle</u>	9	37	31-43	40	32-46	S	141
Brunnich's guillemot <u>Uria lomvia</u>	9	35	31-38	39	27-50	S	141

tend to be less than corresponding liver and kidney levels.[2,32,90,92,94,138,149,156] Feather zinc levels would appear to be variable, relative to other tissues, although where determined, zinc concentrations in feathers are not inconsiderable.[90,92,94,145,149] Mean zinc levels in egg expressed on a dry weight basis in four seabird species are generally similar,[2,157] the highest mean level of 87 µg g^{-1} dry weight being found in eggs of Cory's shearwaters Calonectris diomedea.[157] King et al.[103] found egg zinc values of 8.8-14.0 µg g^{-1} wet weight in royal terns from the Texas coast whilst Blus et al.[13] found egg zinc levels of 4.3-8.3 µg g^{-1} wet weight in brown pelicans from South Carolina and Florida.

2.7.4 Zinc in marine mammals

2.7.4.1 Pinnipeds

Data on the levels of zinc in some seal tissues are presented in Table 2.20. As with the essential element copper, there is generally less variation both within and between species for zinc when compared to the non-essential elements. Species from geographically different localities exhibit similar zinc levels with concentrations tending to be less than 90 µg g^{-1} wet weight in liver tissue.[27,45,46,51,80,84,86,98,180,189] Highest zinc concentrations tend to be found in liver tissue, although this is not always the case. Some studies have revealed kidney zinc concentrations as high as, or in excess of, corresponding liver concentrations.[80,98,123] Whether these high kidney zinc concentrations are in association with elevated cadmium concentrations incorporated in metallothioneins is not clear, there being little documented evidence of this relationship in this marine group. However, it would appear that high zinc levels correspond to high cadmium levels in kidney

TABLE 2.20: Zinc concentrations (μg g^{-1} wet (w) or dry (d) weight) in liver (L), kidney (K) and muscle (M) tissue of Pinnipeds.

Species	No. Sampled	Tis.	Mean	Range	Locality	Ref.
California sea lion	10	L	220.0	166.0-346.0^d	California	123
Zalophus californianus	10	K	173.0	146.0-353.0^d	(females)	
Steller sea lion	17	L	47.0	35.5- 86.0^w	Hokkaido,	80
Eumetopias jubata	17	K	27.0	19.8- 40.4^w	Japan	
	15	M	31.0	24.3- 39.1^w		
Harbour seal	57	L	----	27.0- 56.0^w	German North	45
Phoca vitulina	16	K	----	16.3- 32.5^w	Sea coast	
Ringed seal	29	L	46.0	30.7- 67.3^w	West	98
Phoca hispida	29	K	46.2	27.9- 78.0^w	Greenland	
	29	M	22.2	14.2- 39.5^w		
Grey seal	38	L	55.3	30.0- 97.5^w	Farne Islands,	27
Halichoerus grypus	37	K	28.4	10.5- 75.0^w	England	
					(females)	
Leopard seal	15	L	53.9	32.2- 82.8^w	Antarctic	180
Hydrurga leptonyx	15	M	23.4	14.8- 49.3^w		
Weddell seal	2	L	44.4	41.7- 47.0^w	Antarctic	189
Leptonychotes weddellii	2	K	29.1	27.4- 30.7^w		
	2	M	36.7	33.7- 39.6^w		
Ross seal	20	L	212.4	124.0-406.0^d	Antarctic	117
Ommatophoca rossi						
Elephant seal	1	M	35.6^w	----------	Antarctic	43
Mirounga leonina						

tissue in California sea lions.[123] The high zinc levels in liver tissue of Ross seals reported by McClurg[117] may be diet-linked, no correlation with cadmium being reported. Zinc concentration has been shown to neither increase nor decrease significantly with age in two studies.[45,80]

2.7.4.2 Cetaceans

Data on zinc levels in whale tissues are presented in Table 2.21. The similarity in zinc concentrations reported from all studies is striking, zinc showing little variation between

TABLE 2.21: Zinc concentrations ($\mu g\ g^{-1}$ wet weight) in liver (L), kidney (K) and muscle (M) tissue of Cetaceans.

Species	No. Sampled	Tis.	Mean	Range	Locality	Ref.
Beluga	1	L	32.0	----------	Baltic Sea	84
Delphinapterus leucas	1	K	29.5	----------		
	1	M	20.0	----------		
Narwhal	37	L	38.8	24.0- 63.6	Pond Inlet,	182
Monodon monoceros	54	K	41.1	3.8- 85.8	Canada	
	58	M	17.8	12.4- 28.4		
White-beaked dolphin	1	L	24.0	----------	Kolding Fjord,	4
Lagenorchynchus albirostris	1	M	13.0	----------	Denmark	
Striped dolphin	57	L	44.5	26.5-109.0	East coast,	89
Stenella coeruleoalba	30	K	30.1	22.8- 41.2	Japan	
	59	M	11.4	6.9- 20.4		
Short-finned pilot whale	1	L	36.4	----------	North	41
Globicephala macrorhynchus	1	K	38.1	----------	Queensland	
	1	M	15.9	----------		
Harbour porpoise	17	L	43.2	18.4- 67.6	East coast,	50
Phocoena phocoena	17	K	23.8	19.5- 33.1	Scotland (males)	
Goose-beaked whale	2	L	49.5	40.0- 59.0	Bermuda	104
Ziphius cavirostris	2	K	53.0	52.0- 54.0		
	4	M	11.5	----------		
Bottlenose whale	1	L	23.0	----------	North Sea	84
Hyperoodon ampullatus	1	M	13.5	----------		
Bowhead whale	1	L	43.6	----------	Alaska	26
Balaena mysticetus	2	K	23.8	19.0- 28.5		
	2	M	43.7	36.0- 51.4		

species and geographical location.[4,26,41,50,51,84,89,104,182] Honda _et al._[89] noted a negative correlation between liver zinc concentration and age in striped dolphins, although after an initial decrease in concentration, immature and mature dolphins show little variation in zinc concentration with increasing age. No clear relationship between zinc concentration and age could be elucidated by Falconer _et al._[50] with respect to harbour porpoises. A positive correlation between kidney zinc and cadmium levels was found by Honda et al. [89] in striped dolphins.

2.7.4.3 Sirenians and other groups

Liver zinc levels in dugongs from North Queensland have been shown to range from 58 to 1101 μg g^{-1} wet weight with kidney levels (14-54 μg g^{-1} wet weight) and muscle levels (8-28 μg g^{-1} wet weight) consistently lower. [42] Muscle zinc levels in dugongs from Sulawesi Island (15-30 μg g^{-1} wet weight) [128] are in agreement with the findings of Denton et al. [42] The high liver levels of zinc are not thought to reflect unusually high dietary levels, but may be a result of low dietary copper, zinc being absorbed via vacant copper receptor sites in the intestine. [42] A positive correlation between zinc concentration and age was found in liver and kidney tissue; this may explain the positive correlation between zinc and cadmium in these tissues, as the latter exhibits a similar age-related concentration increase. [42] Alternatively, age-related increases in zinc levels may be due to zinc binding by metallothioneins produced to store cadmium which accumulates with age.

The mean liver concentration of zinc in polar bears from the Canadian Arctic was found to be around 63 μg g^{-1} wet weight. [144]

2.7.5 Conclusions

As with copper, zinc, being an essential element, varies little in concentration between animals studied and there is general agreement regardless of species and geographical location. Maximum zinc concentrations reported for each group covered by this review are 375.0 μg g^{-1} wet weight in liver tissue of black marlin; [118] 688.0 μg g^{-1} dry weight in liver tissue of northern fulmar; [149] 406 μg g^{-1} dry weight in liver tissue of Ross seal;[117] 109 µg g^{-1} wet weight in liver tissue of striped dolphin.[89] Zinc shows little or no age-related accumulation effect, although it has been found to be positively correlated with cadmium levels in several studies.

2.8 OTHER HEAVY METALS

2.8.1 Introduction

Of the many heavy metals for which relatively few data are available for marine vertebrates, the biologically essential metals arsenic, chromium, manganese and nickel[38] will be considered in this section. Each of the above metals will be dealt with separately.

2.8.2 Arsenic

Compared to other marine vertebrates, marine fish tend to exhibit the highest arsenic concentrations. Muscle arsenic levels of over 100 µg g^{-1} dry weight have been reported by several workers from a range of marine fish.[14,15,160] In contrast, other studies have reported arsenic values which rarely exceed 20 µg g^{-1} either on a wet or a dry weight basis for both bony and cartilaginous species.[10,71,75,110,118,187] Bohn[14] noted a positive correlation between arsenic concentration and body weight in several species of marine fish, a relationship also reported by Bohn and Fallis[15] in the shorthorn sculpin *Myoxocephalus scorpius*. Both Bebbington *et al.*[10] and Bohn and Fallis[15] reported arsenic concentrations in fish which exceeded 'standard levels' and 'maximum recommended permissible' levels as defined by the National Health and Medical Research Council and the Canadian Food and Drug Directorate.

Arsenic levels in seabirds and marine mammals are generally low when compared to those in marine fish with concentrations rarely exceeding 1 $\mu g\ g^{-1}$ wet weight in any tissue. [1,13,26,103,119,128,144,145,177]

2.8.3 Chromium

Chromium levels in marine fish have been found to be generally less than 1 $\mu g\ g^{-1}$ wet weight with concentrations often approaching the limits of detection. [71,74,75,132,133,135,152-154] Murray and Portmann [135] reported somewhat higher mean chromium values of 3.8 and 6.4 $\mu g\ g^{-1}$ wet weight in plaice *Pleuronectes platessa* and herring *Clupea harengus* respectively, both samples being taken from the Irish Sea. A similarlarly high chromium concentration of 5.82 $\mu g\ g^{-1}$ dry weight has been reported by Hornung and Ramelow [91] in muscle tissue of *Saurida undosquamis* from the eastern Mediterranean Sea.

Chromium levels in seabirds have been found rarely to exceed 5 $\mu g\ g^{-1}$ either on a wet or dry weight basis in any tissue. [2,13,92,145] Somewhat higher chromium concentrations have been reported by Custer *et al.* [35] who noted levels of up to 18.3 $\mu g\ g^{-1}$ dry weight in liver tissues of common tern chicks, this possibly being the result of local pollution. Anderlini *et al.* [2] noted similar chromium levels in ashy petrels *Oceanodroma homochroa* from California (mean 12.2 $\mu g\ g^{-1}$ dry weight ; liver tissue) and reported correspondingly high concentrations in bone tissue of seabirds from both the Antarctic and North America.

Chromium levels in marine mammals are generally low, reported values being less than 1 $\mu g\ g^{-1}$ wet weight in any tissue. [26,27,41-43,46] McClurg [117] reported chromium levels of up to 3.7 $\mu g\ g^{-1}$ dry weight in liver tissues of Ross seals from the Antarctic.

2.8.4 Manganese

Manganese concentrations in marine fish tend to be less than 1 µg g^{-1} wet weight, often approaching detection limits.[34,71,74,83,152,179] Eustace[49] reported a maximum manganese level of 15 µg g^{-1} wet weight in muscle tissue of a seahorse *Hippocampus* sp. from the Derwent estuary, Tasmania.

Manganese levels in seabirds tend to be less than 5 µg g^{-1} wet weight in any tissue,[90,92,93] although Custer *et al.*[35] noted manganese concentrations of up to 29 µg g^{-1} dry weight in liver tissues of common tern chicks from a somewhat polluted environment.

Manganese concentrations in marine mammals have been found to be generally less than 7 µg g^{-1} wet weight in any tissue.[27,41-43,46,89,104,128,144,189] Higher manganese concentrations have been reported by Martin *et al.*[123] in California sea lions (maximum liver tissue concentration, 24.4 µg g^{-1} dry weight) and by McClurg[117] in Ross seals (maximum liver tissue concentration, 39 µg g^{-1} dry weight), although direct comparison between such data is hindered by presentation of results either on a wet or a dry weight basis.

2.8.5 Nickel

Nickel concentrations in marine fish tend to be less than 1 µg g^{-1} wet weight,[70,71,74,75,83,152] although Vas[179] reported nickel levels of 2 µg g^{-1} wet weight in both muscle and kidney tissues of tope from Liverpool Bay, Irish Sea, and Wright[188] noted a mean nickel concentration of 10.8 µg g^{-1} wet weight in liver tissues of plaice from the Northumberland coast, north east England.

Seabirds exhibit similar nickel levels to those of marine fish with concentrations rarely exceeding 1 µg g^{-1} even on a dry weight basis.[13,35,90] Elevated nickel levels have been reported in feathers of Adelie penguins from the Antarctic (maximum, 3.04 μg g^{-1} fresh weight) by Honda et al.[90] whilst Anderlini et al.[2] noted mean nickel levels of 17 μg g^{-1} dry weight in liver tissues and 16 μg g^{-1} dry weight in bone tissues of ashy petrels from California.

Nickel levels in marine mammals tend to be less than 0.5 μg g^{-1} wet weight with concentrations close to limits of detection,[26,41-43,89,104] although nickel concentrations of up to 1.25 μg g^{-1} wet weight have been reported in muscle tissues of dugong;[128] nickel levels of up to 4.8 μg g^{-1} dry weight in liver tissues of Ross seals from the Antarctic have been noted by McClurg.[117]

2.8.6 Conclusions

Based on the relatively few data for these heavy metals in marine vertebrates, it is difficult to make any assessment as to the effects that they may have on this group. Of the four metals considered, arsenic concentrations would appear to show the most variation with some extremely high levels being reported in some species of marine fish (see section 2.8.2). Such wide variation in metal levels is similar to that reported in the non-essential elements and may be worthy of further investigation.

2.9 DISCUSSION

Of the metals covered in this review, tissue concentrations of the essential elements copper, iron and zinc would appear to be closely regulated metabolically and these elements are, therefore, unlikely to be serious pollution threats in general terms. Localised anthropogenic sources of these metals, however, may result in deleterious effects to the marine environment.

Reported values of cadmium show a wide variation within a given study, in association with skewed distribution patterns,[130] and have been shown to increase in concentration with increasing age/size in several studies of all groups covered in this review. There is some evidence, however, that cadmium when compared to the distribution of, and variation in, mercury levels in seabirds, shows signs of being regulated to a small extent.[130]

Mercury concentrations are the most variable of any metal covered in this review and have been shown to exhibit a markedly skewed distribution pattern.[130] Age-related accumulation trends have been widely reported for mercury with metabolic regulation being minimal by comparison to the essential metals copper, iron and zinc. The trend of a positive correlation between mercury concentration and age/size in marine vertebrates has invariably been reported in terms of total mercury. Given the probable existence of a demethylation process in several species of marine mammals and seabirds which effectively converts a proportion of the dietary organic mercury into the inorganic form, one might expect this correlation to be stronger if inorganic mercury alone was considered. Conversely, a correlation between age/size and organic mercury may prove to be less significant.

In contrast to the amount of work undertaken on cadmium and mercury, there are relatively few data on levels of the non-essential metal lead. Generally, lead concentrations tend to be higher in species inhabiting coastal and estuarine environments[4,24,93,94,131,155] when compared to lead levels in species far from any area of industrialisation.[117] Furthermore, coastal seabird fatalities have been reported as being attributable to elevated lead levels.[24] Further detailed work on lead in marine vertebrates would seem worthwhile given its increasing industrial usage and evidence of global increases in lead levels resulting from atmospheric transport (see chapter by Wolff in this volume). Together with lead, cadmium and mercury would appear to represent the most serious pollution risks and warrant further study whilst further extensive data collection for the essential metals copper, iron and zinc would seem to be of less value.

Despite a relatively large number of studies into the levels of cadmium and mercury in marine vertebrates, there have been few meaningful assessments of the physiological effects of these metals; for example, relatively few data exist on the toxic effects of cadmium and mercury with respect to reproductive processes, on what concentrations are likely to cause reduced breeding success and how the respective effects of different metals combine. Geographical variation in metal concentrations in marine vertebrates has tended to be overlooked, both on local and global scales. However, such studies are hindered by the difficulties associated with sampling highly mobile marine species which have relatively extensive ranges. The limitations of comparing metal levels in different species with distinct geographical distributions should be taken into account, as should the potential bias of using dead seabirds and beached and stranded marine mammals for metal analysis.

2.10 REFERENCES

1. Anas, R.E., Heavy metals in the northern fur seal *Callorhinus ursinus* and harbour seal *Phoca vitulina richardi*, *Fish. Bull.*, 72, 133, 1974.

2. Anderlini, V.C., Connors, P.G., Risebrough, R.W. and Martin, J.H., Concentrations of heavy metals in some Antarctic and North American seabirds, in *Proc. Symp. Conservation Problems Antarctica*, Blacksburg Virginia Polytecnic Institute and State University, 1972, 49.

3. Andersen, A.T., Dommasnes, A. and Hesthagen, I.H., Some heavy metals in sprat (*Sprattus sprattus*) and herring (*Clupea harengus*) from the Inner Oslofjord, *Aquaculture*, 2, 17, 1973.

4. Andersen, S.H. and Rebsdorff, A., Polychlorinated hydrocarbons and heavy metals in harbour porpoise (*Phocoena phocoena*) and whitebeaked dolphin (*Lagenorhynchus albirostris*) from Danish waters, *Aquat. Mamm.*, 4, 14, 1976.

5. Applequist, H., Asbirk, S. and Drabaek, I., Mercury monitoring: mercury stability in bird feathers, *Mar. Pollut. Bull.*, 15, 22, 1984.

6. Arima, S. and Nagakura, K., Mercury and selenium content of Odontoceti, *Bull. Japan. Soc. Sci. Fish.*, 45, 623, 1979.

7. Badsha, K.S. and Sainsbury, M., Uptake of zinc, lead and cadmium by young whiting in the Severn estuary, *Mar. Pollut. Bull.*, 8, 164, 1977.

8. Bakir, F., Damluji, S.F., Amin-Zaki, L., Martadha, M., Khalidi, A., Al-Rawi, N.Y., Tikriti, Z., Dhahir, H.I., Clarkson, T.W., Smith, J.C. and Doherty, R.A., Methyl mercury poisoning in Iraq, *Science*, N.Y., 181, 230, 1973.

9. Barrett, R.T., Skaare, J.V., Norheim, G., Vader, W. and Froslie, A., Persistent organochlorines and mercury in eggs of Norwegian seabirds 1983, *Environ. Pollut. (A)*, 39, 79, 1985.

10. Bebbington, G.N., Mackay, N.J., Chvojka, R., Williams, R.J., Dunn, A. and Auty, E.H., Heavy metals, selenium and arsenic in nine species of Australian commercial fish, *Aust. J Mar. Freshw. Res.*, 28, 277, 1977.

11. Beckett, J.S. and Freeman, H.C., Mercury in swordfish and other pelagic species from the western Atlantic, *Spec. Scient. Rep. Natn. Oceanic Atmos. Adm. U.S. (Fisheries)*, 675, 154, 1974.

12. Bligh, E.G. and Armstrong, F.A.J., Marine mercury pollution in Canada, *Int. Counc. Explor. Sea*, ICES C.M. 1971/E34, 1971.

13. Blus, L.J., Neely, B.S., Lamont, T.G. and Mulhern, B., Residues of organochlorines and heavy metals in tissues and eggs of brown pelicans, 1969-73, *Pestic. Monit. J.*, 11, 40,

1977.

14. Bohn, A., Aresenic in marine organisms from West Greenland, Mar. Pollut. Bull., 6, 87, 1975.

15. Bohn, A. and Fallis, B.W., Metal concentrations (As, Cd, Cu, Pb and Zn) in shorthorn sculpins Myoxocephalus scorpius (Linnaeus) and Arctic char Salvelinus alpinus (Linnaeus) from the vicinity of Strathcona Sound, Northwest Territories, Water Res., 12, 659, 1978.

16. Borg, K., Wanntorp, H., Erne, K. and Hanko, E., Mercury poisoning in Swedish wildlife, J. appl. Ecol., 3, 171, 1966.

17. Born, E.W., Kraul, I. and Kristensen, T., Mercury, DDT and PCB in the Atlantic walrus (Odobenus rosmarus rosmarus) from the Thule District, North Greenland, Arctic, 34, 255, 1981.

18. Botta, J.R., Arsenault, E. and Ryan, H.A., Total mercury content of meat and liver from inshore Newfoundland-caught harp seal (Phoca groenlandica), Bull. Environ. Contam. Toxicol., 30, 28, 1983.

19. Braham, H.W., Lead in the California sea lion (Zalophus californianus), Environ. Pollut., 5, 253, 1973.

20. Braune, B.M., Comparison of total mercury levels in relation to diet and moult for nine species of marine birds, Arch. Environ. Contam. Toxicol., 16, 217, 1987.

21. Brothers, N.P. and Brown, M.J., The potential use of fairy prions (Pachyptila turtur)as monitors of heavy metal levels in Tasmanian waters, Mar. Pollut. Bull., 18, 132, 1987.

22. Bryan, G.W., Pollution due to heavy metals and their compounds, in, Marine Ecology, Vol. 5, Kinne, O. Ed., Wiley, New York, 1984, chap. 3.

23. Buhler, D.R., Claeys, R.R. and Mate, B.R., Heavy metals and chlorinated hydrocarbon residuesin California sea lions (Zalophus californianus californianus), J. Fish. Res. Bd. Can., 32, 2391, 1975.

24. Bull, K.R., Every, W.J., Freestone, P., Hall, J.R., Osborn, D., Cooke, A.S. and Stone, T., Alkyl lead pollution and bird mortalities on the Mersey estuary, UK, 1979-1981, Environ. Pollut. (A), 31, 239, 1983.

25. Bull, K.R., Murton, R.K., Osborn, D., Ward, P. and Cheng, L., High levels of cadmium in Atlantic seabirds and sea-skaters, Nature, 269, 507, 1977.

26. Byrne, C., Balasubramanian, R., Overton, E.B. and Albert, T.F., Concentrations of trace metals in the bowhead whale, Mar. Pollu. Bull., 16, 497, 1985.

27. Caines, L.A., Heavy metal residues in grey seals (Halichoerus grypus) from the Farne Islands, Int. Counc.

Explor. Sea, ICES, C.M. 1978/E: 40, 1978.

28. Cappon, C.J. and Smith, J.C., Mercury and selenium content and chemical form in fish muscle, Arch. Environ. Contam. Toxicol., 10, 305, 1981.

29. Caputi, N., Edmonds, J.S. and Heald, D.I., Mercury content of sharks from south-western Australian waters, Mar. Pollut. Bull., 10, 337, 1979.

30. Cheng, L., Schulz-Baldes, M. and Harrison, C.S., Cadmium in ocean-skaters Halobates sericeus (Insecta) and their seabird predators, Mar. Biol., 79, 321, 1984.

31. Chvojka, R. and Williams, R.J., Mercury levels in six species of Australian commercial fish, Aust. J. Mar. Freshw. Res., 31, 469, 1980.

32. Connors, P.G., Anderlini, V.C., Risebrough, R.W., Gilbertson, M. and Hays, H., Investigations of heavy metals in common tern populations, Can. Field Nat., 89, 157, 1975.

33. Crewther, W.G., Fraser, R.D.B., Lennox, F.G. and Lindley, H., The chemistry of keratins, Adv. Protein Chem., 20, 191, 1965.

34. Cross, F.A., Hardy, L.H., Jones, N.Y. and Barber, R.T., Relation between total body weight and concentrations of manganese, iron, copper, zinc and mercury in white muscle of bluefish (Pomatomus saltatrix) and a bathyl-demersal fish Antimora rostrata, J. Fish. Res. Bd. Can., 30, 1287, 1973.

35. Custer, T.W., Franson, J.C., Moore, J.F. and Myers, J.E., Reproductive success and heavy metal contamination in Rhode Island common terns, Environ. Pollut. (A), 41, 33, 1986.

36. Cutshall, N.H., Naidu, J.R. and Pearcy, W.G., Zinc and cadmium in the Pacific hake Merluccius productus off the western U.S. coast, Mar. Biol., 44, 195, 1977.

37. Cuvin, M.L.A. and Furness, R.W., Uptake and elimination of inorganic mercury and selenium by minnows Phoxinus phoxinus, Aquat. Toxicol., 13, 205, 1988.

38. Da Silva, J.J.R.F., Interaction of the chemical elements with biological systems, in New Trends in Bioinorganic Chemistry, Williams, R.J.P. and Da Silva, J.J.R.F., Eds., Academic Press, London, 1978, 449.

39. Delbeke, K., Joiris, C. and Decadt, G., Mercury contamination of the Belgian avifauna 1970-1981, Environ. Pollut. (B), 7, 205, 1984.

40. Denton, G.R.W. and Breck, W.G., Mercury in tropical marine organisms from north Queensland, Mar. Pollut. Bull., 12, 116, 1981.

41. Denton, G.R.W. and Heinsohn, G.E., unpublished data, cited in, 42.

42. Denton, G.W.R., Marsh, H., Heinsohn, G.E. and Burdon-Jones, C., The unusual metal status of the dugong Dugong dugon, Mar. Biol., 57, 201, 1980.

43. Denton, G.W.R., Marsh, H. and Griffiths, D., Unpublished data, cited in, 42.

44. Doi, R., Ohno, H. and Harada, M., Mercury in feathers of wild birds from the mercury-polluted area along the shore of the Shiranui Sea, Japan, Sci. Tot. Environ., 40, 155, 1984.

45. Drescher, H.E., Harms, U. and Huschenbeth, E., Organochlorines and heavy metals in the harbour seal Phoca vitulina from the German North Sea coast, Mar. Biol., 41, 99, 1977.

46. Duinker, J.C., Hillebrand, M.Th.J. and Nolting, R.F., Organochlorines and metals in harbour seals (Dutch Wadden Sea), Mar. Pollut. Bull., 10, 360, 1979.

47. Dyck, J. and Kraul, I., Environmental pollutants and shell thinning in eggs of the guillemot Uria aalge from the Baltic Sea and the Faeroes, and a possible relation between shell thickness and sea water salinity, Dansk Orn. Foren. Tidsskr., 78, 1, 1984.

48. Essink, K., Monitoring of mercury pollution in Dutch coastal waters by means of the teleostean fish Zoarces viviparus, Neth. J. Sea Res., 19, 177, 1985.

49. Eustace, I.J., Zinc, cadmium, copper and manganese in species of finfish and shellfish caught in the Derwent estuary, Tasmania, Aust. J. Mar. Freshw. Res., 25, 209, 1974.

50. Falconer, C.R., Davies, I.M. and Topping, G., Trace metals in the common porpoise Phocoena phocoena, Mar. Environ. Res., 8, 119, 1983.

51. Fallis, B., unpublished data, cited in, 181.

52. Fimreite, N., Mercury contamination of aquatic birds in northwestern Ontario, J. Wildl. Manag., 38, 120, 1974.

53. Fimreite, N., Brun, E., Froslie, A., Frederichsen, P. and Gundersen, N., Mercury in eggs of Norwegian seabirds, Astarte, 7, 71, 1974.

54. Fimreite, N., Kveseth, N. and Brevik, E.M., Mercury, DDE and PCBs in eggs from a Norwegian gannet colony, Bull. Environ. Contam. Toxicol., 24, 142, 1980.

55. Forrester, C.R., Ketchen, K.S. and Wong, C.C., Mercury content of spiny dogfish (Squalus acanthias) in the Strait of Georgia, British Columbia, J. Fish. Res. Bd. Can., 29, 1487, 1972.

56. Freeman, H.C. and Horne, D.A., Mercury in Canadian seals,

Bull. Environ. Contam. Toxicol., 10, 172, 1973.

57. Freeman, H.C., Horne, D.A., McTague, B. and McMenemy, M., Mercury in some Canadian Atlantic coast fish and shellfish, J. Fish. Res. Bd. Can., 31, 369, 1974.

58. Freeman, H.C., Shum, G. and Uthe, J.F., The selenium content in swordfish (Xiphias gladius) in relation to total mercury content, J. Environ. Sci. Health, A13, 235, 1978.

59. Friberg, L., Piscator, M., Nordberg, G. and Kjellstrom, T., Cadmium in the Environment, 2nd. edn., CRC Press, Cleveland, Ohio, 1974, chap. 8.

60. Fujiki, M., Tajima, S. and Omori, A., The transition of the mercury contamination in Minamata District, Jpn. J. Hyg., 27, 115, 1972.

61. Furness, R.W. and Hutton, M., Pollutant levels in the great skua Catharacta skua, Environ. Pollut., 19, 261, 1979.

62. Furness, R.W. and Hutton, M., Pollutants and impaired breeding success of great skuas Catharacta skua in Britain, Ibis, 122, 88, 1980.

63. Furness, R.W., Muirhead, S.J. and Woodburn, M., Using bird feathers to measure mercury in the environment: relationships between mercury content and moult, Mar. Pollut. Bull., 17, 27, 1986.

64. Ganther, H.E., Goudie, C., Sunde, M.L., Kopecky, M.J., Wagner, P., Oh, S-H. and Hoekstra, W.G., Selenium: relation to decreased toxicity of methylmercury added to diets containing tuna, Science, 175, 1122, 1972.

65. Ganther, H.E. and Sunde, M.L., Effect of tuna fish and selenium on the toxicity of methylmercury: a progress report, J. Food Sci., 39, 1, 1974.

66. Gaskin, D.E., Frank, R., Holdrinet, M., Ishida, K., Walton, C.J. and Smith, M., Mercury, DDT and PCB in harbour seals (Phoca vitulina) from the Bay of Fundy and Gulf of Maine, J. Fish. Res. Bd. Can., 30, 471, 1973.

67. Gaskin, D.E., Ishida, K. and Frank, R., Mercury in harbour porpoises (Phocoena phocoena) from the Bay of Fundy region, J. Fish. Res. Bd. Can., 29, 1644, 1972.

68. Gaskin, D.E., Smith, G.J.D., Arnold, P.W., Louisy, M.V., Frank, R., Holdrinet, M. and McWade, J.W., Mercury, DDT, dieldrin and PCB in two species of Odontoceti (Cetacea) from St. Lucia, Lesser Antilles, J. Fish. Res. Bd. Can., 31, 1235, 1974.

69. Gaskin, D.E., Stonefield, K.I., Suda, P. and Frank, R., Changes in mercury levels in harbour porpoises from the Bay of Fundy, Canada, and adjacent waters during 1969-1977, Arch. Environ. Contam. Toxicol., 8, 733, 1979.

70. Gilmartin, M. and Revelante, N., The concentration of

mercury, copper, nickel, silver, cadmium and lead in the northern Adriatic anchovy Engraulis encrasicholus and sardine Sardina pilchardus, Fish. Bull., 73, 193, 1975.

71. Glover, J.W., Concentrations of arsenic, selenium and ten heavy metals in school shark Galeorhinus australis (Macleay) and gummy shark Mustelus antarcticus Gunther from south-eastern Australian waters, Aust. J. Mar. Freshw. Res., 30, 505, 1979.

72. Gochfeld, M., Mercury levels in some seabirds of the Humboldt Current, Peru, Environ. Pollut. (A), 22, 197, 1980.

73. Greig, R.A. and Krzynonek, J., Mercury concentrations in three species of tunas collected from various oceanic waters, Bull. Environ. Contam. Toxicol., 22, 120, 1979.

74. Greig, R.A. and Wenzloff, D.R., Trace metals in finfish from the New York Bight and Long Island Sound, Mar. Pollut. Bull., 8, 198, 1977.

75. Greig, R.A., Wenzloff, D.R. and Peare, J.B., Distribution and abundance of heavy metals in finfish, invertebrates and sediments collected at a deepwater disposal site, Mar. Pollut. Bull., 7, 185, 1976.

76. Greig, R.A., Wenzloff, D. and Shelpuk, C., Mercury concentrations in fish, north Atlantic offshore waters-1971, Pestic. Monit. J., 9, 15, 1975.

77. Greig, R.A., Wenzloff, D., Shelpuk, C. and Adams, A., Mercury concentrations in three species of fish from north Atlantic offshore waters, Arch. Environ. Contam. Toxicol., 5, 315, 1977.

78. Hall, A.S., Teeny, F.M. and Gauglitz, E.J., Mercury in fish and shellfish of the northeast Pacific. II. Sablefish Anoplopoma fimbria, Fish. Bull., 74, 791, 1976.

79. Hall, A.S., Teeny, F.M., Lewis, L.G., Hardman, W.H. and Gauglitz, E.J., Mercury in fish and shellfish of the northeast Pacific. I. Pacific halibut Hippoglossus stenolepis, Fish. Bull., 74, 783, 1976.

80. Hamanaka, T., Itoo, T. and Mishima, S., Age-related change and distribution of cadmium and zinc concentrations in the Steller sea lion (Eumetopias jubata) from the coast of Hokkaido, Japan, Mar. Pollut. Bull., 13, 57, 1982.

81. Hamanaka, T., Kato, H. and Tgujita, T., Cadmium and zinc in ribbon seal Histriophoca fasciata in the Okhotsk Sea, Res. Inst. N. Pac. Fish. Spec. Vol., 547, 1977.

82. Hardisty, M.W., Kartar, S. and Sainsbury, M., Dietary habits and heavy metal concentrations in fish from the Severn estuary and Bristol Channel, Mar. Pollut. Bull., 5, 61, 1974.

83. Harms, U., 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. Lebensm. Unters.-Forsch., 157, 125, 1975.

84. Harms, U., Drescher, H.E. and Huschenbeth, E., Further data on heavy metals and organochlorines in marine mammals from German coastal waters, Meeresforsch, 26, 153, 1978.

85. Havre, G.N., Underdal, B. and Christiansen, C., Cadmium concentrations in some fish species from a coastal area in southern Norway, Oikos, 24, 155, 1973.

86. Holden, A.V., The accumulation of oceanic contaminants in marine mammals. Rapp. P.-v. Reun. Cons. int. Explor. Mer, 169, 353, 1975.

87. Holt, G., Froslie, A. and Norheim, G., Mercury, DDE and PCB in the avian fauna in Norway 1965-1976, Acta Vet. Scand. Suppl., 70, 1, 1979.

88. Honda, K., Nasu, T. and Tatsukawa, R., Seasonal changes in mercury accumulation in the black-eared kite Milvus migrans lineatus, Environ. Pollut. (A), 42, 325, 1986.

89. Honda, K., Tatsukawa, R., Itano, K., Miyazaki, N. and Fujiyama, T., Heavy metal concentrations in muscle, liver and kidney tissue of striped dolphin Stenella coeruleoalba and their variations with body length, weight, age and sex, Agric. Biol. Chem., 47, 1219, 1983.

90. Honda, K., Yamamoto, Y., Hidaka, H. and Tatsukawa, R., Heavy metal accumulations in Adelie penguins Pygoscelis adeliae and their variations with the reproductive process. Mem. Natl. Inst. Polar Res., Spec. Issue, 40, 443, 1986.

91. Hornung, H. and Ramelow, G.J., Distribution of Cd, Cr, Cu, and Zn in eastern Mediterranean fishes, Mar. Pollut. Bull., 18, 45, 1987.

92. Howarth, D.M., Hulbert, A.J. and Horning, D., A comparative study of heavy metal accumulation in tissues of the crested tern Sterna bergii breeding near industrialised and non-industrialised areas, Aust. Wildl. Res., 8, 665, 1981.

93. Hulse, M., Mahoney, J.S., Schroder, G.D., Hacker, C.S. and Pier, S.M., Environmentally acquired lead, cadmium and manganese in the cattle egret Bubulcus ibis and the laughing gull Larus atricilla, Arch. Environ. Contam. Toxicol., 9, 65, 1980.

94. Hutton, M., Accumulation of heavy metals and selenium in three seabird species from the United Kingdom, Environ. Pollut. (A), 26, 129, 1981.

95. Hutton, M. and Goodman, G.T., Metal contamination of feral pigeons Columba livia from the London area: part 1- tissue accumulation of lead, cadmium and zinc, Environ. Pollut. (A), 22, 207, 1980.

96. Itano, K., Kawai, S., Miyazaki, N., Tatsukawa, R. and

Fujiyama, T., Mercury and selenium levels in striped dolphins caught off the Pacific coast of Japan, Agric. Biol. Chem., 48, 1109, 1984.

97. Jensen, S., Johnels, A.G., Olsson, M. and Westermark, T., The avifauna of Sweden as indicators of environmental contamination with mercury and chlorinated hydrocarbons, Proc. XVth. Int. Ornith. Congr., Leiden, 1972, 455.

98. Johansen, P., Kapel, F.O. and Kraul, I. Heavy metals and organochlorines in marine mammals from Greenland. Int. Counc. Explor. Sea ICES C.M. 1980/E: 32, 1980.

99. Johnels, A.G. and Westermark, T., Mercury contamination of the environment in Sweden, in Chemical Fallout. Current Research on Persistent Pesticides, Millar, M.W. & Berg, G.G., Eds., Charles C. Thomas, Springfield, 1969, 221.

100. Jones, D., Ronald, K., Lavigne, D.M., Frank, R., Holdrinet, M. and Uthe, J.F., Organochlorine and mercury residues in the harp seal (Pagophilus groenlandicus), Sci. Tot. Environ., 5, 181, 1976.

101. Kai, N., Ueda, T., Takeda, M. and Kataoka, A., On mercury and selenium in tuna fish tissues- VIII. The levels of mercury and selenium in albacore from the Indian Ocean, J. Shimonoseki Univ. Fisheries, 31, 69, 1983.

102. Kari, T. and Kauranen, P., Mercury and selenium contents of seals from fresh and brackish waters in Finland, Bull. Environ. Contam. Toxicol., 19, 273, 1978.

103. King, K.A., Lefever, C.A. and Mulhern, B.M., Organochlorine and metal residues in royal terns nesting on the central Texas coast, J. Field Ornithol., 54, 295, 1983.

104. Knap, A.H. and Jickells, T.D., Trace metals and organochlorines in the goosebeaked whale, Mar. Pollut. Bull., 14, 271, 1983.

105. Knauer, G.A. and Martin, J.H., Mercury in a marine pelagic food chain, Limnol. Oceanog., 17, 868, 1972.

106. Koeman, J.H., Peeters, W.H.M., Koudstaal-Hol, C.H.M., Tjioe, P.S. and De Goeij, J.J.M., Mercury-selenium correlations in marine mammals, Nature, 245, 385, 1973.

107. Koeman, J.H., Van de Ven, W.S.M., de Goeij, J.J.M., Tjioe, P.S. and Van Haaften, J.L., Mercury and selenium in marine mammals and birds, Sci. Tot. Environ., 3, 279, 1975.

108. Kureishy, T.W., George, M.D. and Gupta, R.S., Total mercury content in some marine fish from the Indian Ocean, Mar. Pollut. Bull., 10, 357, 1979.

109. Lantzy, R.J. and Mackenzie, F.T., Atmospheric trace metals: global cycles and assessment of man's impact, Geochim. Cosmochim. Acta, 43, 511, 1979.

110. LeBlanc, P.J. and Jackson, A.L., Arsenic in marine fish and

invertebrates, Mar. Pollut. Bull., 4, 88, 1973.

111. Lee, S.S., Mate, B.R., Von der Trenck, K.T., Rimerman, R.A. and Buhler, D.R., Metallothionein and the subcellular localization of mercury and cadmium in the California sea lion, Comp. Biochem. Physiol., 57C, 45, 1977.

112. Leonzio, C., Bacci, E., Focardi, S. and Renzoni, A., Heavy metals in organisms from the northern Tyrrhenian Sea, Sci. Tot. Environ., 20, 131, 1981.

113. Leonzio, C., Focardi, S. and Bacci, E., Complementary accumulation of selenium and mercury in fish muscle, Sci. Tot. Environ., 24, 249, 1982.

114. Lutz and Armstrong, F.A.J., unpublished data, cited in, 181.

115. Lyle, J.M., Mercury concentrations in four Carcharhinid and three hammerhead sharks from coastal waters of the Northern Territory, Aust. J. Mar. Freshw. Res., 35, 441, 1984.

116. Lyle, J.M., Mercury and selenium concentrations in sharks from northern Australian waters, Aust. J. Mar. Freshw. Res., 37, 309, 1986.

117. McClurg, T.P., Trace metals and chlorinated hydrocarbons in Ross seals from Antarctica, Mar. Pollut. Bull., 15, 384, 1984.

118. Mackay, N.J., Kazacos, M.N., Williams, R.J. and Leedow, M.I., Selenium and heavy metals in black marlin, Mar. Pollut. Bull., 6, 57, 1975.

119. McKie, J.C., Davies, I.M. and Topping, G., Heavy metals in grey seals (Halichoerus grypus) from the east coast of Scotland, Int. Counc. Explor. Sea, ICES, 1980/E: 41, 1980.

120. Maedgen, J.L., Hacker, C.S., Schroder, G.D. and Weir, F.W., Bioaccumulation of lead and cadmium in the royal tern and sandwich tern, Arch. Environ. Contam. Toxicol., 11, 99, 1982.

121. Magos, L. and Webb, M., The interaction of selenium with cadmium and mercury, CRC Crit. Rev. Toxicol., 8, 1, 1980.

122. Maher, W.A., Selenium in marine organisms from St. Vincent's Gulf, South Australia, Mar. Pollut. Bull., 14, 35, 1983.

123. Martin, J.H., Elliott, P.D., Anderlini, V.C., Girvin, D., Jacobs, S.A., Risebrough, R.W., Delong, R.L. and Gilmartin, G.W., Mercury-selenium-bromine imbalance in premature parturient California sea lions, Mar. Biol., 35, 91, 1976.

124. Martin, J.H. and Flegal, A.R., High copper concentrations in squid livers in association with elevated levels of silver, cadmium and zinc, Mar. Biol., 30, 51, 1975.

125. Martoja, R. and Viale, D., Accumulation de granules de

seleniure mercurique dans le foie d'Odontocetes (Mammiferes, Cetaces): un mecanisme possible de detoxication du methyl-mercure par le selenium, C. R. hebd. Seanc. Acad. Sci. Paris, (Series D), 285, 109, 1977.

126. Mason, C.F. and Reynolds, P., Organochlorine residues and metals in otters from the Orkney Islands, Mar. Pollut. Bull., 19, 80, 1988.

127. Menasveta, P. and Siriyong, R., Mercury content of several predacious fish in the Andaman Sea, Mar. Pollut. Bull., 8, 200, 1977.

128. Miyazaki, N., Itano, K., Fukishima, M., Kawai, S. and Honda, K., Metals and organochlorine compounds in the muscle of dugong from Sulawesi Island, Sci. Rep. Whales Res. Inst., 31, 125, 1979.

129. Muirhead, S.J., The accumulation, storage and elimination of metals and organochlorines in the great skua *Catharacta skua* and metal accumulation in Atlantic Procellariiformes, Ph.D. thesis, University of Glasgow, 1986.

130. Muirhead, S.J. and Furness, R.W., Heavy metal concentrations in the tissues of seabirds from Gough Island, South Atlantic Ocean, Mar. Pollut. Bull., 19, 278, 1988.

131. Munoz, R.V., Hacker, C.S. and Gesell, T.F., Environmentally acquired lead in the laughing gull *Larus atricilla*, J. Wildl. Dis., 12, 139, 1976.

132. Murray, A.J., Metals, organochlorine pesticides and PCB residue levels in fish and shellfish landed in England and Wales during 1974, Aquat. Environ. Monit. Rep., MAFF Direct. Fish. Res., Lowestoft, 2, 1979.

133. Murray, A.J., Metals, organochlorine pesticides and PCB residue levels in fish and shellfish landed in England and Wales during 1975, Aquat. Environ. Monit. Rep., MAFF Direct. Fish. Res., Lowestoft, 5, 1981.

134. Murray, A.J. and Norton, M.G., The field assessment of effects of dumping wastes at sea. 10: analysis of chemical residues in fish and shellfish from selected coastal regions around England and Wales, Fish. Res. Tech. Rep., MAFF Direct. Fish. Res., Lowestoft 69, 1982.

135. Murray, A.J. and Portmann, J.E., Metals and organochlorine pesticide and PCB residues in fish and shellfish in England and Wales in 1976 and trends since 1970, Aquat. Environ. Monit. Rep., MAFF Direct. Fish. Res., Lowestoft, 10, 1984.

136. Nagakura, K., Arima, S., Kurihara, M., Koga, T. and Fujita, T., Mercury content of whales, Bull. Tokai Reg. Fish. Res. Lab., 78, 41, 1974.

137. National Marine Fisheries Service, 1975 microconstituent resource survey, unpublished data, cited in, Medical and Biological Effects of Environmental Pollutants; Zinc,

National Research Council, Subcommittee on Zinc, University Park Press, Baltimore, 1979, 88.

138. Nicholson, J.K., The comparative distribution of zinc, cadmium and mercury in selected tissues of the herring gull (Larus argentatus), Comp. Biochem. Physiol., 68C, 91, 1981.

139. Nicholson, J.K. and Osborn, D., Kidney lesions in pelagic seabirds with high tissue levels of cadmium and mercury, J. Zool. Lond., 200, 99, 1983.

140. Noble, D.G. and Elliott, J.E., Environmental contaminants in Canadian seabirds, 1968-1984: trends and effects, Technical report series No. 13, Canadian wildlife service, Ottawa, 1986.

141. Norheim, G., Levels and interactions of heavy metals in seabirds from Svalbard and the Antarctic, Environ. Pollut., 47, 83, 1987.

142. Norheim, G. and Kjos-Hanssen, B., Persistent chlorinated hydrocarbons and mercury in birds caught off the west coast of Spitsbergen, Environ. Pollut. (A), 33, 143, 1984.

143. Norheim, G., Somme, L. and Holt, G., Mercury and persistent chlorinated hydrocarbons in Antarctic birds from Bouvetoya and Dronning Maud Land, Environ. Pollut. (A), 28, 233, 1982.

144. Norstrom, R.J., Schweinsberg, R.E. and Collins, B.T., Heavy metals and essential elements in livers of the polar bear (Ursus maritimus) in the Canadian Arctic, Sci. Tot. Environ., 48, 195, 1986.

145. Ohlendorf, H.M., Anderson, D.W., Boellstorff, D.E. and Mulhern, B.M., Tissue distribution of trace elements and DDE in brown pelicans, Bull. Environ. Contam. Toxicol., 35, 183, 1985.

146. Ohlendorf, H.M. and Harrison, C.S., Mercury, selenium, cadmium and organochlorines in eggs of three Hawaiian seabird species, Environ. Pollut. (B), 11, 169, 1986.

147. Osborn, D., A naturally occurring cadmium and zinc binding protein from the liver and kidney of Fulmarus glacialis, a pelagic North Atlantic seabird, Biochem. Pharmacol., 27, 822, 1978.

148. Osborn, D., Every, W.J. and Bull, K.R., The toxicity of trialkyl lead compounds to birds, Environ. Pollut. (A), 31, 261, 1983.

149. Osborn, D., Harris, M.P. and Nicholson, J.K., Comparative tissue distribution of mercury, cadmium and zinc in three species of pelagic seabirds, Comp. Biochem. Physiol., 64C, 61, 1979.

150. Parizek, J. and Ostadalova, I., The protective effect of small amounts of selenite in sublimate intoxication, Experientia, 23, 142, 1967.

151. Perttila, M., Tervo, V. and Parmanne, R., Heavy metals in Baltic herring and cod, Mar. Pollut. Bull., 13, 391, 1982.

152. Plaskett, D. and Potter, I.C., Heavy metal concentrations in the muscle tissue of 12 species of teleost from Cockburn Sound, Western Australia, Aust. J. Mar. Freshw. Res., 30, 607, 1979.

153. Portmann, J.E., The levels of certain metals in fish from coastal waters around England and Wales, Aquaculture, 1, 91, 1972.

154. Portmann, J.E., Chemical monitoring of residue levels in fish and shellfish landed in England and Wales during 1970-73, Aquat. Environ. Monit. Rep., MAFF Direct. Fish. Res., Lowestoft, 1, 1979.

155. Reid, M. and Hacker, C.S., Spatial and temporal variation in lead and cadmium in the laughing gull Larus atricilla, Mar. Pollut. Bull., 13, 387, 1982.

156. Reijnders, P.J.H., Organochlorine and heavy metal residues in harbour seals from the Wadden Sea and their possible effects on reproduction, Neth J. Sea Res., 14, 30, 1980.

157. Renzoni, A., Focardi, S., Fossi, C., Leonzio, C. and Mayol, J., Comparison between concentrations of mercury and other contaminants in eggs and tissues of Cory's shearwater Calonectris diomedea collected on Atlantic and Mediterranean islands, Environ. Pollut. (A), 40, 17, 1986.

158. Rivers, J.B., Pearson, J.E. and Shultz, C.D., Total and organic mercury in marine fish, Bull. Environ. Contam. Toxicol., 8, 257, 1972.

159. Roberts, T.M., Heppleston, P.B. and Roberts, R.D., Distribution of heavy metals in tissues of the common seal, Mar. Pollut. Bull., 7, 194, 1976.

160. Robertson, D.E., Rancitelli, L.A., Langford, J.C. and Perkins, R.W., Battelle-Northwest contribution to the IDOE Baseline Study, in Baseline Studies of Pollutants in the Marine Environment, NSF-IDOE Workshop, Brookhaven, New York, 1972, 209.

161. Ronald, K., Frank, R.J. and Dougan, J., Pollutants in harp seals (Phoca groenlandica). II. Heavy metals and selenium, Sci. Tot. Environ., 38, 153, 1984.

162. Sergeant, D.E. and Armstrong, F.A.J., Mercury in seals from Eastern Canada, J. Fish. Res. Bd. Can., 30, 843, 1973.

163. Shomura, R.S. and Craig, W.L., Mercury in several species of billfishes taken off Hawaii and southern California, Spec. Scient. Rep. Natn. Oceanic Atmos. Adm. U.S. (Fisheries), 675, 160, 1974.

164. Shultz, C.D. and Ito, B.M., Mercury and selenium in blue marlin Makaira nigricans from the Hawaiian islands, Fish.

Bull., 76, 872, 1979.

165. Smith, T.G. and Armstrong, F.A.J., Mercury and selenium in ringed and bearded seal tissues from Arctic Canada, Arctic, 31, 75, 1978.

166. Sorentino, C., Mercury in marine and freshwater fish of Papua New Guinea, Aust. J. Mar. Freshw. Res., 30, 617, 1979.

167. Steinhagen-Schneider, G., Cadmium and copper levels in seals, penguins and skuas from the Weddell Sea in 1982/83, Polar Biol., 5, 139, 1986.

168. Stevens, J.D. and Brown, B.E., Occurrence of heavy metals in the blue shark Prionace glauca and selected pelagic in the N.E. Atlantic Ocean, Mar. Biol., 26, 287, 1974.

169. Stoneburner, D.L., Heavy metals in tissues of stranded short-finned pilot whales, Sci. Tot. Environ., 9, 293, 1978.

170. Stoneburner, D.L. and Harrison, C.S., Heavy metal residues in sooty tern tissues from the Gulf of Mexico and north central Pacific Ocean, Sci. Tot. Environ., 17, 51, 1981.

171. Stoneburner, D.L., Patty, P.C. and Robertson, W.B., Evidence of heavy metal accumulations in sooty terns, Sci. Tot. Environ., 14, 147, 1980.

172. Sumino, K., Yamamoto, R. and Kitamura, S., The role of selenium against methylmercury toxicity, Nature, 268, 73, 1977.

173. Suzuki, T., Miyama, T. and Toyama, C., The chemical form and bodily distribution of mercury in marine fish, Bull. Environ. Contam. Toxicol., 10, 347, 1973.

174. Thompson, D.R., Total and organic mercury concentrations in liver tissue of seabirds, in Seabird Food and Feeding Ecology; Proc. Third Int. Conf. Seabird Group, Tasker, M.L., Ed., 1988, 44.

175. Thomson, J.D., Mercury concentrations of the axial muscle tissues of some marine fishes of the continental shelf adjacent to Tasmania, Aust. J. Mar. Freshw. Res., 36, 509, 1985.

176. Topping, G., Heavy metals in fish from Scottish waters, Aquaculture, 1, 373, 1973.

177. Turner, J.C., Solly, S.R.B., Mol-Krijnen, J.C.M. and Shanks, V., Organochlorine, fluorine and heavy metal levels in some birds from New Zealand estuaries, N. Z. J. Sci., 21, 99, 1978.

178. Van de Ven, W.S.M., Koeman, J.H. and Svenson, A., Mercury and seleium in wild and experimental seals, Chemosphere, 8, 539, 1979.

179. Vas, P., Observations on trace metal concentrations in a Carcharhinid shark Galeorhinus galeus from Liverpool Bay, Mar. Pollut. Bull., 18, 193, 1987.

180. Wagemann, R., unpublished data, cited in, 181.

181. Wagemann, R. and Muir, D.C.G., Concentrations of heavy metals and organochlorines in marine mammals of northern waters: overview and evaluation, Can. Tech. Rep. Fish. Aquat. Sci., No. 1279, 1984.

182. Wagemann, R., Snow, N.B., Lutz, A. and Scott, D.P., Heavy metals in tissues and organs of the narwhal (Monodon monoceros), Can. J. Fish. Aquat. Sci., 40 (Suppl. 2), 206, 1983.

183. Walker, T.I., Effects of species, sex, length and locality on the mercury content of school shark Galeorhinus australis (Macleay) and gummy shark Mustelus antarcticus Guenther from south-eastern Australian waters, Aust. J. Mar. Freshw. Res., 27, 603, 1976.

184. Watling, R.J., McClurg, T.P. and Stanton, R.C., Relation between mercury concentration and size in the mako shark, Bull. Environ. Contam. Toxicol., 26, 352, 1981.

185. Westermark, T., Odsjo, T. and Johnels, A.G., Mercury content of bird feathers before and after Swedish ban on alkyl mercury in agriculture, Ambio, 4, 87, 1975.

186. Wharfe, J.R. and Van Den Broek, W.L.F., Heavy metals in macroinvertebrates and fish from the lower Medway estuary, Kent, Mar. Pollut. Bull., 8, 31, 1977.

187. Windom, H., Stickney, R., Smith, R., White, D. and Taylor, F., Arsenic, cadmium, copper, mercury and zinc in some species of north Atlantic finfish, J. Fish. Res. Bd. Can., 30, 275, 1973.

188. Wright, D.A., Heavy metals in animals from the north east coast, Mar. Pollut. Bull., 7, 36, 1976.

189. Yamamoto, Y., Honda, K., Hidaka, H. and Tatsukawa, R., Tissue distribution of heavy metals in Weddell seals (Leptonychotes weddellii), Mar. Pollut. Bull., 18, 164, 1987.

190. Zonfrillo, B., Sutcliffe, R., Furness, R.W. and Thompson, D.R., Notes on a Risso's dolphin from Argyll with analyses of its stomach contents and mercury levels, Glasgow Nat., 21, 297, 1988.

CHAPTER 3

Materials and methods: sample collection, preparation and mercury analysis

3.1 SAMPLE COLLECTION

3.1.1 Feathers

Feathers have often been used to monitor mercury concentrations in birds. They have the advantage that they can be obtained relatively easily from live birds, removing the necessity of having to kill birds to obtain tissue samples. Work by Furness et al. (1986) indicated that a sample of body feathers would be the most appropriate for the study of mercury levels in birds. This, it was argued, would overcome problems associated with great inter-primary mercury concentration variation, inconsistent numbering for primaries and allow more compatability between studies. However, relationships between levels of mercury in feathers and in other tissues, and relationships with dietary intake, age, sex, moult, toxicology and physiology need to be established before feathers can be used to study mercury pollution with confidence.

Throughout this work, body feathers have been preferentially taken; samples of 4-10 small body feathers from the central back region were placed in mercury-free polythene bags prior to further treatment. Some feathers analysed were not sampled in this way, such cases being outlined in the relevant chapters. For example, eagle feather samples comprised feathers of all available types, including primary and secondary feathers (Chapter 8). Wherever possible, feathers were obtained from live, apparently healthy adult birds during the breeding season when feather moult was suspended. Exceptions to this general pattern were those feather samples obtained from birds found dead, but in a 'fresh' condition, feathers from juveniles or chicks and feathers obtained from birds outside the breeding season and/or in moult. Birds found freshly dead were considered suitable for feather samples since mercury levels in feathers would be unaffected by any internal process which would otherwise alter tissue mercury concentrations. Specific details regarding feather sample collection are given in the chapters to which they apply.

3.1.2 Internal tissues

Mercury analyses of internal tissues were performed to a lesser extent than those of feathers. Internal tissues of birds 'found dead' were not considered suitable for mercury analysis since changes in tissues were likely to have occurred during starvation before death and possibly also post-mortem, thus altering the mercury concentrations.

Where internal tissues have been analysed for mercury, they were obtained, under licence, from freshly killed birds which were apparently healthy and in good physical condition. Wherever possible, birds were immediately deep frozen at ca. -20^{o}C prior to further treatment. Specific collection details for those particular samples obtained in this way are given in the relevant chapters.

3.2 SAMPLE PREPARATION

3.2.1 Feathers

Gross surface contamination, particularly of those feathers obtained from museum study skin collections, was removed by a feather laundering regime as outlined below:-

1. Feathers to be laundered were placed in clean boiling tubes (see 3.4) and covered with chloroform. The tubes were placed in the tank unit of an ultrasonic cleaner (Burndept Ltd., Erith, Kent) for 5 minutes.
2. Used chloroform was decanted off and step 1 repeated.

3. After the second chloroform wash, samples were dried for 1 hour at ca. 50°C to 'drive off' excess chloroform.

4. Feathers were covered with acetone and washed in the ultrasonic bath for 10 minutes. Used acetone was then decanted off.

5. Feathers were then covered with distilled water and washed in the ultrasonic bath for 5 minutes. Used water was decanted off and this step repeated 3 times.

6. Samples were dried at 50°C for 24 hours, then allowed to equilibriate with ambient laboratory temperature (ca. 22°C) prior to weighing.

Note that bound mercury is not removed from feathers by this procedure (Furness, unpublished data). Feather weight was taken as that obtained for a given sample dried at ambient laboratory temperature. In attempting to obtain a 'dry' weight, it was found that feathers quickly increased in weight, once out of the oven, presumably due to the reabsorption of water vapour. It was felt that an accurate dry feather weight could not be obtained with any consistency, and the 'dried at ambient laboratory temperature' weight was used.

3.2.2 Internal tissues

Frozen samples were allowed to thaw and internal tissues, invariably liver, kidney and muscle, were dissected out using stainless steel blades and instruments. 'Wet' samples were weighed and dried to constant weight, determined by repeated weighings, in an oven at 50°C. The water content was determined and used to convert mercury concentrations in dry weight terms to wet weight equivalents where necessary. Dried samples were stored in air-tight glass vials prior to analysis.

3.3 MERCURY ANALYSIS

3.3.1 Total mercury determination

Total mercury concentrations were measured using a cold vapour, atomic absorption spectrophotometry technique, incorporating a Data Acquisition Ltd. DA 1500-DP6 Mercury Vapour Detector. For reasons of logistics and relative convenience, mercury analysis was spread over 2 days. Samples (both feathers and internal tissues) were subjected to the following procedure prior to mercury measurement:-

Day 1

1. Samples of ca. 0.050-0.250 g were weighed out accurately (to 0.001 g) using a Precisa 300MC (Metragram Instruments Ltd., Aspley Guise, Buckinghamshire) top-pan balance and placed in Kjeldahl flasks. Samples were digested using a 4 ml: 1 ml mixture of concentrated sulphuric and concentrated nitric acids in a water bath at 50°C for ca. 2 hours. Flasks were shaken occasionally to aid sample digestion.
2. On complete tissue digestion, the flasks were placed in a refrigerator (ca. 4°C) to cool for 30 minutes.
3. A 5% potassium permanganate solution (25 g potassium permanganate added to 500 ml distilled water) was made up in a dark glass bottle using a magnetic stirrer for at least 3 hours. The solution was cooled in a refrigerator for 30 minutes.
4. The cooled 5% potassium permanganate solution was added to the cooled, digested samples in 2 ml aliquots using a graduated syringe. Flasks were placed back in the refrigerator between additions for ca. 10 minutes to prevent the reaction mixture becoming too hot and developing froth. A total of 14 ml of the 5% potassium permanganate solution was added to each sample which effectively oxidised the tissue present. The flasks were

kept in the refrigerator over night.

5. A 2% potassium permanganate solution (12 g potassium permanganate added to 600 ml distilled water) was made up in another dark glass bottle and left on a magnetic stirrer over night.

6. A 50% sulphuric acid solution was prepared by carefully adding 300 ml of concentrated sulphuric acid to an equal volume of distilled water in a conical flask placed in a cold water bath. The flask was covered and left over night.

7. A reducing agent was prepared by adding 85 g of tin (II) chloride to 250 ml of distilled water in a conical flask, to which was added 250 ml of concentrated hydrochloric acid. This mixture was aerated over night using an aquarium air pump to drive off any mercury impurities which may have been present.

Day 2

1. The excess 5% potassium permanganate solution in the Kjeldahl flasks was dissolved using 30% hydrogen peroxide solution added dropwise.

2. Each sample was poured into a 25 ml volumetric flask and made up to volume with distilled water. The Kjeldahl flasks were rinsed with distilled water and these rinsings made up part of the 25 ml. The volumetric flasks were inverted repeatedly to ensure complete mixing and each sample poured into a 10 ml beaker to await analysis.

3. Standard solutions of mercury (II) nitrate were prepared by adding 100 µl of the 2% potassium permanganate solution and 100 µl mercury (II) nitrate to a 100 ml volumetric flask, made up to volume with distilled water. Replicate standard solutions, usually three, were made up in this way, inverted repeatedly to ensure complete mixing and poured into beakers to await

analysis.

4. The remaining 2% potassium permanganate solution was mixed with the 50% sulphuric acid in a dark glass bottle and cooled in the refrigerator for ca. 15 minutes.

Mercury analysis of samples was performed by adding 1 ml of sample, 20 ml of the acidified potassium permanganate solution and 25 ml distilled water to a Dreshel flask; this mixture was reduced with 10 ml of the reducing agent (see step 7, Day 1) and any free mercury so produced drawn through magnesium perchlorate drying agent and into the analyser as a vapour. 'Background' mercury levels in chemicals used were accounted for by repeating the above procedure, but omitting the 1 ml of sample. All readings were subsequently corrected for the 'blank' reading. Calibration of the analysis was performed with replicate analyses of standard mercury (II) nitrate solutions; 100 µl (equivalent to 100 ng of mercury) of the standard solution was analysed as above. The relationship between the reading obtained and the amount of mercury in the standard solution has been shown to be linear (Muirhead, 1986) and, therefore, only one concentration of mercury (II) nitrate solution was analysed. The above recipe allowed for up to 32 samples to be analysed; blank and standard readings were checked during the course of sample analysis. All chemicals used were of 'Spectrosol', 'Analar' or 'Puranal' analytical grades throughout. The mercury vapour detector was allowed to equilibriate to its working temperature for at least 2 hours prior to every set of analyses.

To determine the mercury concentration in a particular sample, the following steps were followed:-

1. Blank readings were subtracted from standard readings, and the mean 100 ng standard reading obtained.

2. The blank reading was subtracted from the sample reading and the amount of mercury (in ng) determined by...

$$\frac{\text{Reading}}{\text{Mean Standard/100}}$$

3. The mercury concentration (ppm or $\mu g\ g^{-1}$) is given by...

$$\frac{\text{ng Mercury X 25}}{\text{Sample Weight X 1000}}$$

3.3.2 Method accuracy and detection limits

The accuracy and reproducibility of the mercury determination method were tested by analysing International Atomic Energy Agency horse kidney Reference Material H-8. The results obtained from replicate analyses of mercury concentration in this material are presented in Table 3.1 (see also Thompson & Furness, in press; Chapter 7.1). It can be seen that the results obtained agree closely with those presented from other laboratories, indicating that the technique employed is both accurate and reproducible, especially since the mercury concentration in the H-8 material was relatively low (Table 3.1). The lower limit of detection was 0.01 $\mu g\ g^{-1}$ fresh weight of tissue, based on a reading of 1 unit on the digital scale of the analyser. Given that the average 100 ng standard reading was likely to be 200 units and up to 0.250 g of dry tissue could have been analysed, the reading of 1 unit would result in a concentration of ca. 0.05 $\mu g\ g^{-1}$ dry weight or 0.01-0.02 $\mu g\ g^{-1}$ wet weight, depending upon the water content of the tissue analysed.

3.3.3 Extraction method for organic mercury

The analytical method described in 3.3.1 does not

TABLE 3.1: Total mercury concentration ($\mu g\ g^{-1}$ dry weight) of International Atomic Energy Agency horse kidney Reference Material H-8.

Replicates	Mean	95% Conf. limits	s.d.	s.e.	Range	Source
7	0.88	0.86-0.90	0.02	0.008	0.86-0.91	This study
19[a]	0.91	0.83-0.98	0.16	0.040	0.52-1.13	IAEA data

19[a]: 19 accepted laboratory averages combined, based on 85 accepted individual determinations.

discriminate between different forms of mercury which may be present in a given tissue. Because mercury can exist in a variety of fat-soluble organic forms which exhibit different properties when compared to inorganic mercurials, a technique was adapted to extract the organo-mercurials only from a sample. Organic mercury was extracted from samples following the method of Uthe _et al._ (1972). Although the analytical method did not permit identification of specific organo-mercurials, monomethyl mercury was the form of organic mercury normally found in bird tissues by several other authors using gas chromatography techniques (Fimreite, 1974; Norheim _et al._, 1982; Norheim & Froslie, 1978; Osborn _et al._, 1979). It was assumed, therefore, that organic mercury extracted was monomethyl mercury. The steps involved in the extraction method were as follows:-

1. The large keratin molecules in feather samples were initially 'broken down' using 4 ml of 10M sodium hydroxide solution in a water bath at 50°C for ca. 2 hours. The sodium hydroxide solution was subsequently neutralised using 0.85 ml concentrated

sulphuric acid.

2. Feather samples treated in this way, or finely ground tissue samples were then mixed thouroughly with 10 ml 0.1M copper sulphate solution (stock solution, 25 g copper sulphate added to 1 l distilled water), 5 ml acidic sodium bromide solution (stock solution, 250 g sodium bromide added to 565 ml distilled water, to which was added 89 ml concentrated sulphuric acid/89 ml distilled water, all made up to 806 ml with distilled water) and 10 ml toluene in a large centrifuge tube. Whilst mixing, the tubes were covered with 'cling film' to prevent evaporation of the toluene. Methyl mercury was released as methyl mercury bromide which passed into the organic (toluene) phase.

3. Mixed samples then underwent a centrifugation for 15 minutes at ca. 4000 revolutions minute^{-1}; 5 ml of the toluene was removed, using a graduated syringe, to a second, smaller centrifuge tube.

4. The 5 ml of toluene was thouroughly mixed with 2 ml of 0.005M sodium thiosulphate solution (stock 0.05M solution, 12.4 g sodium thiosulphate added to 1 l distilled water; 0.005M solution, 10 ml stock solution made up to 100 ml with distilled water) which converted the methyl mercury bromide into methyl mercury thiosulphate. This latter passed into the aqueous phase.

5. The toluene/sodium thiosulphate mixture underwent a centrifugation for 10 minutes at ca. 2000 revolutions minute^{-1}; 1 ml of the aqueous phase was removed using a graduated syringe and placed in a Kjeldahl flask. Because the analyser was found to be sensitive to toluene, any minute quantities of toluene were driven off by placing the flasks in a water bath at 50^{o}C for 1 hour. The 1 ml extracted sample effectively contained 25% of the methyl mercury originally present.

6. Samples were then analysed as described in 3.3.1.

All solutions were freshly made up prior to use; all chemicals were of 'Puranal', 'Analar' or 'Spectrosol' analytical grades throughout.

3.3.4 Extraction method efficiency and reproducibility

Some of the data presented in this section have been previously published in Thompson & Furness (in press) and appear in Chapter 7.1.

The extraction method efficiency was tested by performing extractions of standard solutions of methyl mercuric chloride. Replicate extractions of ca. 2040 ng (n=13) and ca. 408 ng (n=14) of mercury as methyl mercuric chloride were made and compared to replicate total mercury determinations of the same quantities. The results obtained are presented in Table 3.2. The mean extraction efficiencies for the 2 groups (2040 ng and 408 ng) were not significantly different (2 sample t-test, P=0.805) and were combined, producing an overall extraction efficiency of 90.04% (Table 3.2). All methyl mercury levels obtained in subsequent analyses were corrected for this extraction efficiency.

Inorganic mercury was not extracted by the method. Six replicate extractions of 100 ng, 1000 ng and 10000 ng of mercury as mercury (II) nitrate, together with 6 blank extractions were undertaken. There was no significant difference in the readings obtained from the mercury (II) nitrate extractions and the blank extractions (Kruskal-Wallis 1-Way ANOVA).

Any matrix effects were tested for by performing spiked extractions of Atlantic petrel *Pterodroma incerta* feather samples. From each petrel, 2 samples of equal numbers of small

TABLE 3.2: Methyl mercury extraction efficiency data: initial amount of methyl mercury, mean total mercury measured and mean methyl mercury extracted (ng). Extracted methyl mercury expressed as a percentage of the total mercury measured with standard deviations and ranges.

Calculated initial amount CH_3HgCl	Mean total Hg measured (n)	Mean extracted Hg measured (n)	Mean % extracted (n)	s.d.	Range
2040	2156 (6)	1962 (13)	90.26 (13)	4.79	84.51-98.58
408	415 (4)	373 (14)	89.85 (14)	3.67	84.34-96.87
Overall for both concentrations			90.04 (27)	4.16	84.34-98.58

body feathers (ca. 6) were spiked with a known amount of methyl mercuric chloride and either subjected to the extraction method or analysed for total mercury. After correction for the extraction method efficiency of 90.04% (Table 3.2), the mean values obtained for the 2 respective treatments were similar and there was no significant difference between groups (1 sample t-test, P=0.135, comparing the distribution of the differences between the paired values from each bird around a mean of 0; Table 3.3), indicating that matrix effects did not influence the extraction method. The variation measured within and between

TABLE 3.3: Mercury concentrations ($\mu g\ g^{-1}$ fresh weight) in Atlantic petrel body feathers spiked with methyl mercuric chloride and either analysed for total mercury or 'extracted' and then anlaysed. 'Extracted' values corrected for extraction method efficiency of 90.04%.

	Samples analysed for total mercury	Samples extracted and then analysed
	33.5	37.4
	44.4	42.1
	30.2	41.3
	32.2	36.0
	34.0	41.7
	33.9	38.9
	40.7	40.1
	32.7	28.6
Mean	35.2	38.3
Stand. Dev.	4.8	4.5

1 sample t-test, P=0.135.

both samples reflected the variation between mercury levels in different feathers from the same bird (Table 3.3).

A similar comparison was made using horse kidney reference material H-8 whereby 8 spiked samples underwent the extraction method, the results from which being compared to those from 4 spiked samples measured for total mercury. The results were corrected for the amount of mercury that was present in the H-8 material (based on the mean concentration of 0.88 $\mu g\ g^{-1}$ dry weight; Table 3.1) and for the extraction method efficiency of 90.04% (Table 3.2). The results obtained were found to not differ significantly, again indicating no matrix effects (2 sample t-test, P=0.111; Table 3.4).

TABLE 3.4: Amount of mercury measured (ng) in horse kidney reference material H-8 spiked with methyl mercuric chloride and either analysed for total mercury or 'extracted' and then analysed. All values corrected for amount of mercury present and 'extracted' values for extraction method efficiency of 90.04%.

	Samples analysed for total mercury	Samples extracted and then analysed
	71.0	71.9
	70.9	72.3
	73.4	70.6
	71.2	70.9
		65.3
		69.4
		68.6
		70.4
Mean	71.6	69.9
Stand. Dev.	1.2	2.2

2 sample t-test, P=0.111.

3.4 GLASSWARE LAUNDERING

Glassware was cleaned by soaking in Decon 90 (Decon Laboratories Ltd., Hove, West Sussex) detergent for 24 hours, followed by repeated rinsings with distilled water. Specific labelled items of glassware were used only for one particular solution or acid to reduce the possibilty of contamination.

3.5 STATISTICAL PROCEDURES

Since mercury distribution patterns have been shown to deviate significantly from a Gaussian distribution (Muirhead & Furness, 1988), predominantly non-parametric statistical techniques have been used to assess trends and differences within and between sets of data in this study. However, all data were initially analysed for deviations from a Gaussian distribution using Kolmogorov-Smirnov 1 sample tests. Any data which were not found to deviate significantly from Gaussian were analysed using parametric techniques. Specific details relating to tests used and distribution patterns of particular data are presented in the individual chapters.

3.6 REFERENCES

Fimreite, N. (1974). Mercury contamination of aquatic birds in northwestern Ontario. J.Wildl. Manage. 38, 120-131.

Furness, R.W., Muirhead, S.J. & Woodburn, M. (1986). Using bird feathers to measure mercury in the environment: relationships between mercury content and moult. Mar. Pollut. Bull. 17, 27-30.

Muirhead, S.J. (1986). Accumulation, storage and elimination of pollutants by great skuas Catharacta skua and concentrations of metals in pelagic Atlantic seabirds. Unpubl. Ph.D. thesis, University of Glasgow.

Muirhead, S.J. & Furness, R.W. (1988). Heavy metal concentrations in the tissues of seabirds from Gough Island, south Atlantic Ocean. Mar. Pollut. Bull. 19, 278-283.

Norheim, G. & Froslie, A. (1978). The degree of methylation and organ distribution of mercury in some birds of prey in Norway. Acta Pharmacol. et Toxicol. 43, 196-204.

Norheim, G., Somme, L. & Holt, G. (1982). Mercury and persistent chlorinated hydrocarbons in Antarctic birds from Bouvetoya and Dronning Maud Land. Environ. Pollut. (A) 28, 233-240.

Osborn, D., Harris, M.P. & Nicholson, J.K. (1979). Comparative tissue distribution of mercury, cadmium and zinc in three species of pelagic seabirds. Comp. Biochem. Physiol. 64C, 61-67.

Thompson, D.R. & Furness, R.W. (in press). Comparison of the levels of total and organic mercury in seabird feathers. Mar. Pollut. Bull.

Uthe, J.F., Solomon, J. & Grift, B. (1972). Rapid semimicro method for the determination of methyl mercury in fish tissue. J. Assoc. Off. Anal. Chem. 55, 583-589.

CHAPTER 4

The chemical form of mercury stored in south Atlantic seabirds

4.1 INTRODUCTION

Mercury is one of the heavy metals most likely to cause pollution effects in marine ecosystems (Bryan, 1984). Furthermore, mercury, and more specifically methyl mercury, is the only metal for which evidence exists for widespread and general bioamplification up marine food chains (Bryan, 1979). Only lead has a higher value than mercury for the ratio anthropogenic/natural inputs to the environment (Lantzy & Mackenzie, 1979). Major incidents of mercury contamination of the environment in Japan (Kurland et al., 1960), Sweden (Borg et al., 1969; Johnels & Westermark, 1969) and Iraq (Bakir et al., 1973) all involved predominantly methyl mercury being accumulated by top predators as a result of consumption of prey containing elevated levels of this lipophilic and highly toxic form.

Since the documentation of the above incidents, there have been numerous studies of mercury levels in both marine and terrestrial environments, but the majority of these have dealt with "total" mercury only (for example, Anderlini et al., 1972; Delbeke et al., 1984; Holt et al., 1979; Mackay et al., 1975; McKie et al., 1980; Ronald et al., 1984).

When determined in liver tissue of some marine mammals, methyl mercury levels constitute a small proportion (generally <30%) of the total mercury concentration (for example, Born et al., 1981; Falconer et al., 1983; Gaskin et al., 1979; Itano et al., 1984; Smith & Armstrong, 1978). Conversely, in fish, the methyl mercury level constitutes a relatively high proportion (generally >80%) of the total mercury level (for example, Bebbington et al., 1977; Chvojka, 1988; Kai et al., 1983; Lyle, 1986). This reduction in the relative proportion of methyl mercury between prey and predator has been taken as evidence of a detoxification process, in which methyl mercury is demethylated into an inorganic storage form of mercury (Buhler et al., 1975; Freeman & Horne, 1973; Kari & Kauranen, 1978; Reijnders, 1980; Smith & Armstrong, 1978).

There have been rather few studies of this relationship in birds. A low proportion of methyl mercury has been demonstrated in aquatic birds from north west Ontario (Fimreite, 1974), in birds of prey from Norway (Norheim & Froslie, 1978) and, more recently, by Norheim et al. (1982) in liver tissue of a sample of south polar skuas *Catharacta maccormicki*. In contrast, Osborn et al. (1979) compared methyl and total mercury levels in liver and kidney tissues of three seabird species from St. Kilda and noted that the bulk of the mercury present was in the methyl form.

In the light of the above findings, data are presented in this paper for both total and methyl mercury concentrations in liver tissues of a wide range of seabird species from Gough Island, South Atlantic Ocean. The levels of methyl mercury, relative to total mercury, are compared both within, and between, species. The factors which may influence the observed proportions of the two forms of mercury within this group are discussed.

4.2 MATERIALS AND METHODS

4.2.1 Sample collection and storage

All birds were collected during the breeding season from Gough Island in the Tristan da Cunha group, South Atlantic Ocean, as described by Muirhead & Furness (1988). Livers used in this study had previously been analysed for levels of cadmium, copper, mercury (total) and zinc (Muirhead & Furness, 1988).

4.2.2 Analysis of mercury levels

Total mercury levels were analysed by a cold vapour technique using a Data Acquisition Ltd. DA 1500-DP6 Mercury Vapour Detector, preceded by standard acid digestion of samples (Furness et al., 1986).

For analysis of methyl mercury, an initial fractionation of the sample was performed. The method used is based on that of Uthe et al. (1972). Initially, the dried sample was ground to fine powder, and then mixed with copper sulphate, acidified sodium bromide and toluene. Methyl mercury is released from the tissue and passes into the toluene as methyl mercuric bromide. Part of the organic phase is then removed and added to sodium thiosulphate solution, converting the methyl mercuric bromide into hydrophilic methyl mercuric thiosulphate which passes into the aqueous phase. A sample of the sodium thiosulphate solution, containing the methyl mercuric thiosulphate, is removed, acid digested, and analysed as above. Although the analytical method used in this study is unable to distinguish between specific organo-mercurials, previous studies which used gas chromatography techniques, found that monomethyl mercury is the form in which mercury exists in bird tissues (Fimreite, 1974; Norheim et al., 1982; Norheim & Froslie, 1978; Osborn et al., 1979). The efficiency and reproducibility of this method was tested by using standard solutions of methyl mercuric chloride and was found to be 90.04% efficient and highly reproducible (Thompson & Furness, in press; Chapter 7.1). The extraction method was tested for matrix effects by performing 8 replicate extractions of dried horse kidney tissue spiked with known amounts of methyl mercuric chloride solution. The extraction efficiency of the spiked samples was found to be identical to that of methyl mercuric solution, indicating no significant matrix effects. All results for methyl mercury presented in this paper have been corrected assuming an extraction efficiency of 90.04%.

Mercury concentrations, both total and methyl, are presented as ug g^{-1} dry weight of liver tissue. Since mercury concentrations in seabird liver tissues have been shown to exhibit skewed distribution patterns, deviating markedly from a Gaussian distribution (Muirhead & Furness, 1988), non-parametric Spearman Rank Correlation Coefficients have been calculated in order to compare the trends of total and methyl mercury levels between and within species. The word "significant" has been used in the statistical context only, indicating a probability of chance occurrence of less than 5%.

4.3 RESULTS

4.3.1 Total mercury

Total mercury levels are shown in Table 4.1. These are included for comparison with organic mercury levels, and are not direct dry weight equivalents of total mercury levels reported by Muirhead & Furness (1988) since some samples used in that study were no longer available.

4.3.2 Methyl mercury

Methyl mercury levels (Table 4.1) were found to be less variable than total mercury levels. When expressed as a percentage of the mean total mercury concentration, mean methyl mercury levels were always less than, and in some cases very much less than, 100%. Percentage methyl mercury levels varied from a mean of 2.6% in wandering albatrosses *Diomedea exulans* up to a mean of 92.6% in little shearwaters *Puffinus assimilis*

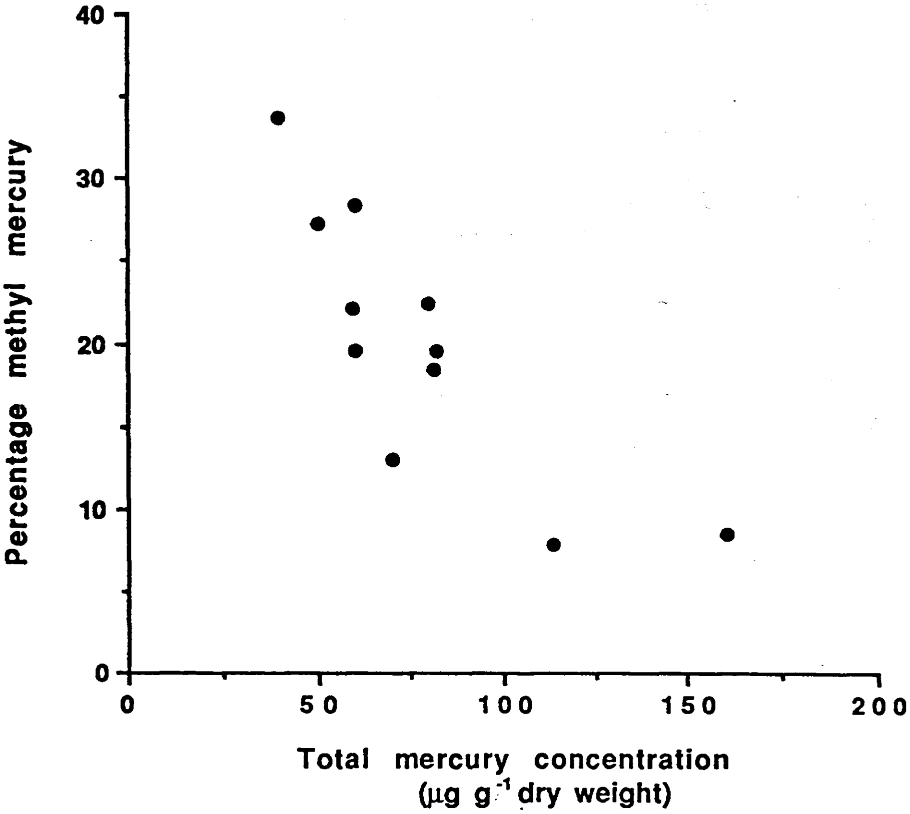

Fig. 4.1 Percentage methyl mercury plotted against total mercury in Atlantic petrel Pterodroma incerta liver samples (r_s = -0.809, P < 0.01)

TABLE 4.1: Total and organic mercury levels ($\mu g\ g^{-1}$ dry weight) in liver tissues of seabirds from Gough Island.

Species	Number Sampled	Total Mercury Mean	Med.	S.D.	Organic Mercury Mean	Med.	S.D.
		(Range)			(Range)		
Rockhopper penguin *Eudyptes crestatus*	12	4.9 (2.2- 7.8)	4.6	1.9	1.9 (0.7- 3.8)	1.8	0.8
Wandering albatross *Diomedea exulans*	2	1343.0 (907.5-1778.5)	---	---	31.3 (30.6-31.9)	---	---
Yellow-nosed albatross *Diomedea chlororhynchos*	9	21.9 (9.4- 63.2)	16.8	16.4	3.8 (1.2- 6.7)	3.5	1.6
Sooty albatross *Phoebetria fusca*	8	472.6 (265.6- 771.3)	393.8	188.8	13.2 (8.3-21.6)	11.7	4.9
Atlantic petrel *Pterodroma incerta*	11	77.8 (39.9- 160.3)	69.6	33.7	13.6 (9.0-18.0)	13.6	2.9
Kerguelen petrel *Pterodroma brevirostris*	7	11.8 (6.7- 17.3)	13.0	4.0	7.9 (4.0-10.7)	8.5	2.4
Soft-plumaged petrel *Pterodroma mollis*	8	50.8 (17.8- 117.9)	39.7	37.5	9.4 (7.1-14.1)	8.1	2.9
Broad-billed prion *Pachyptila vittata*	10	0.8 (0.5- 1.0)	0.9	0.2	0.8 (0.4- 1.1)	0.8	0.2
Great shearwater *Puffinus gravis*	11	4.5 (2.0- 11.9)	3.9	2.6	2.1 (0.6- 3.8)	2.1	0.8
Little shearwater *Puffinus assimilis*	9	3.1 (2.7- 4.1)	3.1	0.4	2.8 (2.1- 3.7)	2.7	0.5
Common diving petrel *Pelecanoides urinatrix*	12	1.1 (0.7- 1.7)	1.1	0.3	1.0 (0.5- 1.3)	1.0	0.3
Tristan skua *Catharacta skua hamiltoni*	13	23.0 (4.8- 57.5)	18.3	17.4	11.5 (3.2-25.2)	10.9	6.9

(Table 4.2). There was a significant negative correlation between methyl mercury expressed as percentage of the total mercury level and total mercury concentration in 5 of the 11 species (Table 4.3; Figure 4.1); (excluding wandering albatrosses due to the small sample size). A significant

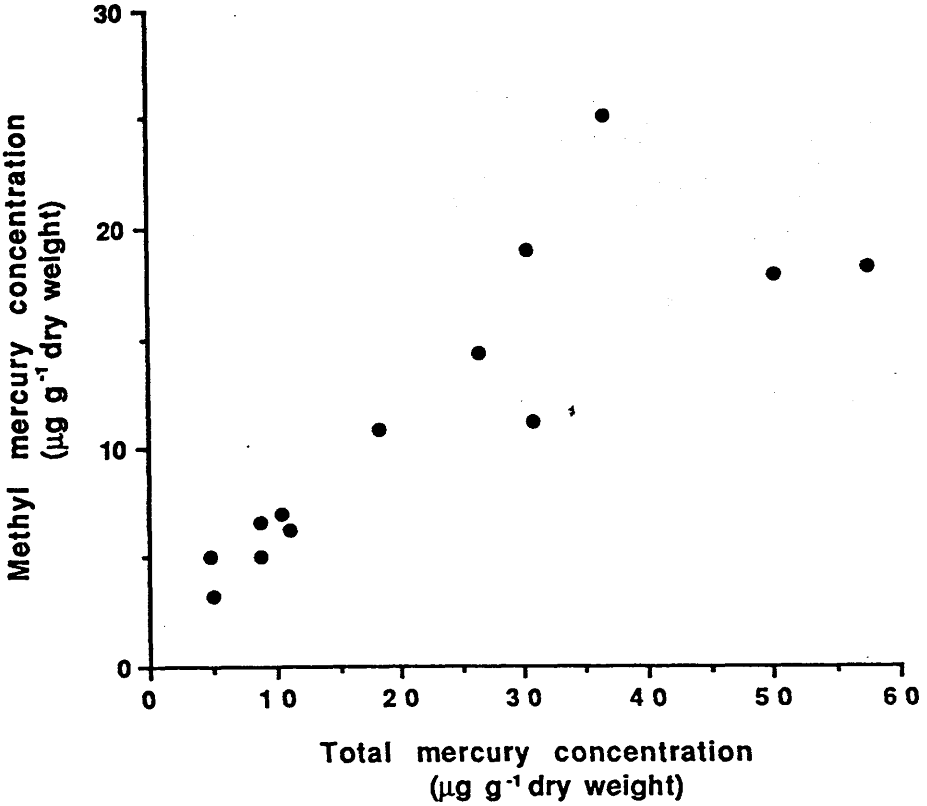

Fig. 4.2 Methyl mercury plotted against total mercury in Tristan skua Catharacta skua hamiltoni liver samples ($r_s = 0.896$, $P < 0.001$)

TABLE 4.2: Organic mercury levels expressed as a percentage of the total mercury level. (Sample sizes as for Table 4.1).

Species	Mean	S.D.	Median
Rockhopper penguin	40.5	13.2	43.4
Wandering albatross	2.6	----	----
Yellow-nosed albatross	23.2	15.7	20.7
Sooty albatross	3.2	1.7	2.9
Atlantic petrel	20.1	8.1	19.6
Kerguelen petrel	69.5	17.5	64.9
Soft-plumaged petrel	25.2	11.9	26.9
Broad-billed prion	91.1	23.4	97.7
Great shearwater	54.9	26.7	56.9
Little shearwater	92.6	20.2	89.7
Common diving petrel	89.5	22.9	89.2
Tristan skua	59.3	19.2	59.4

positive correlation was found between methyl mercury concentration and total mercury concentration in 2 of the 11 species for which sample sizes were sufficiently large (Table 4.3; Figure 4.2). When all 12 species means were considered, a significant negative correlation (r_s= -0.888, P<0.001) was found between mean percentage methyl mercury and mean total mercury (Figure 4.3).

TABLE 4.3: Spearman Rank Order Correlation Coefficients (r_s) between :-

i. organic mercury (expressed as a percentage of total mercury) and total mercury concentration, and

ii. absolute organic mercury concentration and total mercury concentration, in liver tissue of seabirds from Gough Island. Level of significance in parentheses.

Species	(i) % organic mercury vs. total mercury	(ii) Organic mercury vs. total mercury
Rockhopper penguin	-0.364 (n.s.)	0.558 (n.s.)
Yellow-nosed albatross	-0.667 (*)	0.000 (n.s.)
Sooty albatross	-0.690 (n.s.[1])	-0.024 (n.s.)
Atlantic petrel	-0.809 (**)	0.064 (n.s.)
Kerguelen petrel	-0.464 (n.s.)	0.571 (n.s.)
Soft-plumaged petrel	-0.952 (***)	0.738 (*)
Broad-billed prion	-0.236 (n.s.)	0.312 (n.s.)
Great shearwater	-0.645 (*)	-0.089 (n.s.)
Little shearwater	-0.267 (n.s.)	0.033 (n.s.)
Common diving petrel	-0.316 (n.s.)	0.533 (n.s.)
Tristan skua	-0.654 (*)	0.896 (***)

* $P<0.05$; ** $P<0.01$; *** $P<0.001$; n.s. Not Significant.

n.s.[1]; would probably have been significant but for small sample size.

4.4 DISCUSSION

The relatively low proportion of methyl mercury, relative to total mercury, measured in particular tissues of some marine mammals has been taken as evidence of a detoxification process

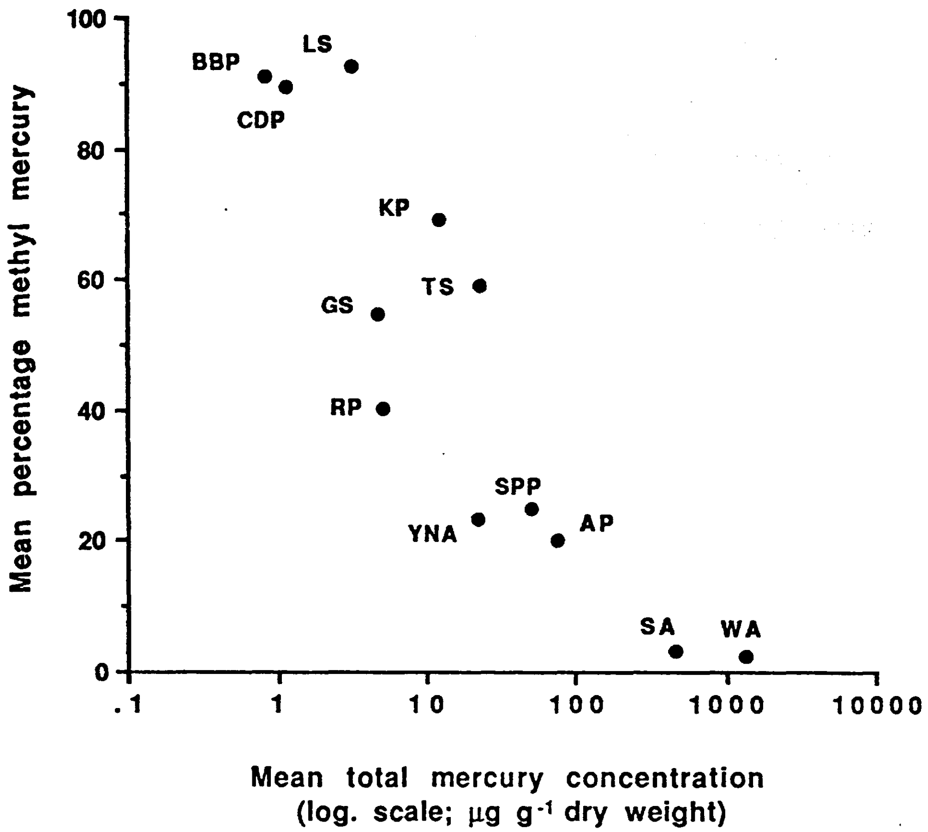

Fig. 4.3 Mean percentage methyl mercury plotted against mean total mercury on a log. scale for all twelve species studied (r_s= -0.888, $P < 0.001$)

Key: RP, rockhopper penguin; WA, wandering albatross; YNA, yellow-nosed albatross; SA, sooty albatross; AP, Atlantic petrel; KP, Kerguelen petrel; SPP, soft-plumaged petrel; BBP, broad-billed prion; GS, great shearwater; LS, little shearwater; CDP, common diving petrel; TS, Tristan skua.

whereby dietary methyl mercury is demethylated into an inorganic storage form of mercury (Buhler et al., 1975; Kari & Kauranen, 1978; Reijnders, 1980; Smith & Armstrong, 1978). This conclusion has been arrived at largely through consideration of the corresponding proportion of methyl mercury in the prey of such predators. In prey, the methyl mercury level constitutes the vast majority of the total mercury level. However, dietary methyl mercury is retained to a greater extent when compared to dietary inorganic mercury, at least in fish (Pentreath, 1976), and this could result in an increase in the proportion of methyl mercury up marine food chains even in the absence of demethylation.

Although the relationship between methyl and inorganic mercury has been investigated less in birds than in marine mammals, several studies have noted a trend of decreasing methyl mercury in percentage terms with increasing total mercury level. There have been various explanations for such findings. In a study of four species of aquatic birds, Fimreite (1974) found that the methyl mercury level, expressed as a percentage of the total mercury concentration, in liver tissues was lowest in goosanders *Mergus merganser* (mean 12.3%; range 5-17%) and highest in pintails *Anas acuta* (mean 51.9%; range 17-70%). The interspecific differences in the proportion of methyl mercury found in these samples were suggested as being the result, at least in part, of gut microfloral activity. Furthermore, the lowest level of methyl mercury, in percentage terms, in goossanders was found in association with the highest mean total mercury concentration.

A similar trend was reported by Norheim & Froslie (1978) in a study of birds of prey from Norway. Of five species, white-tailed eagles _Haliaeetus albicilla_ exhibited the lowest liver methyl mercury levels when expressed as a percentage of the total mercury concentration (range 15-69%) whilst goshawks _Accipiter gentilis_ were found to have the highest percentage of methyl mercury in liver tissue (range 60-95%). Within the sample of white-tailed eagles, those birds with relatively high total mercury levels were found to have low methyl mercury levels expressed in percentage terms. The degree of methylation was reported as being mainly dependent on the total mercury level (Norheim & Froslie, 1978).

Norheim _et al._ (1982) found that mercury levels in liver tissues of a sample of south polar skuas from Dronning Maud land showed a significant negative correlation between percentage methyl mercury and total mercury. Such a relationship has been noted in some marine mammals (Born _et al._, 1981; Falconer _et al._, 1983; Gaskin _et al._, 1972; 1979; Smith & Armstrong, 1978) and is confirmed in five of the species in this study (Table 4.3). Reijnders (1980) reported a decrease in the percentage methyl mercury level with increasing age in liver and brain tissues of a sample of harbour seals _Phoca vitulina_ from the Wadden Sea, and suggested that the demthylation of methyl mercury varied with age.

Whether these trends actually represent demethylation, however, is difficult to say. The data and trends presented in this paper and those cited above could be explained in a number of ways. It could be that the total mercury concentration influences the extent of demethylation, as suggested by Norheim & Froslie (1978), but it is worthwhile considering other factors. Although dietary intake of mercury will influence observed liver mercury concentrations, Muirhead & Furness (1988) found no clear pattern relating mercury levels to diet for the species currently studied. Alternatively, the excretion and biotransformation of mercury could be important in determining observed mercury levels.

Birds are able to diminish their mercury body burdens by placing mercury into growing feathers (for example, Honda et al., 1986). Furthermore, mercury lost from the body in this way is almost entirely organic (methyl) mercury (Thompson & Furness, in press; Chapter 7.1). This eliminatory pathway has been shown to be an important route for the excretion of mercury (Braune & Gaskin, 1987a; 1987b). Therefore, those species with relatively slow moult cycles will be restricted in the amount of methyl mercury they can eliminate in this way. Conversion of a proportion of methyl mercury into an inorganic storage form could be a response to this problem; remaining methyl mercury would be eliminated via growing feathers whilst demethylated mercury would accumulate with age. Conversely, those species with relatively fast moult cycles are not so constrained and demethylation of methyl mercury would not be so important. This trend would be further amplified by the differing life-spans of the seabirds studied. In general, the accumulation of mercury is potentially greater in longer-lived species. Hence, one would predict that a trend of decreasing percentage organic mercury with increasing total mercury concentration, resulting from demethylation, would be observed in those species which have slow moult cycles and which tend to be long-lived. Albatrosses tend to exhibit slow moult cycles (for example, Harris, 1973), completely replacing their feathers over a period of years. The yellow-nosed albatross Diomedea chlororhynchos, for example, has been shown to replace only about 40% of its flight feathers annually (Furness, 1988). Generally, gadfly petrels undergo a partial annual feather moult whilst shearwaters exhibit a complete annual moult (Stresemann & Stresemann, 1966). The life-spans of the study species are not well known; adult survival of wandering albatrosses and sooty albatrosses *Phoebetria fusca* has been determined as 94.4% and 96.3%, respectively (Weimerskirch & Jouventin, 1987; Jouventin & Weimerskirch, 1984) which are undoubtedly higher survival rates than those of any other seabirds on Gough Island. Of the species studied, the albatrosses, and to a lesser extent the gadfly petrels, have the highest concentrations of inorganic mercury, as predicted for relatively slow-moulting and long-lived species.

Although this could be suggested as an explanation of such observations, the life-long accumulation of small quantities of dietary inorganic mercury, coupled with the excretion of methyl mercury, would also account for the observed results. Similarly, the accumulation of inorganic mercury in this way would tend to be more pronounced in those species which are generally long-lived.

One cannot distinguish between these two possible explanations from the present results. In both cases, the accumulation of inorganic mercury to the high levels observed in some of the species in this study (over 1000 µg g^{-1} dry weight in wandering albatrosses; Table 4.1) raises the question of toxic effects, although all birds collected appeared to be healthy and in good condition (Muirhead & Furness, 1988). In a study of red-tailed hawks *Buteo jamaicensis* fed dietary methyl mercury, Fimreite & Karstad (1971) noted pronounced toxic effects and death in birds with liver methyl mercury concentrations of about 20 µg g^{-1} (wet or dry weight not specified). In the present study, only four individuals (3.6%) exhibited methyl mercury levels, on a dry weight basis, in excess of this concentration, although seabirds are likely to be exposed to mercury to a greater extent than terrestrial avian predators. In a study of harp seals Phoca groenlandica, Ronald et al. (1977) found that considerably higher methyl mercury levels could be tolerated by the animals. This may reflect the greater exposure to methyl mercury such animals are likely to receive in the marine environment. In species of marine predator which tend to concentrate high levels of mercury, the accumulation of inorganic mercury may be a toxically less demanding alternative to the accumulation of methyl mercury. Inorganic mercury may, therefore, parallel the age-accumulation of cadmium, as noted in liver and kidney tissues of a sample of great skuas Catharacta skua by Furness & Hutton (1979).

As noted by Muirhead & Furness (1988), the measured mercury levels in these seabirds are likely to be natural. It would seem possible, therefore, that such pelagic seabirds are in a dynamic equilibrium with the mercury they ingest and the amount of mercury they are able to excrete and/or possibly demethylate and accumulate, and that this is the result of exposure to mercury over a long period of time in evolutionary terms. The significant positive correlation between methyl mercury levels in absolute terms and total mercury levels, noted in soft-plumaged petrels Pterodroma mollis and Tristan skuas Catharacta skua hamiltoni (Table 4.3; Figure 4.2), are difficult to interpret in this sense, since they may indicate that these species are unable to deal with all the mercury they ingest. Controlled feeding experiments with species which encounter mercury at relatively high levels, using inorganic and methyl mercury and labelled mercury isotopes, would be useful in determining whether demethylation takes place in seabirds and what factors influence any such transformation of mercury.

4.5 REFERENCES

Anderlini, V.C., Connors, P.G., Riseborough, R.W. & Martin, J.H. (1972). Concentrations of heavy metals in some Antarctic and North American seabirds. Proc. Symp. Conservation Problems Antarctica pp. 49-62. Blacksburg Virginia Polytecnic Institute and State University.

Bakir, F., Damluji, S.F., Amin-Zaki, L., Murtadha, M., Khalidi, A., Al-Rawi, N.Y., Tikriti, S., Dhahir, H.I., Clarkson, T.W., Smith, J.C. & Doherty, R.A. (1973). Methylmercury poisoning in Iraq. Science 181, 230-241.

Bebbington, G.N., Mackay, N.J., Chvojka, R., Williams, R.J., Dunn, A. & Auty, E.H. (1977). Heavy metals, selenium and arsenic in nine species of Australian commercial fish. Aust. J. Mar. Freshw. Res. 28, 277-286.

Borg, K., Wanntorp, H., Erne, K. & Hanko, E. (1969). Alkyl mercury poisoning in Swedish wildlife. Viltrevy 6, 301-379.

Born, E.W., Kraul, I. & Kristensen, T. (1981). Mercury, DDT and PCB in the Atlantic walrus (Odobenus rosmarus rosmarus) from the Thule District, North Greenland. Arctic 34, 255-260.

Braune, B.M. & Gaskin, D.E. (1987a). A mercury budget for the Bonaparte's gull during autumn moult. Ornis Scand. 18, 244-250.

Braune, B.M. & Gaskin, D.E. (1987b). Mercury levels in Bonaparte's gulls (Larus philadelphia) during autumn molt in the Quoddy region, New Brunswick, Canada. Arch. Environ. Contam. Toxicol. 16, 539-549.

Bryan, G.W. (1979). Bioaccumulation of marine pollutants. Phil. Trans. R. Soc. Lond. B 286, 483-505.

Bryan, G.W. (1984). Pollution due to heavy metals and their compounds. In, Marine Ecology, Kinne, O. (ed.), pp. 1289-1431, Wiley, Chichester.

Buhler, D.R., Claeys, R.R. & Mate, B.R. (1975). Heavy metal and chlorinated hydrocarbon residues in California sea lions (Zalophus californianus californianus). J. Fish. Res. Bd. Can. 32, 2391-2397.

Chvojka, R. (1988). Mercury and selenium in axial white muscle of yellowtail kingfish from Sydney, Australia. Mar. Pollut. Bull. 19, 210-213.

Delbeke, K., Joiris, C. & Decadt, G. (1984). Mercury contamination of the Belgian avifauna 1970-1981. Environ. Pollut. (B) 7, 205-221.

Falconer, C.R., Davies, I.M. & Topping, G. (1983). Trace metals in the common porpoise Phocoena phocoena. Mar. Environ. Res. 8, 119-127.

Fimreite, N. (1974). Mercury contamination of aquatic birds in northwestern Ontario. J. Wildl. Manage. 38, 120-131.

Fimreite, N. & Karstad, L. (1971). Effects of dietary methyl mercury on Red-tailed hawks. J. Wildl. Manage. 35, 293-300.

Freeman, H.C. & Horne, D.A. (1973). Mercury in Canadian seals. Bull. Environ. Contam. Toxicol. 10, 172-180.

Furness, R.W. (1988). Influences of status and recent breeding experience on the moult strategy of the yellow-nosed albatross Diomedea chlororhynchos. J. Zool., Lond. 215, 719-727.

Furness, R.W. & Hutton, M. (1979). Pollutant levels in the great skua Catharacta skua. Environ. Pollut. 19, 261-268.

Furness, R.W., Muirhead, S.J. & Woodburn, M. (1986). Using bird feathers to measure mercury in the environment: relationships between mercury content and moult. Mar. Pollut. Bull. 17, 27-30.

Gaskin, D.E., Ishida, K. & Frank, R. (1972). Mercury in harbour porpoises (Phocoena phocoena) from the Bay of Fundy region. J. Fish. Res. Bd. Can. 29, 1644-1646.

Gaskin, D.E., Stonefield, K.I., Suda, P. & Frank, R. (1979). Changes in mercury levels in harbour porpoises from the Bay of Fundy, Canada and adjacent waters during 1969-1977. Arch. Environ. Contam. Toxicol. 8, 733-762.

Harris, M.P. (1973). The biology of the waved albatross Diomedea irrorata of Hood Island, Galapogos. Ibis 115, 483-510.

Holt, G., Froslie, A. & Norheim, G. (1979). Mercury, DDE and PCB in the avian fauna in Norway 1965-1976. Acta Vet. Scand. Suppl. 70, 1-28.

Honda, K., Nasu, T. & Tatsukawa, R. (1986). Seasonal changes in mercury accumulation in the black-eared kite, Milvus migrans lineatus. Environ. Pollut. (A) 42, 325-334.

Itano, K., Kawai, S., Miyazaki, N., Tatsukawa, R. & Fujiyama, T. (1984). Mercury and selenium levels in striped dolphins caught off the Pacific coast of Japan. Agric. Biol. Chem. 48, 1109-1116.

Johnels, A.G. & Westermark, T. (1969). Mercury contamination of the environment in Sweden. In, Chemical Fallout. Current Research on Persistent Pesticides, Millar, M.W. & Berg, G.G. (eds.), pp. 221-239, Thomas, Springfield.

Jouventin, P. & Weimerskirch, H. (1984). L'albatros fuligineux a dos sombre Phoebetria fusca, example de strategie d'adaptation extreme a la vie pelagique. Terre Vie 39, 401-429.

Kai, N., Veda, T., Takeda, M. & Kataoka, A. (1983). On mercury and selenium in tuna fish tissues-VIII The levels of mercury and selenium in albacore from the Indian Ocean. J. Shimonoseki Univ. Fish. 31, 69-73.

Kari, T. & Kauranen, P. (1978). Mercury and selenium contents of seals from fresh and brackish waters in Finland. *Bull. Environ. Contam. Toxicol.* 19, 273-280.

Kurland, L.T., Faro, S.N. & Seidler, H. (1960). Minamata disease. The outbreak of a neurological disorder in Minamata, Japan and its relationship to the ingestion of sea food contaminated by mercuric compounds. *Wld. Neurol.* 1, 370-395.

Lantzy, R.J. & Mackenzie, F.T. (1979). Atmospheric trace metals: global cycles and assessment of man's impact. *Geochim. Cosmo chim. Acta* 43, 511-525.

Lyle, J.M. (1986). Mercury and selenium concentrations in sharks from Northern Australian waters. *Aust. J. Mar. Freshw. Res.* 37, 309-321.

Mackay, N.J., Kazacos, M.N., Williams, R.J. & Leedow, M.I. (1975). Selenium and heavy metals in black marlin. *Mar. Pollut. Bull.* 6, 57-61.

McKie, J.C., Davies, I.M. & Topping, G. (1980). Heavy metals in grey seals (*Halichoerus grypus*) from the east coast of Scotland. *Int. Counc. Explor. Sea (ICES)* 1980/E:41.

Muirhead, S.J. & Furness, R.W. (1988). Heavy metal concentrations in the tissues of seabirds from Gough Island, South Atlantic Ocean. *Mar. Pollut. Bull.* 19, 278-283.

Norheim, G. & Froslie, A. (1978). The degree of methylation and organ distribution of mercury in some birds of prey in Norway. *Acta Pharmacol. et Toxicol.* 43, 196-204.

Norheim, G., Somme, L. & Holt, G. (1982). Mercury and persistent chlorinated hydrocarbons in Antarctic birds from Bouvetoya and Dronning Maud Land. *Environ. Pollut. (A)* 28, 233-240.

Osborn, D., Harris, M.P. & Nicholson, J.K. (1979). Comparative tissue distribution of mercury, cadmium and zinc in three species of pelagic seabirds. *Comp. Biochem. Physiol.* 64C, 61-67.

Pentreath, R.J. (1976). The accumulation of mercury from food by the plaice, *Pleuronectes platessa*. *J. Exp. Mar. Biol. Ecol.* 25, 51-65.

Reijnders, P.J.H. (1980). Organochlorine and heavy metal residues in harbour seals from the Wadden Sea and their possible effects on reproduction. *Neth. J. Sea Res.* 14, 30-65.

Ronald, K., Frank, R.J. & Dougan, J. (1984). Pollutants in harp seals (*Phoca groenlandica*) II. Heavy metals and selenium. *Sci. Tot. Environ.* 38, 153-166.

Ronald, K., Tessaro, S.V., Uthe, J.F., Freeman, H.C. & Frank, R. (1977). Methylmercury poisoning in the harp seal

(Pagophilus groenlandicus). Sci. Tot. Environ. 8, 1-11.

Smith, T.G. & Armstrong, F.A.J. (1978). Mercury and selenium in ringed and bearded seal tissues from Arctic Canada. Arctic 31, 75-84.

Stresemann, E. & Stresemann, V. (1966). Die Mauser der Voegel. J. Orn. Berl. 107.

Thompson, D.R. & Furness, R.W. (in press). A comparison of total and organic mercury levels in seabird feathers. Mar. Pollut. Bull.

Uthe, J.F., Solomon, J. & Grift, B. (1972). Rapid semimicro method for the determination of methyl mercury in fish tissue. J. Assoc. Off. Anal. Chem. 55, 583-589.

Weimerskirch, H. & Jouventin, P. (1987). Population dynamics of the wandering albatross, Diomedea exulans, of the Crozet Islands: causes and consequences of the population decline. Oikos 49, 315-322.

CHAPTER 5

Mercury levels in feathers and tissues of great skuas of known age

5.1 INTRODUCTION

Seabirds have been widely used as monitors of pollutants in the marine environment (Walsh, in press). Mercury has featured prominently in this respect, in part due to the fact that feathers act as relatively stable sites of deposition for this metal (Appelquist et al., 1984; Crewther et al., 1965). Feathers can easily be obtained and analysed to give an indication of the exposure of the birds to mercury (for example, Anderlini et al., 1972; Doi et al., 1984; Gochfeld, 1980; Honda et al., 1986c; Hutton, 1981; Osborn et al., 1979).

By taking into account the effects of moult and the feather type chosen for analysis (Furness et al., 1986) geographical and inter-species differences in mercury burdens can be investigated. However, it is not clear how mercury levels measured in feathers relate to mercury concentrations in the internal tissues, and, furthermore, how mercury levels in both feathers and internal tissues relate to the age of the bird.

Total mercury levels have been found to increase with age in liver and kidney tissues of marine mammals (for example, Arima & Nagakura, 1979; Born et al., 1981; Drescher et al., 1977; Gaskin et al., 1979; Honda et al., 1983; Reijnders, 1980; Ronald et al., 1984). Smith & Armstrong (1978) noted a significant and postive correlation between methyl mercury concentration and age in liver tissue of a sample of ringed seals *Phoca hispida*. Similarly, numerous studies of marine fish have reported positive correlations between mercury concentration and age and/or size (weight or length), particularly in large, pelagic species which tend to exhibit relatively high mercury levels (for example, Caputi et al., 1979; Greig & Krzynonek, 1979; Kai et al., 1983; Lyle, 1984;

Mackay *et al.*, 1975; Shultz & Ito, 1979).

Unlike other marine vertebrates for which length, weight or otolith characteristics (fish) or tooth structure or, to a lesser extent, weight or size (seals and odontocete whales) can be related to age, birds can only be accurately aged by means of a unique and durable indentification marker (for example, the individually numbered and lettered metal leg rings used by the British Trust for Ornithology). There are relatively few bird populations with a large proportion of individuals marked in this way, and it is hardly surprising, therefore, that investigations into age-related changes in mercury concentrations in birds have been relatively few in number.

Several studies have demonstrated an increase in mercury level between chicks, juveniles and adults of various species (Hoffman & Curnow, 1979; Honda *et al.*, 1985; 1986a; Lindberg & Odsjo, 1983) but have been unable to study this trend in adults of varying age, because individually marked birds of known age were not available.

Furness & Hutton (1979) found very weak positive correlations between total mercury concentrations and age in liver tissues, kidney tissues and primary feathers of a small sample of ringed adult great skuas *Catharacta skua* whilst Hutton (1981) found no age-related mercury accumulation trends in herring gulls *Larus argentatus* and great skuas of known age and in oystercatchers *Haematopus ostralegus* aged on plumage characteristics. Similarly, Nicholson (1981) found no significant correlations between age and mercury concentration in internal tissues in a sample of herring gulls. More recently, Furness *et al.* (in press) have demonstrated that there was no significant relationship between body feather mercury levels and age in a sample of adult red-billed gulls *Larus novaehollandiae scopulinus*, and noted that this pattern was in agreement with observations of internal tissue mercury level distributions described in other seabirds (Thompson & Furness, 1989; in press; Chapters 4 & 7.1).

A further problem in obtaining feathers and internal tissues from birds of known age is that marked birds within a population are often the subject of other, long-term studies and acquiring samples for analysis often involves an unacceptable level of disturbance. Compounding factors such as the need for internal tissues of healthy birds to be sampled, since unrepresentative mercury levels tend to be found in birds 'found dead' or 'exhausted' due to tissue wastage, only limit the scope for studies of this kind still further.

In this chapter total, inorganic and methyl mercury data are presented for great skuas of known age from Foula, Shetland. Changes in mercury concentration with age are assessed and possible factors influencing the observed trends are discussed.

5.2 MATERIALS AND METHODS

5.2.1 Sample collection, storage and preparation

The great skua population at Foula, Shetland has been extensively studied and a large proportion (ca. one third) of adult birds on Foula are ringed and of known age (Furness, 1987). All samples were obtained from birds during the breeding season. Feather samples were obtained either from adult birds trapped at the nest during incubation, or trapped at club sites, during 1988. In addition, feathers were obtained from ringed birds found dead on the island in 1986, 1987 and 1988, and from ringed birds shot in 1980, 1983 and 1988. Great skua chick feather samples, together with wing length measurements were obtained from both live and dead chicks in 1987. Wing lengths were converted to age in days using data presented in Furness (1977). For adults and live chicks, four to six large body feathers from the back were taken, but often all that remained of chicks found dead were the wings; in such cases wing coverts were sampled, since it is highly unlikely that mercury levels would differ markedly between these two feather types (Furness et al., 1986). All feather samples were stored in mercury-free polythene bags. Prior to analysis, feathers were dried at ambient laboratory temperature (ca. 22°C). Internal tissues (liver, kidney and muscle) were obtained from 25 birds shot in 1988 and one bird shot in 1980. Further tissue samples, though not of all three types for any given bird, were obtained from birds shot in 1980 and 1983. Birds were shot by crofters under licence from the Nature Conservancy Council and immediately deep frozen at about -20°C prior to transportation to Glasgow where they were maintained deep frozen. After thawing, samples of liver, kidney and muscle tissue were dissected out, oven dried at 50°C to constant weight and stored in air-tight glass vials prior to analysis.

5.2.2 Analysis of mercury levels

Total and methyl mercury levels were determined as described in Chapter 3. All feather mercury concentrations are presented as $\mu g\ g^{-1}$ fresh weight of feather; liver, kidney and muscle mercury concentrations are presented as $\mu g\ g^{-1}$ dry weight of tissue (Chapter 3). Mercury level distribution patterns were found to deviate significantly from a Gaussian distribution in feather and muscle tissues, and deviations from Gaussian were close to statistical significance in other tissues, (Kolmogorov-Smirnov One Sample tests; Table 5.1); all subsequent statistical analyses were performed using non-parametric procedures. Differences in mercury levels between and within tissues were tested by using non-parametric Kruskal-Wallis 1-Way ANOVA and Mann-Whitney U-tests; trends in mercury levels between various tissues and age were assessed by calculating Spearman Rank Order Correlation Coefficients (r_s). The word 'significant' has been used in the statistical context only, indicating a probability of chance occurrence of less than 5%.

5.3 RESULTS

No significant differences were found in mercury levels between 'breeding' (>5 years old) and 'non-breeding' (3-5 years old) adults. Total, inorganic and methyl mercury concentrations, together with methyl mercury expressed as a percentage of the total mercury level, in feathers, liver, kidney and muscle tissues of all adult birds combined are presented in Table 5.2. Total mercury levels decreased in the order liver tissue > kidney tissue > feathers > muscle tissue, this trend being significant (Kruskal-Wallis 1-Way ANOVA, $P<0.0001$). A similar trend was found for methyl mercury with liver levels > kidney levels > muscle levels (Kruskal-Wallis 1-Way ANOVA, $P<0.0001$); feather total mercury levels can be considered as methyl mercury levels (see Chapter 7.1) and as such were higher than in all internal tissues (Table 5.2).

Muscle total and methyl mercury levels were not significantly different (Wilcoxon Sign-Ranks Pairs Test, $P=0.983$), indicating that virtually all the mercury in this tissue is in the methyl form (Table 5.2). Subsequent considerations of muscle mercury concentrations involved total mercury levels only.

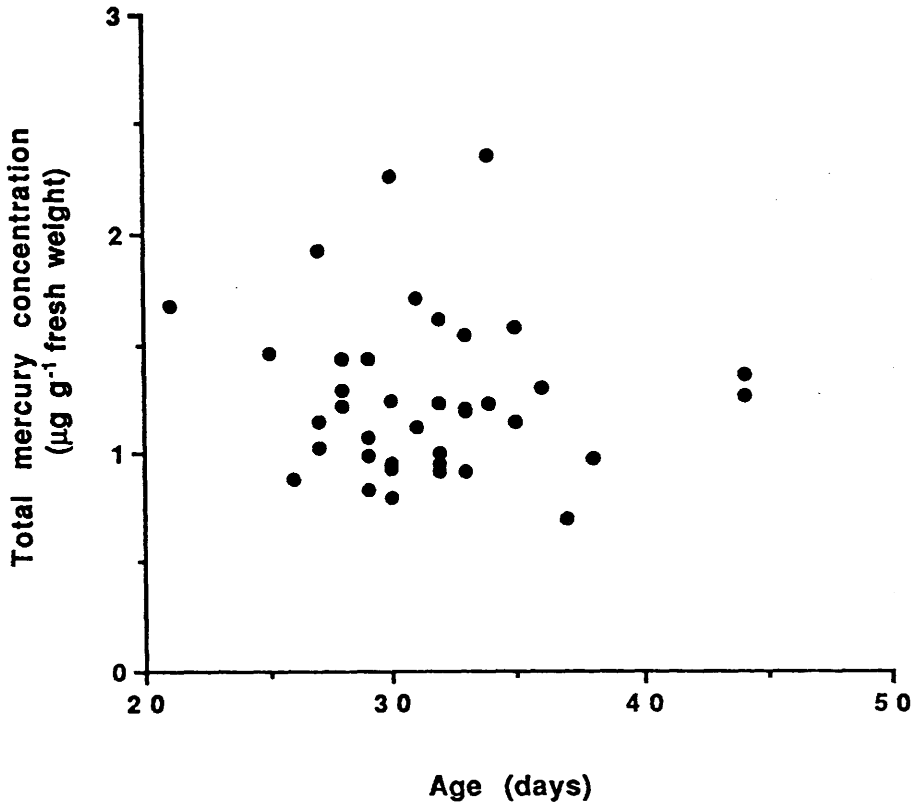

Fig. 5.1 Feather total mercury concentration plotted against age in great skua <u>Catharacta skua</u> chicks (r_s= -0.01, P = 0.94)

TABLE 5.1: Tissue mercury level distributions; tested against Normal distribution using Kolmogorov-Smirnov one sample 'Goodness of Fit' test.

Tissue		Number sampled	K-S Z	P
Feather	All Adults	139	1.945	0.001
	Chicks	40	0.925	0.359
Liver	Total	30	1.035	0.234
	Methyl	29	0.726	0.668
	Inorganic	29	1.069	0.203
Kidney	Total	33	0.909	0.381
	Methyl	33	0.796	0.551
	Inorganic	33	0.717	0.683
Muscle	Total	51	1.694	0.006
	Methyl	51	1.304	0.067

The median body feather mercury level in chicks was found to be 1.2 µg g^{-1} fresh weight (n=40, mean= 1.3 µg g^{-1} fresh weight, s.d.= 0.4, Coefficient of Variation= 30, range= 0.70-2.36 µg g^{-1} fresh weight) which represented 21% of the median body feather mercury concentration of adult birds (Table 5.2). There was no significant trend between chick feather mercury concentration and age (r_s= -0.01; P=0.94; n=40; Figure 5.1).

Methyl mercury levels generally showed less variation than inorganic and total mercury levels (Table 5.2), and when expressed as a percentage of the total mercury level in liver and kidney tissues represented, on average, 52.7% and 51.8% of

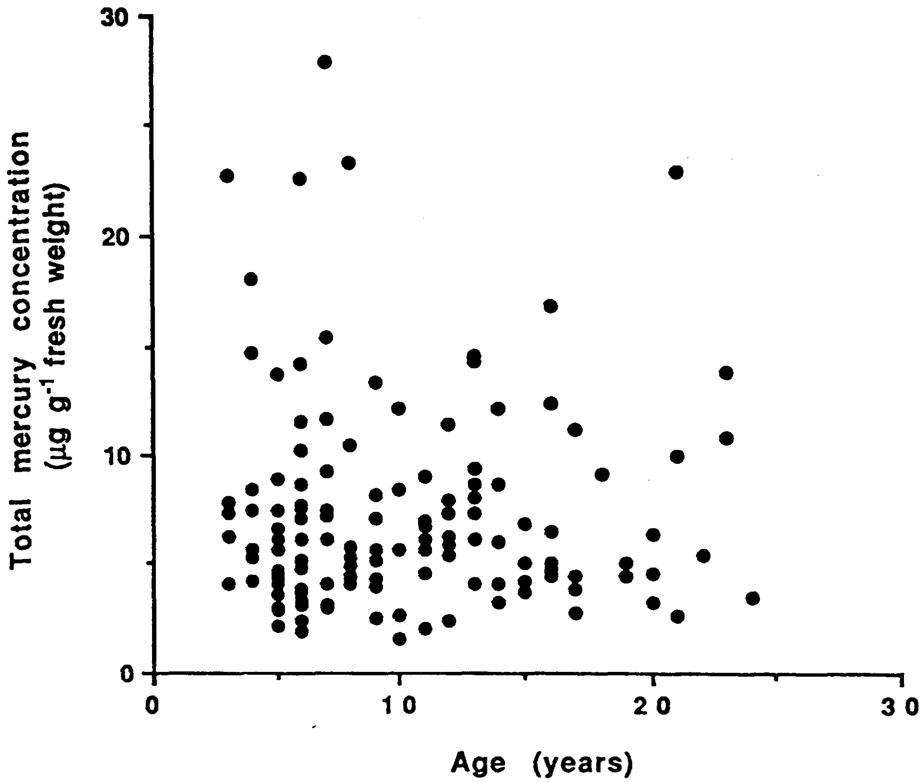

Fig. 5.2 Feather total mercury concentration plotted against age in adult great skuas Catharacta skua (r_s = -0.00, P = 0.96)

TABLE 5.2: Mercury levels ($\mu g\ g^{-1}$ dry weight for soft tissues; $\mu g\ g^{-1}$ fresh weight for feathers; Tot= Total mercury, Inorg= Inorganic mercury, Me= Methyl mercury, %= Methyl mercury expressed as a percentage of the total mercury level) in tissues of all great skuas (adults and juveniles combined).

	Feather	Liver				Kidney				Muscle	
		Tot	Inorg	Me	%	Tot	Inorg	Me	%	Tot	Me
Mean	7.2	11.6	6.2	5.6	52.7	9.7	5.0	4.7	51.8	2.3	2.5
S.D.	4.7	6.2	5.3	2.1	18.4	3.7	3.2	1.8	19.4	1.1	1.1
S.E.	0.4	1.1	1.0	0.4	3.4	0.7	0.6	0.3	3.4	0.2	0.2
Median	5.6	9.8	4.5	5.8	56.6	8.9	4.4	4.7	57.6	2.0	2.4
Max.	28.0	33.4	22.3	11.1	84.3	21.7	13.6	10.5	97.8	6.5	7.2
Min.	1.6	4.5	1.2	1.8	16.0	4.6	0.2	1.9	21.7	0.8	0.6
n	139	30	29	29	29	33	33	33	33	51	51
C.V.	65	53	86	38	35	39	65	38	37	48	44

Key: S.D.= Standard Deviation; S.E.= Standard Error; Max.= Maximum value; Min= Minimum value; n= Number analysed; C.V.= Coefficient of Variation (100 X S.D./Mean).

the total mercury level, respectively (Table 5.2).

Spearman Rank Order Correlation Coefficients (r_s) for comparisons between mercury levels in the various tissues and with age are presented in Table 5.3. Trends for inorganic mercury concentrations have been omitted since they were found to closely match those for total mercury levels. Adult feather mercury levels showed no significant trend with age (Table 5.3; Figure 5.2), but surprisingly, total liver mercury

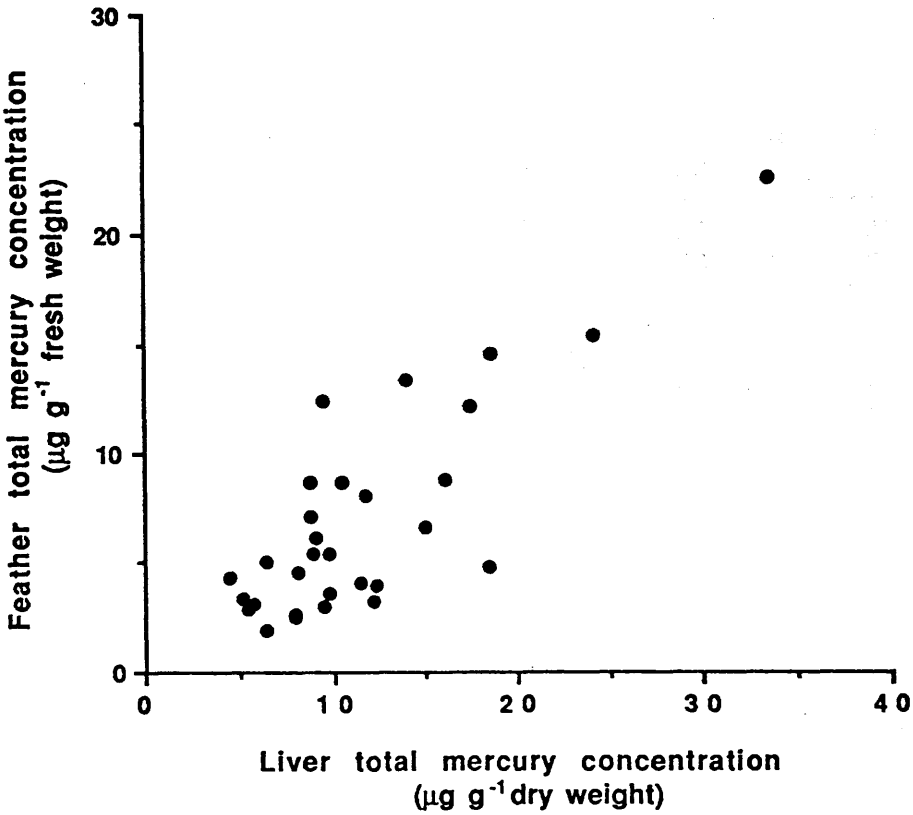

Fig. 5.3 Feather total mercury concentration plotted against total liver concentration in adult great skuas *Catharacta skua* (r_s = 0.66, P = < 0.001)

TABLE 5.3: Spearman Rank Order Correlation Coefficient (r_s) matrix for adult great skuas.

	AGE	F'TH	LT	LM	L%	KT	KM	K%	MuT
AGE	XXX	-.00 NS (139)	-.48 ** (30)	-.27 NS (29)	.40 * (29)	-.17 NS (33)	-.21 NS (33)	.00 NS (33)	-.10 NS (51)
F'TH		XXX	.66 *** (30)	.21 NS (29)	-.46 * (29)	.56 ** (29)	.20 NS (29)	-.24 NS (29)	.31 * (46)
LT			XXX	.54 ** (29)	-.60 *** (29)	.56 ** (28)	.16 NS (28)	-.36 NS (28)	.47 ** (30)
LM				XXX	.22 NS (29)	.36 NS (27)	.17 NS (27)	-.08 NS (27)	.41 * (30)
L%					XXX	-.28 NS (27)	.02 NS (27)	.23 NS (27)	-.21 NS (30)
KT						XXX	.31 NS (33)	-.52 ** (33)	.30 NS (33)
KM							XXX	.57 *** (33)	.18 NS (33)
K%								XXX	-.17 NS (33)
MuT									XXX

Key: NS=Not significant; * P<0.05; ** P<0.01; *** P<0.001 F'TH=Feather; L=Liver tissue; K=Kidney tissue; Mu=Muscle tissue; T=Total mercury; M=Methyl mercury; %=Methyl mercury as a percentage of total. Sample sizes in parentheses.

concentrations were found to be significantly and negatively correlated with age (Table 5.3). There was no significant correlation between age and kidney total mercury concentrations nor muscle total mercury concentrations (Table 5.3). Feather

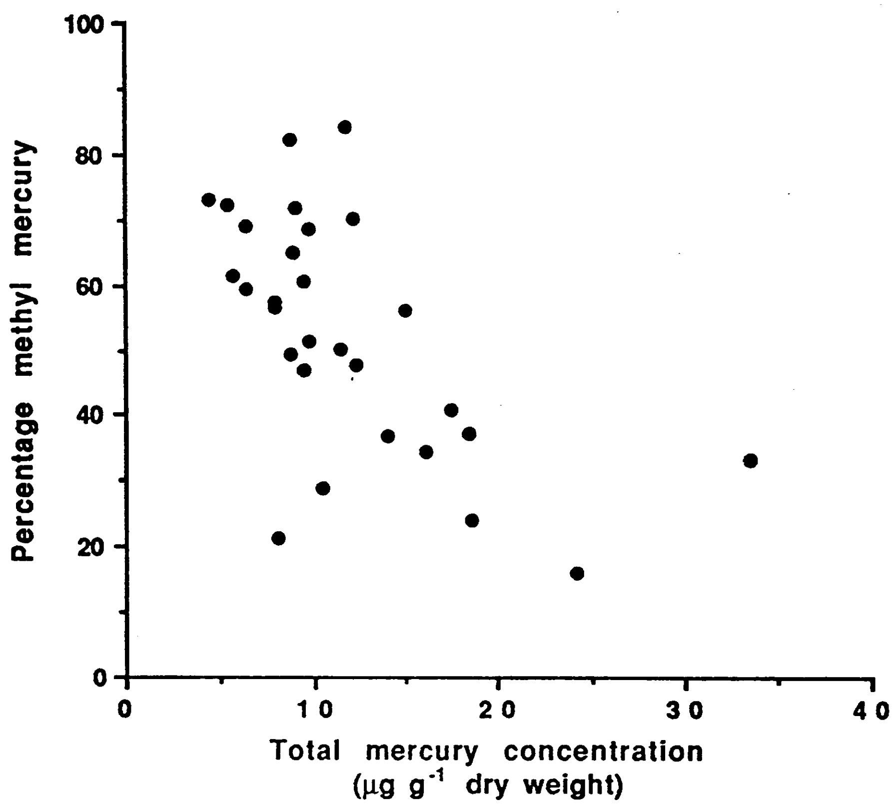

Fig. 5.4 Liver methyl mercury, expressed as a percentage of the total mercury concentration, plotted against liver total mercury concentration in adult great skuas <u>Catharacta skua</u> (r_s = -0.60, P < 0.001)

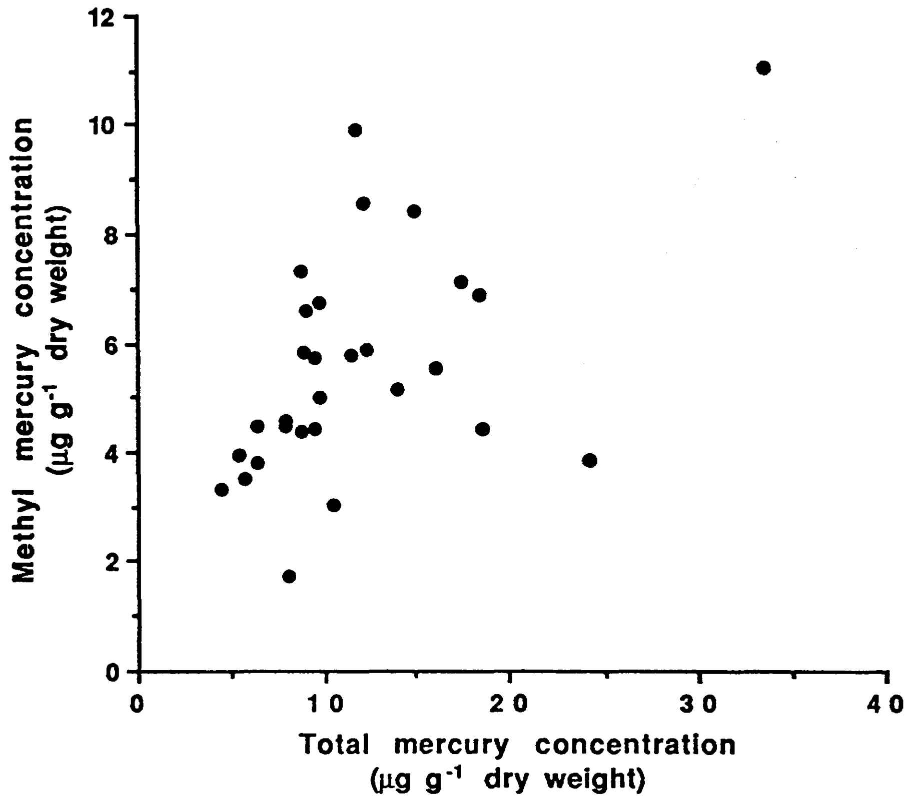

Fig. 5.5 Liver methyl mercury plotted against liver total mercury concentration in adult great skuas Catharacta skua ($r_s = 0.54$, $P < 0.01$)

mercury levels correlated well with liver total mercury levels (Table 5.3; Figure 5.3), and kidney and muscle total mercury levels (Table 5.3). Total mercury concentrations correlated well between internal tissues, but the same was not true for methyl mercury levels (Table 5.3). Both liver and kidney methyl mercury levels when expressed as a percentage of the total mercury level, showed significant negative correlations with total mercury levels (Table 5.3; Figure 5.4), although liver methyl mercury concentrations in absolute terms were significantly and positively correlated with total mercury levels (Table 5.3; Figure 5.5).

5.4 DISCUSSION

The low great skua chick feather mercury concentrations (median= 1.2 µg g^{-1} fresh weight, maximum value= 2.36 µg g^{-1} fresh weight), compared to those of adult birds (median= 5.6 µg g^{-1} fresh weight, maximum value= 27.95 µg g^{-1} fresh weight; Table 5.2), are consistent with similar findings from studies of the chicks/juveniles and adults of red-billed gulls, great blue herons _Ardea herodias_, black-crowned night herons _Nycticorax nycticorax_, great egrets _Casmerodius albus_, eastern great white egrets _Egretta alba modesta_ and peregrine falcons _Falco peregrinus_ (Furness _et al._, in press; Hoffman & Curnow, 1979; Honda _et al._, 1985; 1986a; Lindberg & Odsjo, 1983). The lack of any age-related trend in chick feather mercury levels (Figure 5.1) would tend to suggest that a 'dilution' effect is taking place. During the pre-fledging period, and during years of sufficient food availability, great skua chicks are fed increasingly large daily amounts of food, as their energy demands correspondingly increase (Furness, 1987). This will tend to result in greater absolute amounts of mercury being ingested by older and larger chicks. Since this increase in mercury exposure is associated with increases in feather and body size (and, hence, weight), the mercury concentration would appear to change little during the chick growth period, for a given individual. A similar dilution process was described by Honda et al. (1986a) in eastern great white egret chicks. The increase in feather mercury concentration seen between chicks and adult birds as young as three years of age (one three year-old bird was found to exhibit a feather mercury level of 22.79 $\mu g\ g^{-1}$ fresh weight), presumably reflects the accumulation, via the diet, of mercury between subsequent moults.

Similarly, the lack of any age-related trend in adult feather mercury concentrations (Table 5.3; Figure 5.2) confirms the pattern noted by Furness et al. (in press) for red-billed gulls. It would appear that feather mercury levels are independent of bird age and largely reflect dietary mercury exposure rather than accumulation processes, particularly in those species which have a relatively well-defined and annual or near-annual moult. Hence, once adult status has been achieved, inter-specific comparisons of mercury concentrations in feathers can be made without the need to apply a correction for adult age.

Furthermore, only total mercury concentrations in liver tissue showed a significant trend with age, this being negative (Table 5.3). This result was surprising since it seems hard to imagine a process or mechanism by which the total (and, hence, inorganic) mercury concentration in internal tissues would decrease with age in any marine top predator. A wide range of studies have demonstrated the opposite of the present finding in numerous species of marine fish and mammals (see Thompson, in press; Chapter 2). Recent work by Thompson & Furness (1989; Chapter 4) would tend to suggest that relatively long-lived species of seabirds in which the excretion of methyl mercury via the feathers is relatively limited, due mainly to slow moult cycles, exhibit levels of inorganic mercury in liver tissue which are both appreciable and likely to be the result of biotransformation and accumulation over time. The presence of relatively high levels of inorganic mercury in both liver and kidney tissues of great skuas (Table 5.2) would suggest that the excretion of methyl mercury via the feathers is insufficient to deal with all of the methyl mercury ingested, and that a proportion is demethylated and stored in internal tissues. It is highly likely that the mercury ingested by the skuas is virtually all organic, methyl mercury. Numerous studies have demonstrated that generally >80%, and in many cases a higher percentage, of measured mercury in fish was organic mercury (for example, Chvojka, 1988; Chvojka & Williams, 1980; Thomson, 1985). The seabird prey of skuas on Foula, mainly auks (Alcidae), and kittiwakes Rissa tridactyla are also likely to exhibit high proportions of methyl mercury in their internal tissues; all such species undergo a complete annual moult, typical of those species with high proportions of methyl mercury (Thompson & Furness, 1989; Chapter 4) and mercury in guillemots Uria aalge from north west Scotland was found to be virtually all methyl (Chapter 6).

The possibility that inorganic mercury is stored in internal tissues is further supported by the significant and negative relationship between methyl mercury, expressed as a percentage of the total mercury concentration, and the total mercury level for both liver and kidney tissues (Table 5.3; Figure 5.4). Such trends have been reported in other seabirds (Norheim et al., 1982; Thompson & Furness, 1989; Chapter 4). In addition, the significant and positive correlation between liver methyl mercury concentrations and liver total mercury concentrations (Table 5.3; Figure 5.5) may indicate that the amount of methyl mercury ingested via the diet is too great for the demethylation process, as noted for Tristan skuas *Catharacta skua hamiltoni* by Thompson & Furness (1989; Chapter 4), although it is not clear why this should be. It seems likely, therefore, that the negative correlation between total mercury concentration and age (Table 5.3), although statistically significant, is likely to be a chance result, since the above-mentioned trends would tend to result in the storage, and hence, accumulation of inorganic (and total) mercury in internal tissues.

Alternatively, it may be that immature great skuas differ in exposure to mercury because of their different geographical distribution outside the breeding season and different diets (Furness, 1987). Great skuas feed on a wide range of prey species and some individuals within a colony show marked preferences for one particular prey type (Furness, 1979). Therefore, dietary specialisation with individuals consistently feeding on different prey types, covering several trophic levels with associated differences in mercury concentration, would tend to reduce the effect of age as a strong determinant of mercury levels of internal tissues. A skua which feeds predominantly upon seabirds, for example, is likely to exhibit higher mercury concentrations than a bird which tends to feed on whitefish discards, regardless of age. One might expect that within birds with similar dietary preferences, an age-related increase in inorganic mercury concentration would be observed, although it has not been possible to investigate such a pattern, due to the lack of detailed dietary data for each bird analysed. In species with diets which are fairly uniform, being composed of prey species of similar trophic status, the accumulation of inorganic mercury with age is likely to be more pronounced. The extremely high levels of inorganic mercury measured in wandering albatrosses Diomedea exulans from Gough Island have been suggested as being indicative of accumulation over time (Thompson & Furness, 1989; Chapter 4). This seems probable given the relative uniformity of such species' diets (see Prince & Morgan, 1987).

The strong, positive correlations between adult feather mercury concentrations and total mercury concentrations of internal tissues (Table 5.3; Figure 5.3) are similar to those reported in a wide range of other species (Fimreite, 1974; Furness & Hutton, 1979; Hutton, 1981; Ohlendorf et al., 1985; see also Chapter 6). Although not well documented, great skuas are thought to undergo a complete post-nuptial moult (Ginn & Melville, 1983), but some body feathers may be replaced every two years (Furness, 1987). Feather mercury levels measured from a sample taken in 1988 would, therefore, reflect the previous summer's (1987) internal tissue mercury concentration. The mercury concentration of internal tissues measured in 1988 represent the accumulation of mercury that year. The significant correlation between these two mercury concentrations effectively represents a year to year trend which would suggest that a given individual with relatively high feather mercury levels would be likely to exhibit similarly high feather levels in future years

(Table 5.3; Figure 5.3). One might expect, however, that feather mercury concentrations would correlate more strongly with tissue methyl mercury concentrations, than with total mercury levels. Feather mercury has been shown to be virtually all methyl mercury (Thompson & Furness, in press; Chapter 7.1). Feathers act as the most important eliminatory pathway for mercury (Braune & Gaskin, 1987), as the 'body pool' of accumulated mercury diminishes during feather growth (Honda et al., 1986b). Hence, a strong correlation between feather methyl mercury concentration (total mercury concentration) and body tissue methyl mercury concentration would be expected. There may be several reasons why this was not observed (Table 5.3) and why significant and postive correlations were observed between feather mercury levels and tissue total mercury levels (Table 5.3; Figure 5.3). Total mercury concentrations in internal tissues exhibited greater variation (Coefficient of Variation= 53, liver tissue; Table 5.2) than did methyl mercury levels (Coefficient of Variation= 38, liver tissue; Table 5.2). A significant relationship would be statistically easier to detect for total mercury concentrations, since they covered a greater range of values when compared to the relatively restricted range of methyl mercury values. It is of note that liver total mercury concentrations were significantly and positively correlated with liver methyl mercury levels (Table 5.3). It may be that tissue methyl mercury levels correlate more strongly with those mercury levels of first-moulted feathers, since mercury levels in feathers moulted later during the process are likely to reflect the correspondingly reduced 'body pool' of mercury within internal tissues.

It is clear that despite the presence of inorganic mercury in liver and kidney tissues of great skuas, a straight forward age-accumulation trend does not exist. Dietary variation and specialisation appear to be more important as determinants of mercury concentrations.

5.5 REFERENCES

Anderlini, V.C., Connors, P.G., Risebrough, R.W. & Martin, J.H. (1972). Concentrations of heavy metals in some Antarctic and North American seabirds. Proc. Symp. Conservation Problems Antarctica pp.49-62. Blacksburg Virginia Polytecnic and State University.

Appelquist, H., Asbirk, S. & Drabaek, I. (1984). Mercury monitoring: mercury stability in bird feathers. Mar. Poll. Bull. 15, 22-24.

Arima, S. & Nagakura, K. (1979). Mercury and selenium content of Odontoceti. Bull. Japan. Soc. Sci. Fish. 45, 623-626.

Born, E.W., Kraul, I. & Kristensen, T. (1981). Mercury, DDT and PCB in the Atlantic walrus (Odobenus rosmarus rosmarus) from the Thule District, north Greenland. Arctic 34, 255-260.

Braune, B.M. & Gaskin, D.E. (1987). Mercury levels in Bonaparte's gulls (Larus philadelphia) during autumn molt in the Quoddy Region, New Brunswick, Canada. Arch. Environ. Contam. Toxicol. 16, 539-549.

Caputi, N., Edmonds, J.S. & Heald, D.I. (1979). Mercury content of sharks from south-western Australian waters. Mar. Pollut. Bull. 10, 337-340.

Chvojka, R. (1988). Mercury and selenium in axial white muscle of yellowtail kingfish from Sydney, Australia. Mar. Pollut. Bull. 19, 210-213.

Chvojka, R. & Williams, R.J. (1980). Mercury levels in six species of Australian commercial fish. Aust. J. Mar. Freshw. Res. 31, 469-473.

Crewther, W.G., Fraser, R.D.B., Lennox, F.G. & Lindley, H. (1965). The chemistry of keratins. Adv. Prot. Chem. 20, 191-346.

Doi, R., Ohno, H. & Harada, M. (1984). Mercury in feathers of wild birds from the mercury-polluted area along the shore of the Shiranui Sea, Japan. Sci. Tot. Environ. 40, 155-167.

Drescher, H.E., Harms, U. & Huschenbeth, E. (1977). Organochlorinews and heavy metals in the harbour seal Phoca vitulina from the German North Sea coast. Mar. Biol. 41, 99-106.

Fimreite, N. (1974). Mercury contamination of aquatic birds in northwestern Ontario. J. Wildl. Manage. 38, 120-131.

Furness, R.W. (1977). Studies on the breeding biology and population dynamics of the great skua Catharacta skua Brunnich. Unpublished Ph.D. Thesis, University of Durham.

Furness, R.W. (1979). Foods of great skuas Catharacta skua at north Atlantic breeding localities. Ibis 121, 86-92.

Furness, R.W. (1987). The Skuas. T. & A.D. Poyser, Calton.

Furness, R.W. & Hutton, M. (1979). Pollutant levels in the great skua Catharacta skua. Environ. Pollut. 19, 261-268.

Furness, R.W., Lewis, S.A. & Mills, J.A. (in press). Mercury levels in the plumage of red-billed gulls Larus novaehollandiae scopulinus of known sex and age. Environ. Pollut.

Furness, R.W., Muirhead, S.J. & Woodburn, M. (1986). Using bird feathers to measure mercury in the environment: relationships between mercury content and moult. Mar. Pollut. Bull. 17, 27-30.

Gaskin, D.E., Stonefield, K.I., Suda, P. & Frank, R. (1979). Changes in mercury levels in harbour porpoises from the Bay of Fundy, Canada, and adjacent waters during 1969-1977. Arch. Environ. Contam. Toxicol. 8, 733-762.

Ginn, H.B. & Melville, D.S. (1983). Moult in birds. British Trust for Ornithology, Tring.

Gochfeld, M. (1980). Mercury levels in some seabirds of the Humboldt current, Peru. Environ. Pollut. (A) 22, 197-205.

Greig, R.A. & Krzynonek, J. (1979). Mercury concentrations in three species of tunas collected from various oceanic waters. Bull. Environ. Contam. Toxicol. 22, 120-127.

Hoffman, R.D. & Curnow, R.D. (1979). Mercury in herons, egrets and their foods. J. Wildl. Manage. 43, 85-93.

Honda, K., Min, B.Y. & Tatsukawa, R. (1985). Heavy metal distribution in organs and tissues of the eastern great white egret Egretta alba modesta. Bull. Environ. Contam. Toxicol. 35, 781-789.

Honda, K., Min, B.Y. & Tatsukawa, R. (1986). Distribution of heavy metals and their age-related changes in the eastern great white egret, Egretta alba modesta, in Korea. Arch. Environ. Contam. Toxicol. 15, 185-197.

Honda, K., Nasu, T. & Tatsukawa, R. (1986). Seasonal changes in mercury accumulation in the black-eared kite, Milvus migrans lineatus. Environ. Pollut. (A) 42, 325-334.

Honda, K., Tatsukawa, R., Itano, K., Miyazaki, N. & Fujiyama, T. (1983). Heavy metal concentrations in muscle, liver and kidney tissue of striped dolphin, Stenella coeruleoalba, and their variations with body length, weight, age and sex. Agric. Biol. Chem. 47, 1219-1228.

Honda, K., Yamamoto, Y., Hidaka, H. & Tatsukawa, R. (1986). Heavy metal accumulations in Adelie penguin, Pygoscelis adeliae, and their variations with the reproductive process. Mem. Natl. Inst. Polar Res., Spec. Issue 40, 443-453.

Hutton, M. (1981). Accumulation of heavy metals and selenium in three seabird species from the United Kingdom. Environ. Pollut. (A) 26, 129-145.

Kai, N., Ueda, T., Takeda, M. & Kataoka, A. (1983). On mercury and selenium in tuna fish tissues-VIII The levels of mercury and selenium in albacore from the Indian Ocean. J. Shimonoseki University Fish. 31, 69-73.

Lindberg, P. & Odsjo, T. (1983). Mercury levels in feathers of peregrine falcon Falco peregrinus compared with total mercury content in some of its prey species in Sweden. Environ. Pollut. (B) 5, 297-318.

Lyle, J.M. (1984). Mercury concentrations in four Carcharhinid and three hammerhead sharks from coastal waters of the Northern Territory. Aust. J. Mar. Freshw. Res. 35, 441-451.

Mackay, N.J., Kazacos, M.N., Williams, R.J. & Leedow, M.I. (1975). Selenium and heavy metals in black marlin. Mar. Pollut. Bull. 6, 57-61.

Nicholson, J.K. (1981). The comparative distribution of zinc, cadmium and mercury in selected tissues of the herring gull (Larus argentatus). Comp. Biochem. Physiol. 68C, 91-94.

Norheim, G., Somme, L. & Holt, G. (1982). Mercury and persistent chlorinated hydrocarbons in Antarctic birds from Bouvetoya and Dronning Maud Land. Environ. Pollut. (A) 28, 233-240.

Ohlendorf, H.M., Anderson, D.W., Boellstorff, D.E. & Mulhern, B.M. (1985). Tissue distribution of trace elements and DDE in brown pelicans. Bull. Environ. Contam. Toxicol. 35, 183-192.

Osborn, D., Harris, M.P. & Nicholson, J.K. (1979). Comparative tissue distribution of mercury, cadmium and zinc in three species of pelagic seabirds. Comp. Biochem. Physiol. 64C, 61-67.

Prince, P.A. & Morgan, R.A. (1987). Diet and feeding ecology of Procellariiformes. In Seabirds: feeding ecology and role in marine ecosystems. Croxall, J.P. (ed.). pp.135-172. Cambridge University Press, Cambridge.

Reijnders, P.J.H. (1980). Organochlorine and heavy metal residues in harbour seals from the Wadden Sea and their possible effects on reproduction. Neth. J. Sea Res. 14, 30-65.

Ronald, K., Frank, R.J. & Dougan, J. (1984). Pollutants in harp seals (Phoca groenlandica) II. Heavy metals and selenium. Sci. Tot. Environ. 38, 153-166.

Shultz, C.D. & Ito, B.M. (1979). Mercury and selenium in blue marlin, Makaira nigricans, from the Hawaiian Islands. Fish. Bull. 76, 872-879.

Smith, T.G. & Armstrong, F.A.J. (1978). Mercury and selenium in ringed and bearded seal tissues from Arctic Canada. Arctic 31, 75-84.

Thomson, J.D. (1985). Mercury concentrations of the axial muscle tissues of some marine fishes of the continental shelf adjacent to Tasmania. Aust. J. Mar. Freshw. Res. 36, 509-517.

Thompson, D.R. (in press). Metals in marine vertebrates. In, Heavy Metals in the Marine Environment. Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

Thompson, D.R. & Furness, R.W. (1989). The chemical form of mercury stored in south Atlantic seabirds. Environ. Pollut. 60, 305-317.

Thompson, D.R. & Furness, R.W. (in press). Comparison of total and organic mercury levels in seabird feathers. Mar. Pollut. Bull.

Walsh, P.M. (in press). The use of seabirds as monitors of metal levels in oceans. In, Heavy Metals in the Marine Environment. Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

CHAPTER 6

Seasonal variation in mercury concentrations in common guillemots

6.1 INTRODUCTION

Mercury concentration data have been published for a wide range of terrestrial and marine organisms. The vast majority of these data, however, have represented the mercury level in tissues of a given species at a particular time or point within the season and variations in mercury levels on a seasonal basis have seldom been studied. The influences of such factors as metabolic, physiological and/or dietary variations, for example, upon mercury levels over a period of time for a given species have received little attention.

Boalch *et al.* (1981), in a study of mussels *Mytilus edulis*, concluded that there was no evidence of any overall seasonal pattern in metal levels in that species, although mercury concentrations were shown to decrease markedly between August and September. Similarly, De Clerck *et al.* (1974) found no seasonal trend in total mercury concentrations in shrimps *Crangon crangon* caught in Belgian coastal waters. Crustacea, such as shrimps, are potentially able to lose metals from the body into the new exoskeleton following moult, but De Clerck *et al.* (1974) noted that only 12% of the measured mercury was in the 'shell', and they made no mention of the particular form of mercury they measured. Recent reviews of metal levels and fluxes in marine invertebrates, including crustaceans, would tend to suggest that the dynamics of mercury in this group and the role of moult, as an eliminatory pathway for mercury, are subjects requiring further work before firm conclusions can be drawn (Phillips, in press; Rainbow, in press).

Essink (1985) concluded that there was no seasonal variation in the total mercury contents of eelpout *Zoarces viviparus* from Dutch coastal waters. The lack of any pronounced seasonal fluctuation in mercury levels in marine fish such as eelpout is, perhaps, not surprising given that methyl mercury, the predominant form of the metal in fish (see Thompson, in press; Chapter 2, for references), has been shown to exhibit a relatively long biological half-life in plaice *Pleuronectes platessa* (Pentreath, 1976).

Reproductive processes could lead to differences in mercury dynamics between males and females in higher vertebrates. Methyl mercury can cross the placental barrier, as demonstrated in experimental studies (see Nordberg & Skerfving, 1972) and field investigations (Reinjders, 1980; Ronald *et al.*, 1984). Furthermore, methyl mercury has been reported to be excreted in the milk of lactating female marine mammals (Born *et al.*, 1981; Kim *et al.*, 1974). Since losses of mercury via these routes are unavailable to males, one might predict that there would be differences between the sexes with respect to mercury level fluctuations over the breeding season. The published data, however, shed little light on this aspect of mercury monitoring. Itano *et al.* (1984) reported that mercury levels were similar in tissues of male and female (pregnant, lactating and resting) striped dolphins *Stenella coeruleoalba* whilst Ronald *et al.* (1984) noted significantly higher mercury levels in tissues of female harp seals *Phoca groenlandica* compared to those in males. Furthermore, mercury has been measured in the fur and hair of some marine mammals (Freeman & Horne, 1973; Kim *et al.*, 1974; Mason & Reynolds, 1988; Yamamoto *et al.*, 1987). Since hair is periodically moulted and regrown, it represents an eliminatory pathway by which mercury would be lost from the body. The relative importance of this process with respect to mercury dynamics, in conjunction with mercury losses through reproductive processes, appear not to have been studied to any great extent in marine mammals.

Birds are able to lose mercury from their internal tissues via two main routes; the most important of these is via the growth of new feathers during moult. Braune & Gaskin (1987) reported that feathers accounted for 93% of the body content of total mercury lost during the moulting process in a sample of Bonaparte's gulls *Larus philadelphia*. Honda *et al.* (1986a) clearly demonstrated that as primary moult proceeded in the black-eared kite *Milvus migrans lineatus*, the mercury concentration of internal tissues decreased as the body burden of mercury diminished and was excreted into growing feathers.

Egg production offers a second route by which females can eliminate mercury from the body. Honda *et al.* (1986b) concluded, however, that mercury loss via this pathway was negligible when compared to the mercury burden of female Adelie penguins *Pygoscelis adeliae*. Indeed, mercury levels tend to be generally low in seabird eggs, rarely exceeding 0.5 µg g^{-1} wet weight (For example, Barrett *et al.*, 1985; Ohlendorf & Harrison, 1986). Becker *et al.* (1989) reported similarly low mercury concentrations in eggs of herring gulls *Larus argentatus*, but suggested that the loss of mercury via this route acted as a method of 'depollution' for the female.

Since many species of birds undergo a complete post-nuptial moult, there are likely to be pronounced changes in the mercury concentrations of internal tissues of such birds during the course of the breeding season and the subsequent moult. Inter-sex differences in mercury levels and dynamics may arise as a result of egg production in females. In this chapter, mercury concentration data are presented for common guillemots *Uria* aalge, collected at 3 times during the year corresponding to the pre-laying, post-laying/pre-moult and post-moult periods, respectively. Changes in mercury levels and tissue weights are compared between males and females and between the above periods, and the importance of egg production and moult as means of eliminating body mercury are discussed.

6.2 MATERIALS AND METHODS

6.2.1 Sample collection, storage and preparation

Up to a maximum of 30 guillemots were shot at sea, under licence from the Nature Conservancy Council, from an inflatable boat around the Summer Isles, off the north west coast of Scotland (Grid Reference of the jetty from which the boat was launched NB 983 112). Three collections were made during 1988; 30 birds were obtained on 26 April, 27 birds on 25 June and 25 birds over 1-2 November. For each bird, wing length (to the nearest mm), bill length (in mm to 0.1 mm), bill depth (in mm to 0.1 mm), head and bill length (to the nearest mm), gonad size (largest follicle for females, testes dimensions for males; in mm to 0.1 mm), cloacal bursa if present (in mm to 0.1 mm) and fresh weight (in g to 10 g) were measured. Such measurements were obtained in the field wherever possible, although inclement weather and/or failing light (November) resulted in readings being taken in the laboratory.

In addition, each bird's stomach, for dietary analysis (Dr. Nancy Harrison, NCC), and liver were dissected out (removal of the liver occurring with that of the stomach). Birds were individually tagged and, along with the removed livers, brought back to Glasgow, each liver weighed accurately (to 0.001 g) and each carcass and liver then deep frozen at ca. -20^{o}C prior to further treatments. On thawing, internal tissue samples were dissected out; as much of the kidneys were removed as possible (in some individuals, gun-shot damage made complete removal of all kidney tissue impossible), together with one whole pectoral muscle (for fat extraction) and a sample from the remaining pectoral muscle (for mercury analysis). These, together with the thawed liver, were dried to constant weight in an oven at 50^{o}C. An approximate estimation of total pectoral muscle dry weight was made by doubling the dry weight value obtained for the one whole pectoral muscle removed. A sample of four to ten small body feathers were taken from the central back region of each bird, washed (see Chapter 3) to remove any blood, dried at ambient laboratory temperature (ca. 22^{o}C) and placed in mercury-free polythene bags to await analysis. The sex of each bird was determined, although gun-shot damage prevented unequivocal indentification in one individual.

6.2.2 <u>Mercury analysis</u>

Internal tissues from birds from the first collection were analysed for methyl and total mercury. All subsequent analyses of internal tissues (collections 2 and 3) were of total mercury only. Feather samples were analysed for total mercury throughout (see Chapter 3 for details of methodology).

6.2.3 <u>Comparisons between collections</u>

In order to investigate the possibility that birds sampled at a given time of year were migrants from another, distinct population with dietary differences and, hence, differences in exposure to mercury, a measure of bird size was determined. This involved combining wing length, bill (length and depth) and head and bill measurements. For each of these four parameters and for each bird, a 'z-score' (Norusis, 1984) was determined as follows:-

for example, wing length...

weighted or
z-score= $z_{wing} = \dfrac{\text{wing length- Mean wing length (for all birds)}}{\text{Standard deviation (of wing l for all birds)}}$

This calculation was repeated for bill length, bill depth and head and bill length, and all four 'z-scores' combined, for each bird, to give a 'size index'. By treating each measurement in this way, 'weighted' measurements were produced which overcame differences due to scale. A mean 'size index' was calculated for each collection and mean 'size indices' compared between collections using 1-Way ANOVA.

The distribution patterns of mercury concentrations in the various tissues were assessed using Kolmogorov-Smirnov one sample tests; differences between total and methyl mercury levels in tissues of birds from the first (April) collection were investigated by using one sample t-tests, comparing the distribution of the differences (total mercury level-methyl mercury level) around a mean of zero. Trends in mercury levels, tissue mercury contents and tissue weights with time (sampling date) were assessed using 2-Way ANOVA for each tissue. Product Moment Correlation Coefficients (r) were calculated to assess relationships in mercury concentrations between different tissues.

6.3 RESULTS

The mean 'size indices' for each collection of birds (Sample 1=268.0, s.d.=7.5; Sample 2=265.7, s.d.=9.1; Sample 3=265.4, s.d.=10.4) were not significantly different from each other (1-Way ANOVA, P=0.527), indicating that, on the basis of

TABLE 6.1: Total mercury concentrations (μg g^{-1} dry weight of internal tissues; μg g^{-1} fresh weight of feathers) in tissues of guillemots collected in April, 1988 (Sample=1), June, 1988 (Sample=2) and November, 1988 (Sample=3).

Group (Sample size)	Sample	Liver Mean (s.d.) Range	Kidney Mean (s.d.) Range	Muscle Mean (s.d.) Range	Feather Mean (s.d.) Range
Adults (n=24)	1	3.66 (1.05) 1.78--6.92	3.93 (1.06) 2.44--7.12	1.76 (0.62) 0.55--2.96	2.15 (0.52) 0.80--2.93
Adults (n=21)	2	2.52 (0.99) 0.72--5.38	2.54 (0.89) 0.92--4.75	0.84 (0.38) 0.31--1.67	2.09 (0.75) 1.14--4.13
Adults (n=20)	3	0.87 (0.28) 0.34--1.47	0.84 (0.24) 0.53--1.22	0.47 (0.26) 0.19--1.17	1.71 (0.57) 0.85--3.12
Juveniles (n=6)	1	2.40 (0.34) 1.85--2.74	3.43 (0.58) 2.13--3.70	1.27 (0.30) 1.01--1.74	1.26 (0.33) 0.81--1.67
Juveniles (n=6)	2	1.57 (0.53) 1.02--2.56	1.91 (0.60) 1.23--2.78	0.65 (0.27) 0.39--1.09	2.68 (1.64) 1.33--5.73
Juveniles (n=5)	3	1.06 (0.44) 0.63--1.74	1.02 (0.25) 0.78--1.41	0.52 (0.18) 0.34--0.81	0.87 (0.42) 0.23--1.26
All birds (n=30)	1	3.41 (1.08) 1.78--6.92	3.67 (1.08) 2.13--7.12	1.66 (0.60) 0.55--2.96	1.98 (0.60) 0.80--2.93
All birds (n=27)	2	2.31 (0.98) 0.72--5.38	2.40 (0.86) 0.92--4.75	0.80 (0.36) 0.31--1.67	2.22 (1.01) 1.14--5.73
All birds (n=25)	3	0.90 (0.32) 0.34--1.74	0.87 (0.25) 0.53--1.41	0.48 (0.24) 0.19--1.17	1.54 (0.63) 0.23--3.12

the four dimensions measured, the birds were similar enough to be able to assume that they were from the same population.

Mercury level distribution patterns did not differ significantly from Gaussian (Kolmogorov-Smirnov one sample tests; $P>0.05$), regardless of tissue or form of mercury. Furthermore, there were no significant differences between methyl and total mercury concentrations in liver, kidney nor muscle tissues (one sample t-tests; P=0.128, 0.468, 0.208, respectively) of birds from the first collection, indicating that virtually all the mercury present was in the methyl form.

Total mercury levels in tissues and feathers of adult, juvenile and all birds combined are presented in Table 6.1. Both juvenile and adult birds exhibited similar patterns of mercury concentrations in internal tissues and feathers over the three sampling dates. A 2-way ANOVA of mercury level by age (juvenile/adult) and collection showed significant differences between the two age groups for each tissue, except feathers (Liver; age, $F_{1,80}=10.8$, $P<0.01$: Kidney; age, $F_{1,80}=8.7$, $P<0.01$: Muscle; age, $F_{1,80}=4.0$, $P<0.05$: Feather; age, $F_{1,80}=3.7$, $P=0.058$). Generally, juveniles exhibited lower mercury concentrations than those of adults; on average, juvenile tissue mercury levels represented from 80 to 94% of the corresponding adult mercury concentrations, depending on the particualr tissue (Table 6.1). All subsequent analyses involved adult birds only.

Total mercury levels in tissues and feathers of male and female adult birds, together with dry weights and mercury contents of liver and pectoral muscle tissues, are presented in Table 6.2. Generally, males and females exhibited closely similar or identical seasonal trends in mercury levels and tissue weights. A 2-way ANOVA revealed that neither sex nor sampling date were significant factors with respect to liver weight (Sex; $F_{1,63}=1.5$, $P=0.233$: Sample; $F_{1,63}=1.2$, $P=0.321$). Similarly, sample date did not affect pectoral muscle weight significantly ($F_{2,63}=1.8$, $P=0.182$), although a significant

TABLE 6.2: Tissue dry weights (g), total mercury concentrations ($\mu g\ g^{-1}$ dry weight of internal tissues; $\mu g\ g^{-1}$ fresh weight of feathers) and mercury content (μg) of liver, kidney and pectoral muscle (Pect. Mus.) tissues and feathers of male (M) and female (F) adult guillemots from the 3 collections. All values are means with (s.d.).

Sample	Feather	Liver			Kidney	Pect. Mus.		
	conc.	conc.	wt.	cont.	conc.	conc.	wt.	cont.
1 M (n=18)	2.14 (0.4)	3.62 (0.8)	14.00 (2.0)	50.38 (11.2)	3.79 (0.8)	1.81 (0.6)	57.8 (4.5)	103.3 (33.1)
1 F (n=6)	2.21 (0.8)	3.78 (1.7)	15.58 (1.9)	58.01 (25.9)	4.33 (1.6)	1.60 (0.5)	55.6 (5.4)	90.2 (32.0)
2 M (n=12)	2.44 (0.7)	2.15 (0.6)	13.57 (1.8)	28.83 (8.5)	2.37 (0.7)	0.79 (0.4)	59.1 (5.5)	46.9 (24.1)
2 F (n=9)	1.64 (0.5)	3.00 (1.2)	13.71 (2.4)	41.45 (17.8)	2.77 (1.1)	0.91 (0.4)	54.1 (4.4)	48.7 (19.4)
3 M (n=13)	1.82 (0.6)	0.91 (0.3)	14.10 (1.6)	12.78 (4.3)	0.85 (0.3)	0.45 (0.2)	60.1 (4.4)	27.0 (9.9)
3 F (n=6)	1.58 (0.4)	0.79 (0.2)	14.29 (1.8)	11.14 (3.2)	0.76 (0.2)	0.56 (0.4)	58.9 (6.7)	31.3 (19.8)

conc.= mercury concentration; wt.= organ weight; cont.= mercury content; n= sample size.

difference was found between the sexes ($F_{1,63}$=4.9, P<0.05). The significant decrease in mercury content in liver and muscle tissues over the sampling period (Table 6.2) was likely, therefore, to have been a function of mercury concentration, rather than tissue weight. Sex was not a significant factor with

TABLE 6.3: Testes dimensions (length X width in mm) in male guillemots from the three collections.

	Collection 1	Collection 2	Collection 3
Sample size	18	12	13
Mean dimensions	33.0 X 13.3	14.9 X 4.5	9.9 X 3.7
Standard dev.	6.6 3.7	2.5 1.6	1.2 0.6

respect to tissue mercury content (2-way ANOVA: Liver; sample, $F_{2,63}=55.3$, $P<0.001$; sex, $F_{1,63}=4.0$, $P=0.051$: Muscle; sample, $F_{2,63}=47.5$, $P<0.001$; sex, $F_{1,63}=0.1$, $P=0.732$).

Internal tissue mercury concentrations showed a general decline from sample 1 through to sample 3. Two-way ANOVA, for each internal tissue, of mercury concentration for the three sampling dates and between males and females showed significant differences between the time of collection (Liver; $F_{2,63}=57.2$, $P<0.001$: Kidney; $F_{2,63}=73.2$, $P<0.001$: Muscle; $F_{2,63}=43.8$, $P<0.001$), but not between the sexes (Liver; $F_{1,63}=2.2$, $P=0.144$: Kidney; $F_{1,63}=1.5$, $P=0.223$: Muscle; $F_{1,63}=0.0$, $P=0.993$).

Feather mercury concentration showed less seasonal variation than that of internal tissues. Two-way ANOVA of mercury concentration by sampling date and sex showed no significant difference between time of collection ($F_{2,63}=3.0$, $P=0.059$), although there was a significant difference between the sexes ($F_{1,63}=4.9$, $P<0.05$). The seasonal trends in mercury levels in adult birds are presented in Figure 6.1a,b.

Testes dimensions for male guillemots from each of the three collections are presented in Table 6.3 whilst fresh weights of birds (adults, juveniles and all birds combined) for

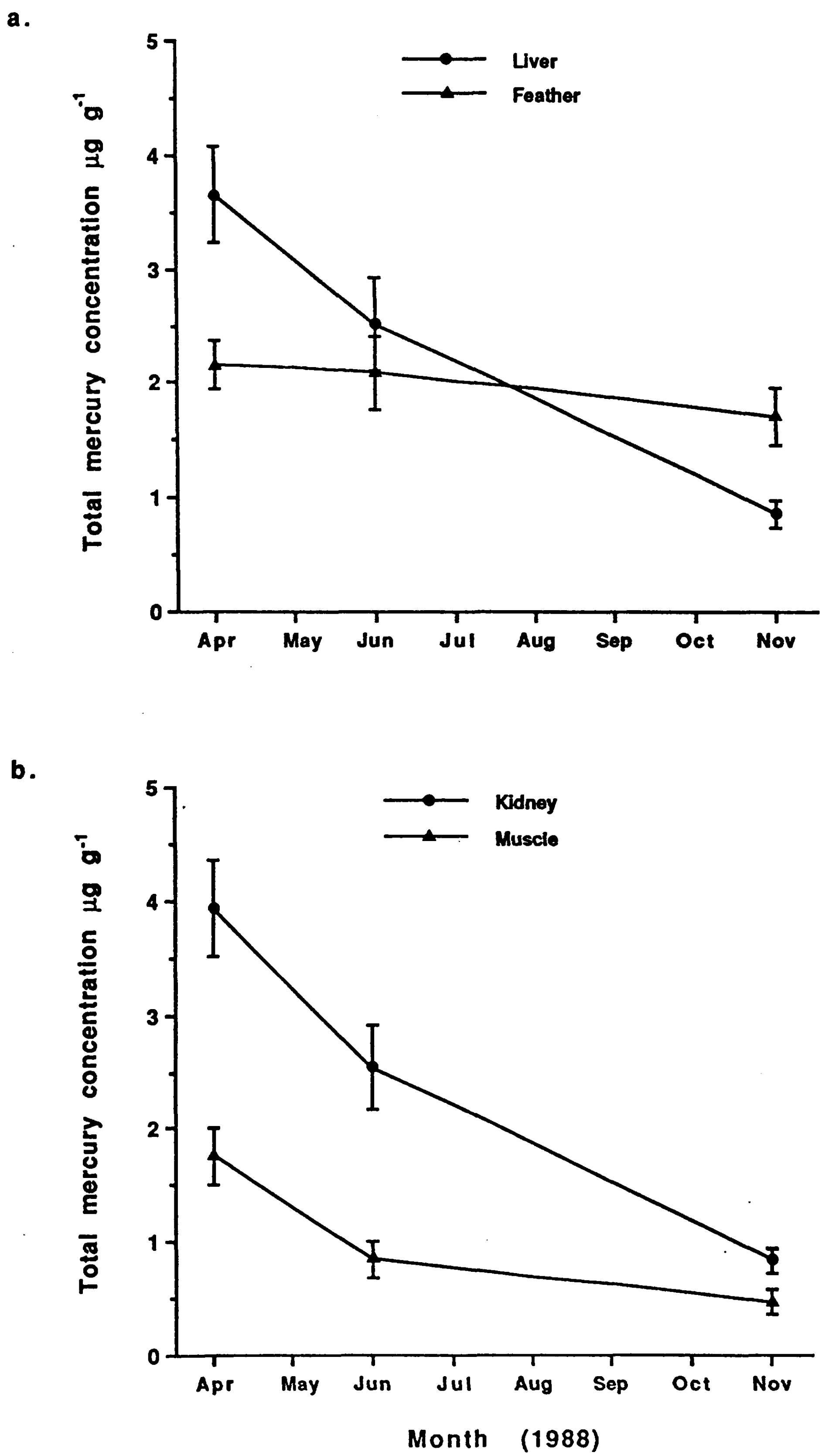

Fig. 6.1 Seasonal changes in total mercury concentration in tissues of adult common guillemots <u>Uria aalge</u> a. liver and feather, b. kidney and muscle (Points are means with 95% confidence limits)

all samples are presented in Table 6.4.

There were few inter-tissue mercury concentration correlations. Mercury levels in liver and kidney tissues were found to be positively and significantly correlated in birds from all three collections (Sample 1; $r=0.77$, $P<0.05$: Sample 2; $r=0.81$, $P<0.001$: Sample 3; $r=0.48$, $P<0.05$). Mercury levels in liver and muscle tissues were significantly and positively correlated in birds from collections 1 and 2 only (Sample 1; $r=0.59$, $P<0.01$: Sample 2; $r=0.51$, $P<0.05$). Feather mercury concentrations were found to be positively and significantly correlated with liver mercury levels in birds from the third collection only ($r=0.47$, $P<0.05$).

TABLE 6.4: Whole bird fresh weights (g) for adult, juvenile and all guillemots from the three collections. Values are means with (standard deviations).

	Collection 1	Collection 2	Collection 3	All
Adults	1030 (65.5) (n=24)	970 (74.8) (n=21)	1040 (71.9) (n=20)	1010 (74.8) (n=65)
Juveniles	990 (59.1) (n= 6)	1020 (79.6) (n= 6)	1020 (86.2) (n= 5)	1010 (71.3) (n=17)
All	1020 (65.1) (n=30)	980 (77.1) (n=27)	1030 (73.4) (n=25)	1010 (73.7) (n=82)

n= sample size.

6.4 DISCUSSION

The dates of the three guillemot collections spanned two of the major processes likely to influence mercury levels in internal tissues and feathers; namely, reproduction and moult. Precise data for the time of egg laying were not obtained for the birds sampled, but most eggs would almost certainly have been laid in May, between the first (26 April) and second (25 June) collections. Birkhead (1980) found that the median laying date of guillemots on Skomer Island, south west Wales varied between 16 and 20 May in three years whilst Harris & Wanless (1988) noted median laying dates in guillemots on the Isle of May, Firth of Forth to be generally in the first two weeks of May (with isolated dates at the end of April). Although laying date varies with latitude (see Harris & Birkhead, 1985), the guillemots sampled in this study are unlikely to have differed markedly in their date of laying.

Guillemots undergo a complete post-nuptial moult which generally commences in July in British birds. The primaries, secondaries and tail feathers are dropped simultaneously, though at slightly different times depending on the feather type, once the adults leave the nesting ledges. Body feather moult may commence before the birds depart for the sea (Birkhead & Taylor, 1977; Ginn & Melville, 1983). Hence, birds will have undergone, and largely completed, post-nuptial moult between the second (25 June) and third (1-2 November) collections. It is of note, however, that two juvenile (that is, one year old) birds obtained during the second collection had already dropped, and were regrowing, their primary feathers. No adult birds sampled at that time were found to be at a similar stage of moult.

The decline in mercury concentrations in internal tissues measured in adult birds between collections 1 and 2 (Tables 6.1 & 6.2) could, therefore, be associated with mercury losses via egg production (females) or testes maturation (males). It has been suggested that the egg represents an eliminatory pathway, via which female birds are able to reduce their body burden of mercury. Becker _et al._ (1989) reported mean egg mercury levels higher than those in liver tissues of a sample of female herring gulls, and indicated that the egg served a 'depolluting' function, as described above. Many studies, however, have reported egg mercury levels for a range of species, some of which have been relatively elevated (>0.5 $\mu g\ g^{-1}$ wet weight), but have made no assessment as to the significance of this route for mercury loss (For example, Becker et al., 1985; Renzoni et al., 1986; see also, Thompson, in press; Chapter 2).

The reduction in mercury concentration in liver and muscle tissues of the female guillemots between collections 1 and 2, and the resultant decrease in mercury content of those tissues (Table 6.2) are worth considering further. On average, females exhibited a drop in mercury content of at least 16 µg in liver tissue and nearly 42 µg mercury in pectoral muscle tissue over the egg laying period (Collections 1 to 2; Table 6.2). Could it be that this mercury is being lost via the egg ? Although no eggs were collected as part of the sampling procedure in this study, it was possible to estimate the potential eggs provide as an excretory pathway for mercury. Birkhead & Harris (1985) provided an equation (log. egg weight as % of adult body weight = 1.801-0.251 X log. adult body weight) which allows the approximate egg weight to be determined for a given adult body weight. Using the overall adult body weight value of 1010 g (Table 6.4), and substituting into the above equation, an egg weight of approximately 112.5 g can be calculated. By subtracting the weight of the shell (Ratcliffe (1970) gave a value of 12.5 g for British guillemots), a value of roughly 100 g was obtained which can be thought of as that weight of egg contents into which the female could potentially have deposited mercury. Recent work by Barrett et al. (1985) reported mean egg mercury concentrations in Norwegian guillemots as ranging from 0.08 to 0.13 µg g^{-1} wet weight whilst Dyck & Kraul (1984) reported a mean egg mercury value of 0.31 µg g^{-1} wet weight in guillemots from the Baltic Sea. Since fauna from in and around the Baltic Sea have been shown to be relatively contaminated with a range of pollutants, including mercury (For example, Falandysz et al., 1988; Kari & Kauranen, 1978), it is extremely unlikely that mercury levels in eggs of the birds analysed in this study would exceed the 0.31 µg g^{-1} level (Dyck & Kraul, 1984). Hence, by using this as a maximum concentration, a guillemot egg would be likely to contain no more than 0.31 X 100 µg = 31 µg mercury. The highest mean value reported by Barrett et al. (1985) would have resulted in 0.13 X 100 µg = 13 µg mercury being deposited in an egg. The reduction of 16 µg mercury in the liver and 42 µg mercury in the pectoral muscle for the birds in this study (Table 6.2) would combine to produce a figure of 58 µg which failed to take account of losses in other tissues such as the kidney (although the kidney mercury level fell significantly between collections 1 and 2 (Tables 6.1 & 6.2), a corresponding drop in mercury content was not assessed due to difficulties in determining accurate kidney weights). However, despite this conservative estimate, it is clear that the figure of 58 µg exceeds the likely mercury content of an average guillemot egg from a female in this study, especially when the lower mercury concentration of Barrett et al. (1985) was used.

This would tend to suggest that the potential 'mercury carrying capacity' of the egg was not being used fully, even at these relatively low mercury levels. The reduction in mercury concentration and content of the internal tissues was likely, therefore, to have been associated with lipid and protein mobilisation, as part of egg formation. Furthermore, it would seem evolutionarily sensible to excrete as little mercury, in this case methyl mercury, as possible into the egg, especially in such a species as the guillemot which produce one large egg per year (disregarding replacement eggs). Being highly toxic, methyl mercury could reduce the viability of the developing embryo. It would seem plausible, therefore, that in 'normal' circumstances (wild bird populations in environments not heavily contaminated with pollutants from anthropogenic sources), birds would preferentially deposit mercury into growing feathers or demethylate any excess methyl mercury which could not be lost in this way, before 'over-loading' the egg(s) with methyl mercury. At what levels mercury in eggs of wild seabirds become toxic to the embryo is difficult to say, based on the experimental feeding of captive birds, since these latter studies often involved terrestrial species which were fed relatively ('unnaturally') high levels of organic mercury (For example, Heinz, 1974; Scott et al., 1975; Spann et al., 1972). The finding that the egg does not represent a major eliminatory pathway for mercury in the guillemot agrees with the similar conclusion drawn by Honda et al. (1986b) for Adelie penguins.

The male guillemots also showed significant decreases in mercury concentrations of internal tissues over the same period (collections 1 to 2), resulting in, on average, approximately 22 μg and 56 μg mercury being lost from liver and pectoral muscle tissues, respectively (Table 6.2). Since it is unlikely that this reduction in mercury content is associated with feather growth (moult not having commenced at this stage), the possibility that the reduction represents redistribution of mercury with lipid and protein mobilisation for testes maturation and sperm production would seem appropriate. The testes showed marked seasonal fluctuations in size (Table 6.3), presumably involving correspondingly marked variations in mobilisation of tissue products for reproduction.

The fact that mercury levels in internal tissues did not return to those measured prior to egg laying may be due to the onset of moult. Between collections 2 and 3, internal tissue mercury levels dropped still further (Tables 6.1 & 6.2) as moult and feather growth was underway. This loss of mercury via the feathers, once mobilised as a consequence of reproduction, clearly points towards the feathers as being the major eliminatory pathway for mercury. Such a finding agrees with the well-documented examples for other species (Braune & Gaskin, 1987; Furness et al., 1986; Honda et al., 1986a). It is of note that the mercury levels in guillemot feather samples exhibited no significant seasonal trend over the three collection dates (Table 6.1 & 6.2).

There was a fair degree of correlation of mercury concentrations between internal tissues (particularly liver and kidney tissues), birds with relatively high mercury levels in one tissue tending to have correspondingly high levels in other tissues (see Results section). Such inter-tissue correlations have been found in a variety of other species (Fimreite, 1974; Furness & Hutton, 1979; Hutton, 1981; Ohlendorf et al., 1985; see also Chapter 5) and would indicate that mercury is able to accumulate in a range of internal tissues, although highest levels have been invariably found in liver and kidney tissues (Table 6.1). The single, weak correlation between liver and body feather mercury concentrations in sample 3 birds only (r=0.47,

$P<0.05$) may be a result of body feathers being relatively unimportant in terms of mercury loss (see above). It may be, as with great skuas *Catharacta skua* (Chapter 5), that internal tissue mercury concentrations would correlate more strongly with those mercury levels in first-moulted feathers (flight feathers).

Overall, it would appear that for birds which undergo a complete annual feather moult and which are exposed to relatively low levels of mercury, feather growth, following moult, would constitute the major eliminatory pathway for mercury. The egg, although likely to contain mercury at levels comparable to those found in other studies of this species (Barrett *et al.*, 1985; Dyck & Kraul, 1984), appeared to be relatively unimportant as an excretory route. More mercury than was calculated to be contained in the egg was found to be lost from internal tissues over the egg laying period. The processes by which mobilisation of mercury takes place during the reproductive process, and those which would appear to prevent larger amounts of mercury being lost via the egg(s) would seem to warrant further investigation.

6.5 REFERENCES

Barrett, R.T., Skaare, J.U., Norheim, G., Vader, W. & Froslie, A. (1985). Persistent organochlorines and mercury in eggs of Norwegian seabirds 1983. Environ. Pollut. (A) 39, 79-93.

Becker, P.H., Conrad, B. & Sperveslage, H. (1989). Chlororganische Verbindungen und Schwermetalle in weiblichen Silbermowen (Larus argentatus) und ihren Eiern mit bekannter Legefolge. Die Vogelwarte 35, 1-10. (English summary).

Becker, P.H., Ternes, W. & Russel, H.A. (1985). Schadstoffe in Gelegen von Brutvogeln der deutschen Nordseekuste. II. Quecksilber. J. Orn. 126, 253-262. (English summary).

Birkhead, T. R. (1980). Timing of breeding of common guillemots Uria aalge on Skomer Island, Wales. Ornis Scand. 11, 142-145.

Birkhead, T.R. & Harris, M.P. (1985). Ecological adaptations for breeding in the Atlantic Alcidae. In, The Atlantic Alcidae. Nettleship, D.N. & Birkhead, T.R. (eds.). Academic Press, London.

Birkhead, T.R. & Taylor, A.M. (1977). Moult of the guillemot Uria aalge. Ibis 119, 80-85.

Boalch, R., Chan, S. & Taylor, D. (1981). Seasonal variation in the trace metal content of Mytilus edulis. Mar. Pollut. Bull. 12, 276-280.

Born, E.W., Kraul, I. & Kristensen, T. (1981). Mercury, DDT and PCB in the Atlantic walrus (Odobenus rosmarus rosmarus) from the Thule District, north Greenland. Arctic 34, 255-260.

Braune, B.M. & Gaskin, D.E. (1987). Mercury levels in Bonaparte's gulls (Larus philadelphia) during autumn moult in the Quoddy Region, New Brunswick, Canada. Arch. Environ. Contam. Toxicol. 16

De Clerck, R., Vanderstappen, R. & Vyncke, W. (1974). Mercury content of fish and shrimps caught off the Belgian coast. Ocean Manage. 2, 117-126.

Dyck, J. & Kraul, I. (1984). Environmental pollutants and shell thinning in eggs of the guillemot Uria aalge from the Baltic Sea and the Faeroes, and a possible relation between shell thickness and sea water salinity. Dansk Orn. Foren. Tidsskr. 78, 1-14.

Essink, K. (1985). Monitoring of mercury pollution in Dutch coastal waters by means of the teleostean fish Zoarces viviparus. Neth. J. Sea Res. 19, 177-182.

Falandysz, J., Jakuczun, B. & Mizera, T. (1988). Metals and organochlorines in four female white-tailed eagles. Mar. Pollut. Bull. 19, 521-526.

Fimreite, N. (1974). Mercury contamination of aquatic birds in northwestern Ontario. J. Wildl. Manage. 38, 120-131.

Freeman, H.C. & Horne, D.A. (1973). Mercury in Canadian seals. Bull. Environ. Contam. Toxiol. 10, 172-180.

Furness, R.W. & Hutton, M. (1979). Pollutant levels in the great skua Catharacta skua. Environ. Pollut. 19, 261-268.

Furness, R.W., Muirhead, S.J. & Woodburn, M. (1986). Using bird feathers to measure mercury in the environment: relationships between mercury content and moult. Mar. Pollut. Bull., 17, 27-30.

Ginn, H.B. & Melville, D.S. (1983). Moult in BIrds. British Trust for Ornithology, Tring.

Harris, M.P. & Birkhead, T.R. (1985). Breeding biology of the Atlantic Alcidae. In, The Atlantic Alcidae. Nettleship, D.N. & Birkhead, T.R. (eds.). Academic Press, London.

Harris, M.P. & Wanless, S. (1988). The breeding biology of guillemots Uria aalge on the Isle of May over a six year period. Ibis 130, 172-192.

Heinz, G. (1974). Effects of low dietary levels of methyl mercury on mallard reproduction. Bull. Environ. Contam. Toxicol. 11, 386-392.

Honda, K., Nasu, T. & Tatsukawa, R. (1986a). Seasonal changes in mercury accumulation in the black-eared kite, Milvus migrans lineatus. Environ. Pollut. (A) 42, 325-334.

Honda, K., Yamamoto, Y., Hidaka, H. & Tatsukawa, R. (1986b). Heavy metal accumulations in Adelie penguins Pygoscelis adeliae and their variations with the reproductive process. Mem. Natl. Inst. Polar Res., Spec. Issue 40, 443-453.

Hutton, M. (1981). Accumulation of heavy metals and selenium in three seabird species from the United Kingdom. Environ. Pollut. (A) 26, 129-145.

Itano, K., Kawai, S., Miyazaki, N., Tatsukawa, R. & Fujiyama, T. (1984). Mercury and selenium levels in striped dolphins caught off the Pacific coast of Japan. Agric. Biol. Chem. 48, 1109-1116.

Kari, T. & Kauranen, P. (1978). Mercury and selenium contents of seals from fresh and brackish waters in Finland. Bull. Environ. Contam. Toxicol. 19, 273-280.

Kim, K.C., Chu, R.C. & Barron, G.P. (1974). Mercury in tissues and lice of northern fur seals. Bull. Environ. Contam. Toxicol. 11, 281-284.

Mason, C.F. & Reynolds, P. (1988). Organochlorine residues and metals in otters from the Orkney Islands. Mar. Pollut. Bull. 19, 80-81.

Nordberg, G.F. & Skerfving, S. (1972). Metabolism. In, Mercury in the Environment. Friberg, L. & Vostal, J. (eds.). CRC Press, Cleveland, Ohio.

Norusis, M.J. (1984). Advanced Statistics SPSS/PC+. SPSS Inc., Chicago, Illinois.

Ohlendorf, H.M., Anderson, D.W., Boellstorff, D.E. & Mulhern, B.M. (1985). Tissue distribution of trace elements and DDE in brown pelicans. Bull. Environ. Contam. Toxicol. 35, 183-192.

Ohlendorf, H.M. & Harrison, C.S. (1986). Mercury, selenium, cadmium and organochlorines in eggs of three Hawaiian seabird species. Environ. Pollut. (B) 11, 169-191.

Pentreath, R.J. (1976). The accumulation of mercury from food by the plaice, Pleuronectes platessa. J. exp. mar. Biol. Ecol. 25, 51-65.

Phillips, D.J.H. (in press). Use of macroalgae and invertebrates as monitors of metal levels in estuaries and coastal waters. In, Heavy Metals in the Marine Environment. Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

Rainbow, P.S. (in press). Heavy metal levels in marine invertebrates. In, Heavy Metals in the Marine Environment. Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

Ratcliffe, D.A. (1970). Changes attributable to pesticides in egg breakage frequency and eggshell thickness in some British birds. J. appl. Ecol. 7, 67-107.

Reijnders, P.J.H. (1980). Organochlorine and heavy metal residues in harbour seals from the Wadden Sea and their possible effects on reproduction. Neth. J. Sea Res. 14, 30-65.

Renzoni, A., Focardi, S., Fossi, C., Leonzio, C. & Mayoz, J. (1986). Comparison between concentrations of mercury and other contaminants in eggs and tissues of Cory's shearwater Calonectris diomedea collected on Atlantic and Mediterranean islands. Environ. Pollut. (A) 40, 17-35.

Ronald, K., Frank, R.J. & Dougan, J. (1984). Pollutants in harp seals (Phoca groenlandica). II. Heavy metals and selenium. Sci. Tot. Environ. 38, 153-166.

Scott, M.L., Zimmermann, J.R., Marinsky, S., Mullenhoff, P.A., Rumsey, G.L. & Rice, R.W. (1975). Effects of PCBs, DDT and mercury compounds upon egg production, hatchability and shell quality in chickens and Japanese quail. Poultry Sci. 54, 350-368.

Spann, J.W., Heath, R.G., Kreitzer, J.F. & Locke, L.N. (1972). Ethyl mercury p-toluene sulfonanilide: lethal and reproductive effects on pheasants. Science 175, 328-331.

Thompson, D.R. (in press). Metal levels in marine vertebrates.

In, Heavy Metals in the Marine Environment. Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

Yamamoto, Y., Honda, K., Hidaka, H. & Tatsukawa, R. (1987). Tissue distribution of heavy metals in Weddell seals (*Leptonychotes weddellii*). *Mar. Pollut. Bull.* 18, 164-169.

CHAPTER 7

The form of mercury in seabird feathers and historical changes in mercury levels in some British seabirds

7.1 A COMPARISON OF THE LEVELS OF TOTAL AND ORGANIC MERCURY IN SEABIRD FEATHERS

Within the marine environment, mercury can exist in both organic and inorganic forms. Of these, organic (methyl) mercury is generally more toxic to marine organisms (Bryan, 1984) and tends to accumulate up marine food chains to a greater extent than inorganic mercury or other metals (Bryan, 1979). Because methyl mercury is lipid soluble while inorganic mercury is not, their distributions between animal tissues differ. Marine vertebrates have been shown to exhibit different proportions of these two forms of mercury, depending on such factors as trophic status, tissue analysed, age and adaptive abilities to biotransform organic mercury into inorganic mercury (Thompson, in press). The relative proportions of the two forms of mercury have been studied less in seabirds than in marine fish and mammals. All such studies of birds have concentrated on mercury determinations for internal tissues (Fimreite, 1974; Norheim _et al._, 1982; Norheim & Froslie, 1978; Osborn _et al._, 1979). In this paper data are presented for total and organic mercury concentrations in seabird feathers from a range of species. The implications for studies using feather samples from museum collections to investigate historical trends in mercury contamination are discussed.

All feather samples were taken from apparently healthy adult birds during the breeding season. Samples of four to ten body feathers were taken (Furness _et al._, 1986), dried at 15-25^{o}C and stored in mercury-free polythene bags. The species and sites sampled were as follows: wandering albatross _Diomedea exulans_ from Gough Island (South Atlantic Ocean) and Marion Island (Indian Ocean); sooty albatross _Phoebetria fusca_ from

Gough Island; northern fulmar Fulmarus glacialis, shag Phalacrocorax aristotelis, great skua Catharacta skua, Arctic skua Stercorarius parasiticus, kittiwake Rissa tridactyla, razorbill Alca torda, common guillemot Uria aalge and puffin Fratercula arctica from Foula (Shetland). For comparisons between total and organic mercury levels, sufficiently large feathers were split longitudinally, the halves being analysed either for total or organic mercury. For species where the body feathers were too small to split in this way, discrete samples of several small feathers were analysed separately for total or for organic mercury.

The method used for organic mercury extraction from feathers was adapted from that described by Uthe et al. (1972) for methyl mercury extraction from fish tissue. Initially, the large feather keratin molecules were 'broken down' using 4ml 10M sodium hydroxide in a water bath at 60^{o}C for 2 hours which was subsequently neutralised using sulphuric acid. Organic mercury was then removed in the form of methyl mercuric thiosulphate for subsequent analysis (see Uthe et al., 1972). Because the analyser used is sensitive to the presence of toluene, problems with minute quantities of toluene contaminating the sodium thiosulphate were overcome by placing the sample in a water bath at 60^{o}C for 1 hour prior to proceeding with mercury analysis. This resulted in traces of toluene being driven off.

Extracted organic mercury and total (organic plus inorganic) mercury levels were determined by a cold vapour absorption spectrophotometry technique using a Data Acquisition Ltd. DA 1500-DP6 Mercury Vapour Detector, preceeded by standard acid digestion of samples as outlined by Furness et al. (1986).

The efficiency and repeatability of the organic mercury extraction method was tested by using standard solutions of methyl mercuric chloride. Thirteen replicate extractions of ca. 2040 ng mercury and 14 replicate extractions of ca. 408 ng mercury as methyl mercuric chloride were made and compared to total mercury determinations of the same quantities. The efficiency of the extractions was found to average 90.04% (0.81 s.e.). The method was further tested for matrix effects by performing organic mercury extractions of eight feather samples spiked with known amounts of methyl mercuric chloride solution. The extraction efficiency of the spiked samples was found to be identical to that of methyl mercuric chloride solution, indicating no significant matrix effects. All feather organic mercury levels presented in this paper have been corrected for the 90.04% efficiency found for the method. Six samples each of 100 ng, 1000 ng and 10,000 ng mercuric (II) nitrate, together with six blank samples, were subjected to the extraction procedure; no inorganic mercury was extracted, there being no statistically significant difference in the mean readings obtained from blank extractions and from inorganic mercury extractions (Kruskal-Wallis 1-way ANOVA). Blank mercury levels were usually between 3 and 4 ng. The precision and accuracy of mercury determination were tested by analysis of International Atomic Energy Agency horse kidney Reference Material H-8 for total mercury. The results obtained (mean= 0.88 $\mu g\ g^{-1}$ dry weight; s.d.= 0.02; n= 7) were well within the 95% confidence limits of the mean of the accepted results presented by the Agency (mean= 0.91 $\mu g\ g^{-1}$ dry weight; s.d.= 0.16; 95% confidence limits= 0.83-0.98; n= 19 accepted laboratory averages combined, based on 85 accepted individual determinations). All solutions were freshly made up prior to use; chemicals used were of

'Puranal', 'Analar' or 'Spectrosol' grades throughout.

The results of the total mercury and organic mercury analyses are presented in Table 7.1.1. Mercury level data (both total and organic) for wandering albatrosses from Gough Island and Marion Island have been combined since there was no significant difference between the concentrations from these two localities. None of the ten species showed a statistically significant difference between mean organic and mean total mercury levels measured in feathers. For the ten species taken together, organic mercury represented an average of 100.8% of total mercury, implying that virtually all mercury in the feathers was organic. Deviations from 100% for particular species appear to be due to chance effects alone.

The fact that all mercury deposited into seabird feathers during their growth is organic mercury, and the fact that inorganic mercury is not extracted by the technique described above, have implications for the measurement of mercury in feather samples used to elucidate changes in historical levels of mercury contamination of the environment. Several authors have used total mercury measurements of feathers taken from museum specimens to investigate trends in mercury levels over time (Appelquist et al., 1985; Berg et al., 1966; Doi et al., 1984; Somer & Appelquist, 1974). These studies took no account of the form of mercury present in the feathers analysed and several encountered problems due to contamination through study skin preservation processes which often involved the application of inorganic mercury. This problem is clearly demonstrated by a total mercury level of 495 $\mu g\ g^{-1}$ measured in a feather sample taken from a white-tailed eagle Haliaeetus albicilla killed in 1890 and preserved in the Royal Scottish Museum, Edinburgh. Such

TABLE 7.1.1: Total and organic mercury levels (µg g^{-1} fresh weight) in seabird body feathers. Organic mercury levels are corrected for the measured mean extraction efficiency of 90.04%.

Species	No. Sampled	Total Mercury Mean	s.d.	Median	Organic Mercury Mean	s.d.	Median	Organic Hg as % of Total
Wandering albatross	26	30.7	11.7	29.2	29.2	11.6	32.3	95
Sooty albatross	7	9.4	3.9	8.5	9.1	4.0	8.8	97
Northern fulmar	15	1.8	0.8	1.8	2.0	0.7	2.0	111
Shag	14	1.7	0.7	1.5	2.0	0.8	1.8	118
Great skua	14	6.8	4.4	5.8	7.3	5.5	4.9	107
Arctic skua	9	2.2	1.7	1.9	1.7	1.8	1.3	77
Kittiwake	14	2.4	0.6	2.4	2.2	0.7	2.3	92
Razorbill	16	2.1	0.3	2.1	2.1	0.6	2.2	100
Common guillemot	17	1.5	0.4	1.4	1.7	0.5	1.8	113
Puffin	10	5.2	2.7	4.8	5.1	2.1	4.1	98

Wandering albatrosses from Gough Island and Marion Island; sooty albatrosses from Gough Island; all other species from Foula, Shetland Isles. s.d.= Standard deviation.

a value is clearly due to museum contamination with inorganic mercury since levels in uncontaminated contemporary specimens are generally less than 10 µg g^{-1} (Thompson, unpublished data). Such erroneous results can be discarded, but it is difficult to draw a line between high natural levels and slightly contaminated ones.

The results presented in this paper for organic mercury content of seabird feathers indicate that all the mercury is present as organic mercury. Therefore, by applying an organic mercury extraction method to museum feather samples, any problems due to inorganic mercury contamination will be avoided. This provides reliable and meaningful results and should make the subjective discarding of apparently contaminated results (for example, Berg _et_ _al._, 1966) unnecessary.

The fact that all the mercury in body feathers of all seabirds studied is organic mercury is of interest since it has been found that wandering and sooty albatrosses accumulate extremely large quantities of inorganic mercury in their liver tissues (Thompson & Furness, 1989). Although the vast majority (more than 90%) of the mercury in the albatrosses' liver tissues is inorganic, none or only a tiny proportion of the feather mercury was found to be in this form. This would appear to indicate that inorganic mercury in the liver is immobilised and, unlike organic mercury, cannot circulate in the blood and become incorporated into feathers. Thus feathers provide a means of measuring organic mercury levels in birds that avoids problems due to post-mortem contamination with inorganic mercury, but feathers cannot provide information on the stores of inorganic mercury held in the liver of some seabird species.

7.2 HISTORICAL CHANGES IN MERCURY LEVELS IN SOME BRITISH SEABIRDS

7.2.1 Introduction

Examples of local, relatively well-defined pollution due to anthropogenic emissions of mercury to the environment have been well documented. Mercury, of both industrial and agricultural origin, has been shown to be the cause of major toxicological problems, and in some cases human fatalities, in Japan (Kurland et al., 1960), Iraq (Bakir et al., 1973) and Sweden (Borg et al., 1969; Johnels & Westermark, 1969). Demonstrating a general and widespread increase in mercury concentrations within whole environments, associated with an increase in human use, and atmospheric and marine transportation of mercury, over the past 150 years, has proved more difficult.

Attempts have been made to measure mercury concentrations in polar ice-core samples (for example, Appelquist et al., 1978), in order to assess any changes in mercury deposition in these relatively remote regions. Such investigations have been hampered by the analytical difficulties associated with the measurement of the extremely low mercury levels (ca. 1-10 pg g^{-1}) in ice samples. Furthermore, the low mercury levels have led to problems with sample contamination and reliable mercury data have been difficult to obtain (see Wolff, in press).

Complementary to the use of ice-core samples have been the various studies incorporating mercury determinations in historical and contemporary biological samples. Since biological samples accumulate mercury to concentrations five to nine orders of magnitude higher than found in ice/snow samples, analytical difficulties in measuring the mercury levels are much reduced, and any contamination of samples, although undesirable, becomes less of a problem. Peat core samples have been used to investigate changes in mercury deposition (Madsen, 1981), since mercury is taken up by bog plants and retained by the humic substances in peat. Madsen (1981) found an increase in mercury deposition in two bogs in Denmark which paralleled known trends in consumption of mercury in Europe between 1740 and 1980. In addition, volcanic activity in Iceland was suggested as being the likely cause of some relatively well-defined periods of elevated mercury deposition rates.

Following the confiscation of large, pelagic, commercial fish, such as swordfish, marlin and tuna, by the U.S. Food and Drug Administration when it was thought that the relatively high mercury levels measured in these groups were the result of anthropogenic emissions of mercury to the marine environment, several workers investigated the trends in mercury concentration in marine fish over time (Barber et al., 1972; Miller et al., 1972). These studies concluded that mercury levels were not significantly different between old and contemporary fish samples. However, the sample sizes in both studies were small. Miller et al. (1972) compared mercury concentrations between seven preserved tuna and one preserved swordfish head with five contemporary tuna and six contemporary swordfish. Similarly, Barber et al. (1972) compared mercury levels between fresh benthopelagic fish with those in only two preserved specimens, of different species. Clearly, any historical change in mercury concentration will be difficult to detect given such small sample sizes, especially since mercury levels in muscle tissues of such pelagic species of fish tend to exhibit great individual variation (for example, Mackay et al., 1975).

Human hair has also been utilised to assess changes in mercury levels over time. Mercury concentrations in hair samples from mummified Inuit from northwest Greenland have been compared to contemporary samples, and these indicate an increase in hair mercury content over the past 500 years (Hansen, in press).

In a study of mercury levels in preserved and contemporary polar bear *Ursus maritimus* hair samples, Eaton & Farant (1982) concluded that no real increase in mercury levels had taken place. It would seem likely, however, that many of the historical samples analysed in that study had suffered contamination with inorganic mercury, probably as part of the preservation process, a fact recognised by the authors. If organic mercury alone was considered, the form of mercury in which the vast majority of mercury exists in polar bear hair (Eaton & Farant, 1982), in those adult animals from a comparable geographical location, a four-fold increase in mercury levels is observed between 1910-27 and 1977. Andersen & Rebsdorff (1976) determined the mercury concentration in the skin of three harbour porpoises *Phocoena phocoena* from 1936-1943 which had been preserved in 70% ethanol, and compared the results with contemporary specimens. Such small sample sizes, however, preclude any firm conclusions.

Analysis of time series of feather samples from bird populations has also proved to be a popular approach for the elucidation of historical trends in mercury contamination (Appelquist *et al.*, 1985; Berg *et al.*, 1966; Doi *et al.*, 1984; Somer & Appelquist, 1974). Berg *et al.* (1966) noted an increase in mercury levels in birds' feathers associated with the use of alky mercury as a seed dressing in Sweden. Appelquist *et al.* (1985), in a study of guillemots *Uria aalge*, *U. lomvia* and *Cepphus grylle*, noted an increase in mercury burdens during this century in those birds from the Baltic Sea, compared to fairly constant mercury levels in birds from Greenland and the Faeroe Islands. However, the form of mercury in bird feathers was not considered and measurements of total mercury were made using neutron activation analysis techniques. Even if feather samples are thoroughly washed, it is very difficult to remove all inorganic mercury, often applied as a preservative. Hence, 'total' mercury determinations are likely to incorporate any such contamination, leading to erroneous, elevated results. This has led to the subjective discarding of high mercury values (Berg et al., 1966), an approach which requires a thorough understanding of mercury levels in a given species, but one which will always be prone to the discarding of values which are naturally high. Despite these problems, birds make ideal subjects for work of this nature: preserved study skin collections are large and well documented, allowing relatively large numbers of feather samples to be obtained from accurately dated birds. Mercury bound to the feather keratin molecules is resistent to a variety of treatments (Appelquist et al., 1984) and feathers are likely to be less prone to physical and chemical change compared to internal tissues, such as fish muscle samples. Furthermore, recent work has shown that virtually all the mercury present in seabird feathers is organic (methyl) mercury (Thompson & Furness, in press; Chapter 7.1). The authors of that study concluded that by measuring feather methyl mercury alone, as opposed to feather total mercury, more meaningful and reliable results would be obtained from historical samples which may have been contaminated with inorganic mercury.

In this study, feather samples from a range of British seabird species from the past 150 years have been obtained from museum collections and analysed for methyl mercury, the mercury levels being compared to contemporary mercury concentrations to assess any changes in mercury burdens of these seabirds over this time period.

7.2.2 Materials and methods

7.2.2.1 Sample collection and preparation

Contemporary feather samples were obtained from apparently healthy adult (unless otherwise stated) birds during the breeding season. Species and sites sampled were as follows: northern fulmar from St. Kilda and Foula, Shetland; Manx shearwater *Puffinus puffinus* (dead adults) from Skomer, south west Wales; gannet *Sula bassana* adults and juveniles from the Bass Rock; great skua from Foula; puffin from Foula. In all cases, four to ten body feathers were taken if available (Furness *et al.*, 1986) and placed in mercury-free polythene bags prior to analysis. In a few cases wing covert feathers were taken when bodies were not available.

Historical feather samples, from the same species as outlined above, were obtained from preserved study skins held in the Royal Scottish Museum, Edinburgh, the Hancock Museum, Newcastle upon Tyne and the British Museum (Natural History), Tring. In all cases, body feathers were taken and placed in mercury-free polythene bags prior to washing and analysis. Historical and contemporary feather samples were also obtained from herring gulls *Larus argentatus*, lesser black-backed gulls *Larus fuscus*, great black-backed gulls *Larus marinus* and guillemots. For these species there was insufficient geographical compatability within historical samples, and hence, between historical and contemporary samples, to allow a meaningful assessment of trends in the mercury burdens of these species. Although feather mercury levels in puffins were compared from a variety of locations, there was a strong south and west bias to the historical samples (see Appendix 1).

Although the organic mercury extraction technique discriminates against inorganic mercury (Thompson & Furness, in press; Chapter 7.1), such mercury, applied as a preservative, and other contamination will alter the weight of the feathers; all museum feather samples were subjected to the washing regime described in Chapter 3 in order to remove any gross surface contamination. Washed, historical feather samples were then subjected to the organic mercury extraction procedure (Chapter 3).

7.2.2.2 Analysis of mercury levels

Historical feather samples were analysed for methyl mercury by performing an initial fractionation of the sample to remove only the methyl mercury present (Thompson & Furness, in press; Chapters 3 & 7.1). For 142 individuals of a range of seabird species (n=10), the feather methyl mercury level was found to represent 100.8% of the total mercury level and, for any given species, there was no significant difference between mean methyl and mean total mercury concentrations (Thompson & Furness, in press; Chapter 7.1). Hence, methyl mercury determinations of historical samples, once corrected for the level of efficiency of the extraction technique (90.04%), were equivalent to total mercury levels, the latter measurement being made for contemporary samples (Chapter 3).

Spearman Rank Order Correlation Coefficients (r_S) were calculated for each species in order to assess any change in mercury levels over time. Mann-Whitney U-tests were used to compare between median feather mercury levels before and after 1950 (all contemporary samples, except one adult gannet sample from 1951, were obtained during the 1980s). The word 'significant' has been used in the statistical context only, indicating a chance occurrence of less than 5%.

7.2.3 Results

Spearman Rank Order Correlation Coefficients (r_s) for feather mercury concentrations with change in time for all species studied are presented in Table 7.2.1. Manx shearwaters from south-west Britain, juvenile gannets from the Bass Rock, great skuas from Shetland/Orkney, and puffins from all locations exhibited significant positive trends in feather mercury levels over time; fulmars from Shetland/Orkney exhibited a significant and negative trend in feather mercury levels over time whilst for other comparisons (n=2) trends were not significant (Table 7.2.1; Figures 7.1-7.5). For puffins, mercury levels in historical samples alone exhibited a significant positive trend over time (r_s= 0.32, $P<0.05$; covering the years 1842-1921, inclusive). Changes in median mercury levels before and after 1950 are presented in Table 7.2.2. Mercury concentration data for contemporary samples are summarised in Table 7.2.3. All historical samples analysed, including some results not presented here, are included in Appendix 1.

7.2.4 Discussion

Although no historical samples were analysed for total mercury in order to assess the extent of inorganic mercury contamination from the museum collections sampled (there was generally insufficient material from such unique samples to

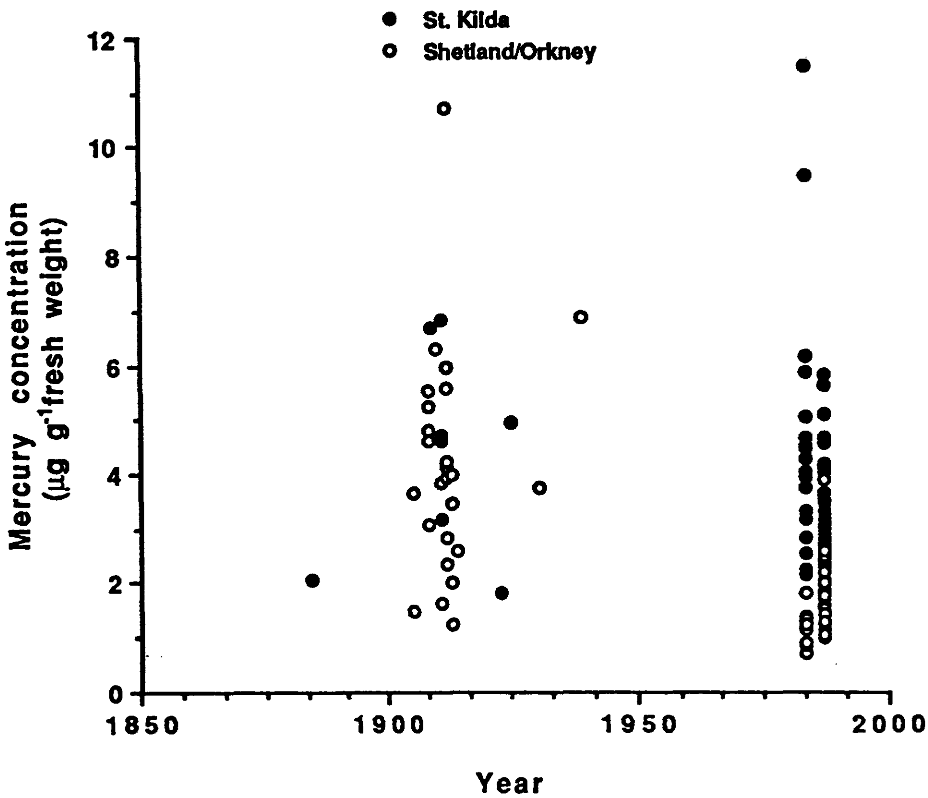

Fig. 7.1 Temporal changes in feather mercury concentration of fulmars _Fulmarus glacialis_ from St. Kilda (r_s= -0.09, N.S., n= 93) and Shetland/Orkney (r_s= -0.55, P< 0.0001, n= 53)

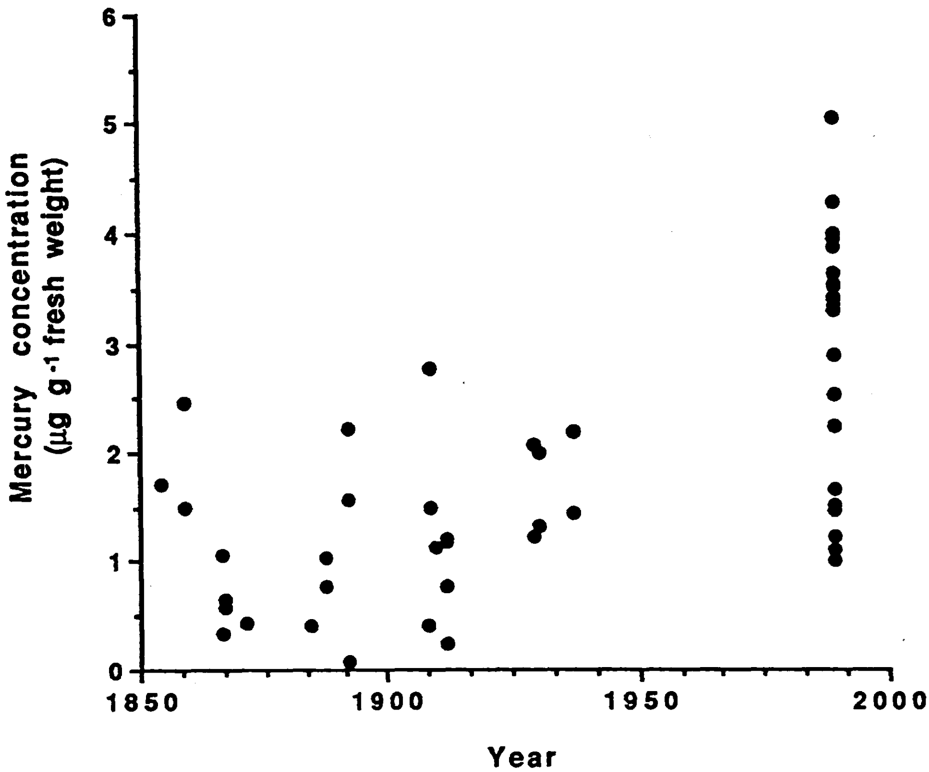

Fig. 7.2 Temporal changes in feather mercury concentration of Manx shearwaters Puffinus puffinus from south-west Britain and Ireland (r_s= 0.65, $P < 0.0001$, n= 50)

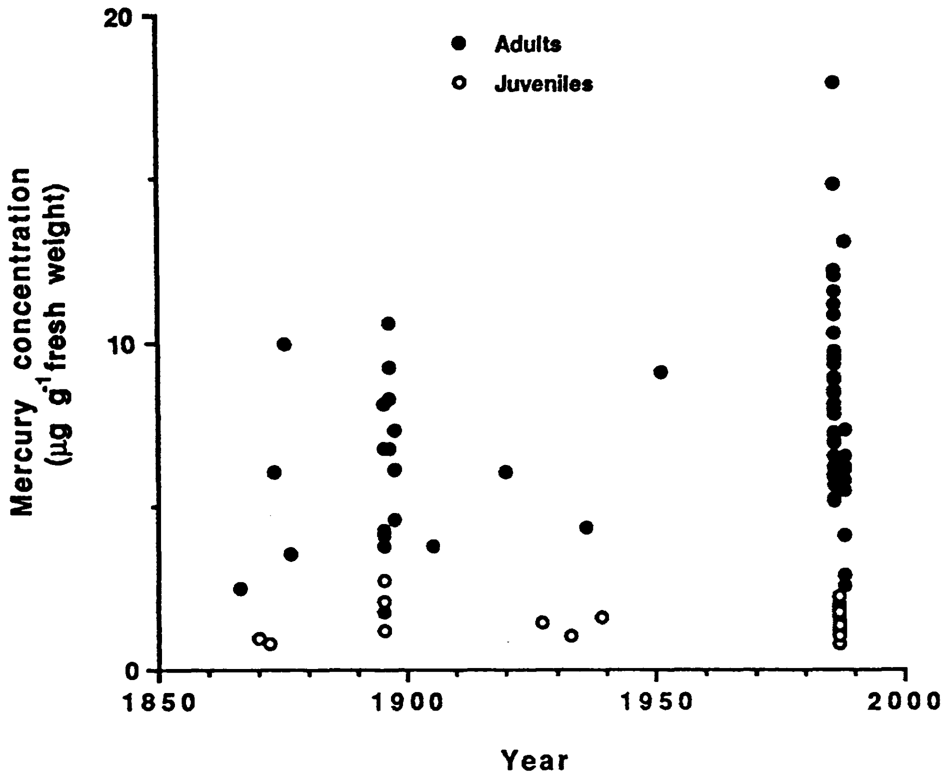

Fig. 7.3 Temporal changes in feather mercury concentration of gannets Sula bassana from the Bass Rock (Adults r_s= 0.13, N.S., n= 66; Juveniles r_s= 0.33, P< 0.05, n= 38)

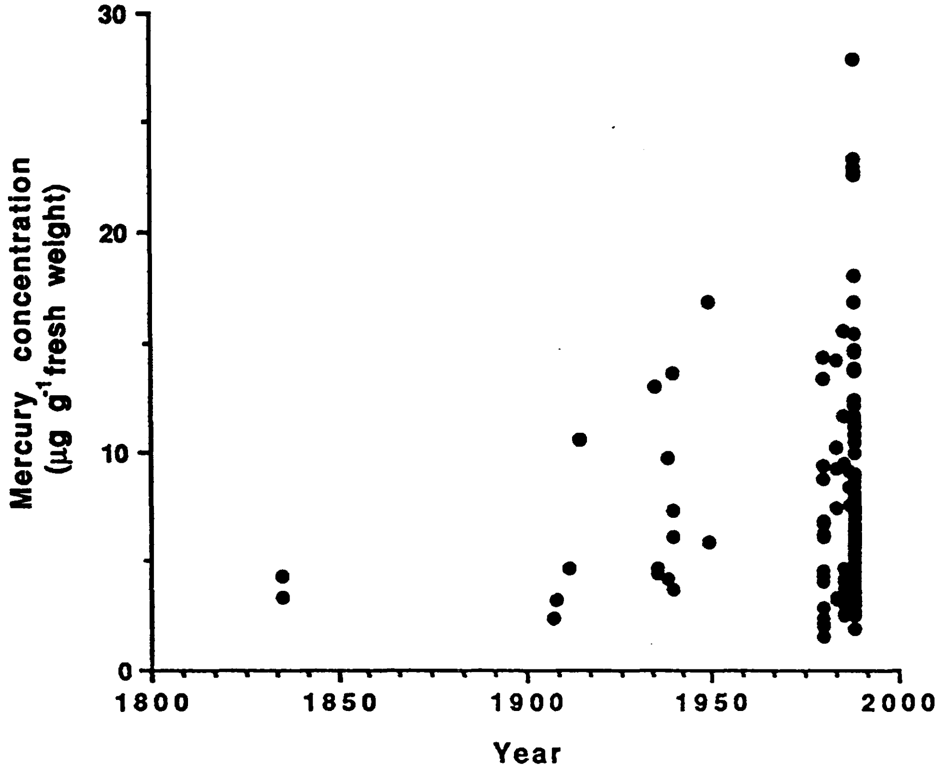

Fig. 7.4 Temporal changes in feather mercury concentration of great skuas Catharacta skua from Shetland and Orkney (r_s= 0.24, $P < 0.01$, n= 169)

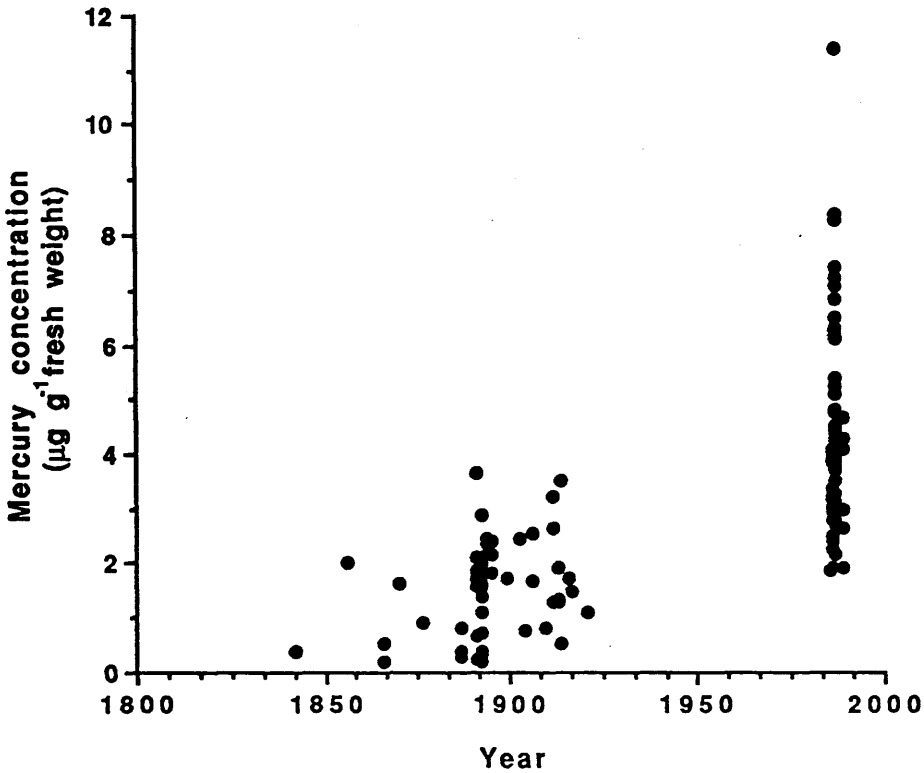

Fig. 7.5 Temporal changes in feather mercury concentration of puffins <u>Fratercula arctica</u> from throughout Britain and south and west Ireland (r_s= 0.74, P< 0.0001, n= 116)

TABLE 7.2.1: Spearman Rank Order Correlation Coefficients (r_s) between feather mercury concentrations and year of sampling for British seabirds.

Species	Location	Number birds analysed (years covered)	r_s	Significance
Fulmar	St. Kilda	93 (1884-1987)	-0.09	N.S.
	Shetland/ Orkney	53 (1905-1987)	-0.55	$P<0.0001$
Manx Shearwater	S-W Britain/ S-W Ireland	50 (1854-1989)	0.65	$P<0.0001$
Gannet (Ad.)	Bass Rock	66 (1866-1988)	0.13	N.S.
(Juv.)	Bass Rock	38 (1870-1987)	0.33	$P<0.05$
Great skua	Shetland/ Orkney	169 (1835-1988)	0.24	$P<0.01$
Puffin	All Britain/ S-W Ireland	116 (1842-1989)	0.74	$P<0.0001$

Ad.= Adult; Juv.= Juvenile; N.S.= Not significant.

allow for two destructive analyses to be performed), it was clear that many feathers obtained from study skins were heavily coated with preservative. Indeed, Muirhead (1986) reported total mercury levels in feather samples from preserved Faeroese and Icelandic great skuas from the British Museum (Natural History, Tring) which were considerably greater than those found for the same individuals analysed in this study using the extraction technique (see Appendix 1). Such variations were presumably due to inorganic mercury preservative.

It is clear from the results of assessments of changes in

TABLE 7.2.2: Changes in median feather mercury levels before and after 1950 for the species studied; Mann-Whitney U-test comparing the median mercury levels of the two periods.

Species	Pre-1950	Post-1950	% Change	M-W U-test
Fulmar				
St. Kilda	4.68 (8)	2.82 (85)	-66	N.S.
Shetland/ Orkney	3.97 (26)	1.32 (27)	-201	P<0.0001
Manx shearwater	1.19 (28)	3.33 (22)	+180	P<0.0001
Gannet				
Adult	6.00 (22)	7.24 (44)	+21	P<0.05
Juvenile	1.34 (8)	1.48 (30)	+10	N.S.
Puffin	1.63 (54)	3.98 (62)	+144	P<0.0001

Values in brackets are sample sizes.

mercury burdens with time (Tables 7.2.1 & 7.2.2) that there is no one, clear pattern. Four of the five species studied exhibited significant increases in body feather mercury concentrations over time whilst one species showed a significant negative trend. No significant trends in body feather mercury levels over time were noted in St. Kildan fulmars.

A similar pattern is seen when pre-1950 and post-1950 mercury levels were compared, although using this approach, adult gannets exhibited a significant increase in mercury levels between the two periods (Mann-Whitney U-test, $P<0.05$) whilst the increase in great skua feather mercury levels was not

TABLE 7.2.3: Body feather mercury concentrations ($\mu g\ g^{-1}$ fresh weight) from contemporary seabirds.

Species	Locality	Year	n	Mean	S.D.	Median
Fulmar	Foula	1983	12	1.14	0.31	1.17
	Foula	1987	15	1.84	0.76	1.77
	St. Kilda	1983	19	4.58	2.40	4.04
	St. Kilda	1987	66	2.92	0.94	2.77
Manx shearwater	Skomer	1989	22	2.92	0.94	3.33[a]
Gannet (Ad.)	Bass Rock	1986	32	8.82	2.82	8.46[b]
	Bass Rock	1988	12	5.55	2.55	5.61[b]
(Juv.)	Bass Rock	1987	30	1.47	0.31	1.48[b]
Great skua	Foula	1980	17	5.80	3.86	4.47
	Foula	1988	108	7.45	4.92	5.85
	Noss	1985	13	5.55	4.06	3.75
Puffin	Foula	1986	20	3.11	0.65	3.11
	Foula	1987	13	5.41	2.52	5.11
	St. Kilda	1987	23	5.08	1.57	4.84
	Great Saltee	1989	6	3.44	1.08	3.56

n= Sample size; S.D.= Standard deviation; Ad.= Adult; Juv.= Juvenile; a= Samples collected by Dr C.M. Perrins from adults found dead at the colony; b= P.M. Walsh, unpublished data.

significant (Table 7.2.2).

Although virtually all samples analysed, both historical and contemporary, were obtained from birds during the breeding season, factors which may influence mercury levels outside this part of the year, when many of the species included in this study would be dispersed from the breeding areas, cannot be easily quantified. However, all of the species investigated undergo a complete post-nuptial moult (Ginn & Melville, 1983) which would tend to result in feather levels which would be representative of mercury accumulation in internal tissues since the preceding moult, and hence, in part, over the summer months when birds would have been breeding. The accumulation of mercury outwith the breeding season may mask any historical trend for a given breeding locality. The use of feather samples obtained from juveniles fledged during the year of sampling may overcome any such problems, since their feather mercury levels would tend to reflect the level of mercury contamination of a more clearly-defined area; that is, the area, radiating out from the breeding site, over which their parents forage for food.

Despite such potential limitations of this type of approach to the elucidation of historical trends in mercury contamination of the marine environment, several species studied showed distinct and significant changes in body feather mercury concentrations over time.

Mercury levels of feather samples obtained from fulmars from St. Kilda exhibited no significant change over time whilst those of feathers from Shetland/Orkney birds declined significantly during this century (Tables 7.2.1 & 7.2.2; Figure 7.1). St. Kilda (57^{o} $49^{'}$N 08^{o} $35^{'}$W) is a remote, oceanic island group which has held a breeding population of fulmars for several hundreds of years. Being on the edge of the continental shelf and far from any source of anthropogenic mercury, St. Kildan fulmars would have been unlikely to have experienced any dramatic change in exposure to mercury via the diet over the period from which samples were obtained. Hence, the lack of any significant trend in feather mercury levels over time was not entirely unexpected. A similar result was obtained for historical changes in mercury levels in guillemots from the Faeroe Islands and Greenland, both of which are relatively remote and far from anthropogenic sources of pollution (Appelquist _et al._, 1985).

Feather samples obtained from preserved 19th. century fulmars from Shetland/Orkney would, almost certainly, have consisted of individuals colonising these islands from Faeroe or Iceland. Foula was the first British island, other than St. Kilda, to hold breeding fulmars, the first proved breeding attempt being in 1878. It was thought that these colonists originated from the Faeroe Islands, and by 1911 there were approximately 100 pairs breeding in Orkney (Fisher, 1952). Hence, during the end of the 19th. century and the first 15 years of the 20th. century, the Shetland/Orkney fulmar population would have been made up, at least in part, of Faeroese birds, the proportion of which would presumably have declined with time as birds fledged from these new breeding locations were eventually recruited into the breeding population. The significant decline in feather mercury concentrations in fulmars from Shetland/Orkney with time (Tables 7.2.1 & 7.2.2; Figure 7.1) may, therefore, reflect a change in structure of the breeding population, rather than a drop in the mercury contamination of the environment. The are no available comparative data which would shed any light on mercury levels in Faeroese fulmars, past or present, although unpublished data (Furness) would indicate that mercury levels in other species tend to be somewhat higher from Iceland and Faeroe, compared to corresponding levels in birds from the north of Scotland. Work by Furness & Todd (1984) showed that the diets of fulmars breeding at St. Kilda and Foula were markedly different, there being vitually no overlap in species taken. Sandeels *Ammodytes marinus* and fish offal were found to be the major prey items of Foula birds (86% of samples) whilst pelagic zooplankton formed the major part of the diet of St. Kildan fulmars (71% of samples). This dietary difference is probably the major factor influencing the mercury levels in these two groups of fulmars, contemporary St. Kildan birds exhibiting significantly higher feather mercury concentrations than those at Foula (Mann-Whitney U-test, $P<0.0001$). Indeed, fish and whale offal availability was cited by Fisher (1952) as an important factor influencing the spread southwards of the fulmar, and by implication, the diet of Faeroese birds was and is likely to contain more pelagic zooplankton than the diet of Shetland/Orkney fulmars. It could be argued that if such a dietary difference existed between the colonising Faeroese birds and those of Shetland/Orkney origin, the former exhibiting higher mercury concentrations, a trend of decreasing feather mercury concentration with time would result, as the proportion of these birds in the population declined.

Great skuas from Shetland/Orkney exhibited a weak, but significant, increase in feather mercury concentrations over time (Table 7.2.1; Figure 7.4). Unlike the fulmars which colonised this region at and around the end of the 19th. century, great skuas have bred at two Shetland sites at least since 1774 (Furness, 1987). Immigration of birds was unlikely to have been important once the colonies became established, especially since declines in numbers due to persecution during the 19th. century did not seem to be 'offset' by continued immigration of individuals. Hence, compounding factors which may have influenced trends in mercury levels of fulmars at the same locations can be largely discounted for the great skua. The detected increase in feather mercury levels was not pronounced when compared to those measured in Manx shearwaters and puffins (Tables 7.2.1 & 7.2.2; Figures 7.2 & 7.5), generally from the south and west of Britain, but may reflect a general increase in the mercury burden of the marine environment.

It is interesting to note that, for those species for which contemporary individuals were compared with historical samples from the same, coastal locality, the most pronounced increase in feather mercury concentrations occurred in the south-west of Britain (Manx shearwaters and, to a lesser extent, puffins), with a modest increase in the north and east of Britain (great skuas and gannets; Tables 7.2.1 & 7.2.2; Figures 7.3 and 7.4, respectively). Gardner (1975) suggested that mercury, originating from industrial sources and carried by jet-streams, was eventually deposited along certain belts below such jet-streams. This resulted in elevated sea water mercury concentrations, including relatively high values obtained from the south-west approaches to the British Isles, in the north-east Atlantic. Furthermore, British coastal waters exhibited relatively high mercury concentrations, in part through surface run-off, but large amounts of suspended matter in the water, to which mercury has a high affinity, resulted in lower mercury concentrations compared to those resulting from jet-stream deposition (Gardner, 1975). Hence, sea water approaching Britain from the south-west is relatively rich in mercury, a significant component of which is of essentially industrial origin. As this water moves northwards around the Shetland and Orkney Isles and then southwards into the northern North Sea, there would be great potential for the mercury to be assimilated into the food chain and/or sequestered by suspended matter, and be gradually reduced in concentration. Indeed, Gardner (1975) commented that in areas of upwelling, rich in nutrients as well as in mercury, periodic blooms of plankton could strip mercury from the water and result in slightly lower sea water mercury concentrations, the mercury being transferred up the food chain. In a survey of mercury levels in British coastal waters, Baker (1977) found that mercury concentrations were generally higher towards the south and west, although localised 'hot-spots' (often associated with sewage dumping and/or riverine inputs) and sampling conditions influenced this overall view.

It could be argued, therefore, that mercury would be gradually removed from the water column as the flow of sea water progresses around the north of Scotland and into the North Sea. The likely results of such a pattern would not only be relatively high mercury concentrations in biota from the south-west of Britain, but also more pronounced historical increases in mercury levels in biota from these areas as a result of the jet-stream deposition of additional, industrial mercury. This pattern of a south-west to north-east 'mercury gradient' is supported by recent work on mercury levels in gannets from a range of British sites which clearly showed that burdens tend to be highest towards the south and west with lowest levels reported in birds from the Bass Rock off the east coast of Scotland (Walsh, 1988). The comparison of mercury levels in feathers from puffins in this study may well be conservative given this finding. Since the majority of historical samples were from the south and west of Britain and Ireland, it could be argued that such birds would tend to exhibit relatively high mercury levels as a result of breeding closer to naturally mercury-rich waters approaching Britain, regardless of time of sampling. Contemporary birds sampled from Foula and St. Kilda (Table 7.2.3) may, therefore, exhibit lower mercury levels than contemporary birds from the south and west.

In conclusion, it would appear that time series of feather samples, coupled with the organic mercury extraction procedure, provides a means by which historical changes in mercury contamination of the environment can be assessed. From these results, mercury concentrations in British seabirds seem to have generally increased over the last 150 years, although geographical clines of mercury availability, population movements and geographical compatability of samples all need to be considered in the interpretation of these data.

7.2.5 References

Andersen, S.H. & Rebsdorff, A. (1976). Polychlorinated hydrocarbons and heavy metals in harbour porpoise (Phocoena phocoena) and whitebeaked dolphin (Lagenorhynchus albirostris) from Danish waters. Aquat. Mamm. 4, 14-20.

Appelquist, H., Asbirk, S. & Drabaek, I. (1984). Mercury monitoring: mercury stability in bird feathers. Mar. Pollut. Bull. 15, 22-24.

Appelquist, H., Drabaek, I. & Asbirk, S. (1985). Variation in mercury content of guillemot feathers over 150 years. Mar. Pollut. Bull. 16, 244-248.

Appelquist, H., Jensen, K.O., Sevel, T. & Hammer, C. (1978). Mercury in the Greenland ice sheet. Nature 273, 657-659.

Baker, C.W. (1977). Mercury in surface waters of seas around the United Kingdom. Nature 270, 230-232.

Bakir, F., Damluji, S.F., Amin-Zaki, L., Murtadha, M., Khalidi, A., Al-Rawi, N.Y., Tikriti, S., Dhahir, H.I., Clarkson, T.W., Smith, J.C. & Doherty, R.A. (1973). Methylmercury poisoning in Iraq. Science 181, 230-241.

Barber, R.T., Vijayakumar, A. & Cross, F.A. (1972). Mercury concentrations in recent and ninety-year-old benthopelagic fish. Science 178, 636-639.

Berg, W., Johnels, A., Sjostrand, B. & Westermark, T. (1966). Mercury content in feathers of Swedish birds from the past 100 years. Oikos 17, 71-83.

Borg, K., Wanntorp, H., Erne, K. & Hanko, E. (1969). Alkyl mercury poisoning in Swedish wildlife. Viltrevy 6, 301-379.

Bryan, G.W. (1979). Bioaccumulation of marine pollutants. Phil. Trans. R. Soc. Lond. B 286, 483-505.

Bryan, G.W. (1984). Pollution due to heavy metals and their compounds. In, Marine Ecology, Kinno, O. (ed.). Wiley, Chichester. pp. 1289-1431.

Doi, R., Ohno, H. & Harada, M. (1984). Mercury in feathers of wild birds from the mercury polluted area along the shore of the Shiranui Sea, Japan. Sci. Tot. Environ. 40, 155-167.

Eaton, R.D.P. & Farant, J.P. (1982). The polar bear as a biological indicator of the environmental mercury burden. Arctic 35, 422-425.

Fimreite, N. (1974). Mercury contamination of aquatic birds in northwestern Ontario. J. Wildl. Manage. 38, 120-131.

Fisher, J. (1952). The Fulmar. Collins, London.

Furness, R.W. (1987). The Skuas. T. & A.D. Poyser, Calton.

Furness, R.W., Muirhead, S.J. & Woodburn, M. (1986). Using bird feathers to measure mercury in the environment: relationships between mercury content and moult. Mar. Pollut. Bull. 17, 27-30.

Furness, R.W. & Todd, C.M. (1984). Diets and feeding of fulmars Fulmarus glacialis during the breeding season: a comparison between St. Kilda and Shetland colonies. Ibis 126, 379-387.

Gardner, D. (1975). Observations on the distribution of dissolved mercury in the ocean. Mar. Pollut. Bull. 6, 43-46.

Ginn, H.B. & Melville, D.S. (1983). Moult in Birds. British Trust for Ornithology, Tring.

Hansen, J.C. (in press). Human exposure to metals through consumption of marine foods: a case study of exceptionally high intake among Greenlanders. In, Heavy Metals in the Marine Environment. Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

Johnels, A.G. & Westermark, T. (1969). Mercury contamination of the environment in Sweden. In, Chemical Fallout. Current Research on Persistent Pesticides. Millar, M.W. & Berg, G.G. (eds.). Thomas, Springfield. pp. 221-239.

Kurland, L.T., Faro, S.N. & Seidler, H. (1960). Minamata disease. The outbreak of a neurological disorder in Minamata, Japan and its relationship to the ingestion of sea food contaminated by mercuric compounds. Wld. Neurol. 1, 370-395.

Mackay, N.J., Kazacos, M.N., Williams, R.J. & Leedow, M.I. (1975). Selenium and heavy metals in black marlin. Mar. Pollut. Bull. 6, 57-61.

Madsen, P.P. (1981). Peat bog records of atmospheric mercury deposition. Nature 293, 127-130.

Miller, G.E., Grant, P.M., Kishore, R., Steinkruger, F.J., Rowland, F.S. & Guinn, V.P. (1972). Mercury concentrations in museum specimens of tuna and swordfish. Science 175, 1121-1122.

Muirhead, S.J. (1986). The accumulation, storage and elimination of metals and organochlorines in the great skua Catharacta skua skua and metal accumulation in Atlantic Procellariiformes. Unpubl. Ph.D. thesis, University of Glasgow.

Norheim, G. & Froslie, A. (1978). The degree of methylation and organ distribution in mercury of some birds of prey in Norway. Acta Pharmacol. et Toxicol. 43, 196-204.

Norheim, G., Somme, L. & Holt, G. (1982). Mercury and persistent chlorinated hydrocarbons in Antarctic birds from Bouvetoya and Dronning Maud Land. Environ. Pollut. (A) 28, 233-240.

Osborn, D., Harris, M.P. & Nicholson, J.K. (1979). Comparative tissue distribution of mercury, cadmium and zinc in three spe cies of pelagic seabirds. Comp. Biochem. Physiol. 64C, 61-67.

Somer, E. & Appelquist, H. (1974). Changes and differences in mercury level in the Baltic and Kattegat compared to the north Atlantic using Uria sp. (guillemot sp.) and Cepphus grylle (black guillemot) as indicators. Paper presented at the 9th. Conf. Baltic Oceanographers, Kiel, West Germany.

Thompson, D.R. (in press). Metal levels in marine vertebrates. In, Heavy Metals in the Marine Environment, Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

Thompson, D.R. & Furness, R.W. (1989). Differences in the chemical form of mercury stored in south Atlantic seabirds. Environ. Pollut. 60, 305-317.

Thompson, D.R. & Furness, R.W. (in press). Comparison of the levels of total and organic mercury in seabird feathers. Mar. Pollut. Bull.

Uthe, J.F., Solomon, J. & Grift, B. (1972). Rapid semimicro method for the determination of methyl mercury in fish tissue. J. Ass. Off. Anal. Chem. 55, 583-589.

Walsh, P.M. (1988). Geographical variation in mercury levels of north Atlantic gannets Sula bassana. In, Seabird Food and Feeding Ecology; Proceedings of third internatinal conference of the Seabird Group. p.46.

Wolff, E. (in press). Evidence for historical changes in global metal pollution: snow and ice samples. In, Heavy Metals in the Marine Environment. Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

CHAPTER 8

Mercury levels in Scottish golden and white-tailed eagles

8.1 INTRODUCTION

Effects of pollutants on the breeding success of birds of prey have been widely studied. The use of organochlorine compounds as pesticides during the 1940's and 1950's in Britain led to decreases in eggshell weight and thickness in raptors which in turn led to reduced productivity through increased egg-breakage (Ratcliffe, 1965; 1967; 1970). Declines in the numbers and breeding success of sparrowhawks _Accipiter nisus_, kestrels _Falco tinnunculus_, peregrines _Falco peregrinus_ and golden eagles _Aquila chrysaetos_ in areas of Britain testify to this phenomenon (Cramp, 1973; Lockie & Ratcliffe, 1964; Newton, 1974; Ratcliffe, 1980). Similarly, elevated levels of organochlorines elsewhere have been associated with reduced breeding success and possibly death in bald eagles _Haliaeetus leucocephalus_ (Belisle _et al._, 1972; Grier, 1974; Krantz _et al._, 1970; Reichel _et al._, 1984; Wiemeyer _et al._, 1984), with death in marsh harrier _Circus aeruginosus_, sparrowhawk, buzzards _Buteo buteo_ and kestrels from the Netherlands (Koeman _et al._, 1969) and with population decline and reduced breeding success in ospreys _Pandion haliaetus_ (Henny _et al._, 1977; Wiemeyer _et al._, 1975), white-tailed eagles _Haliaeetus albicilla_ (Helander _et al._, 1982; Koeman _et al._, 1972), prairie falcons _Falco mexicanus_ and merlins _Falco columbarius_ (Fyfe _et al._, 1976), marsh harriers (Odsjo & Sondell, 1977) and Cooper's hawks _Accipiter cooperii_ (Snyder _et al._, 1973).

Since the widespread use of such organochlorines in the environment has been greatly reduced or eliminated altogether in western Europe, there has been evidence of lower organochlorine burdens within several raptor species (Koivusaari _et al._, 1980; Lockie _et al._, 1969; Newton _et al._, 1988; 1989).

By comparison, there have been rather few studies which have looked for associations between poor breeding success and elevated mercury concentrations. This may have been due partly to masking effects of organochlorine compounds whereby any effect on breeding success cannot be attributed to mercury directly since effects may be the result of high levels of organochlorine residues. In eggs in particular, levels of pollutants of all types tend to be intercorrelated (for example, Newton et al., 1989). Egg pollutant levels could reflect concentrations of fat-soluble pollutants accumulated and stored in body tissues, in which case all individual contaminant levels are likely to be relatively high. Alternatively, pollutant levels in the egg may reflect levels in food which, in a terrestrial system in particular, are likely to be relatively and uniformly low. Hence, eggs derived from a high proportion of body tissue products and a low proportion of recently-digested food products are likely to exhibit relatively high levels of all contaminants. Newton et al. (1989) found that DDE, HEOD and PCB concentrations were intercorrelated in peregrine eggs. A multiple regression analysis of levels of the above pollutants on brood size revealed that DDE was significantly and negatively correlated with brood size, and that the other pollutants did not explain any more of the variation in brood size than did DDE alone. Furthermore, egg mercury concentrations, found to correlate positively with DDE and negatively, but weakly, with brood size, were thought to possibly reduce brood size over and above any effects of DDE alone, since mercury and DDE combined explained significantly more of the variation in brood size than they did alone (Newton et al., 1989).

In Sweden, alkyl mercury was widely used in seed dressings between 1940 and 1966. This resulted in elevated mercury burdens and population decline in some raptors (Berg et al., 1966; Jensen et al., 1972). Elevated mercury levels in white-tailed eagles breeding near to the Baltic Sea have been suggested as being the cause of death in some individuals (Falandysz et al., 1988; Henriksson et al., 1966; Koeman et al., 1972; Oehme, 1981) whilst Koeman et al. (1969) reported high mercury levels in the internal tissues of buzzards and kestrels, found dead in the Netherlands, as being the probable cause of death. More recently, Newton et al. (1988) found a significant negative relationship between mercury levels in British merlin eggs and breeding success and Furness et al. (1989) have suggested that relatively high mercury concentrations in golden eagles from the Isle of Rhum may be related to reduced breeding success.

In this chapter, mercury concentration data are presented which greatly add to those published in Furness et al. (1989) for Scottish golden eagles. In addition, mercury concentration data are presented for white-tailed eagles reintroduced to Scotland. The possible link between high mercury levels in some Scottish golden eagles and reduced breeding success is discussed and the mercury levels in Scottish white-tailed eagles, in relation to those mercury concentrations suggested as being harmful or even lethal in Baltic birds, are assessed.

8.2 MATERIALS AND METHODS

8.2.1 Sample collection, storage and preparation

Moulted golden eagle and white-tailed eagle feathers were collected from nest and roost sites by members of the Raptor Study Groups and other workers during 1987, 1988 and 1989, although several samples were obtained prior to this. All feathers were dried at ambient laboratory temperature (ca. 22^{o}C) and placed in mercury-free polythene bags prior to analysis. Results from all feather types for both species were pooled since mercury levels were not significantly different between body feathers and flight feathers for sites from which both feather types could be compared (one sample t-test, comparing the distribution of the differences between each pair of values around a mean of 0, $P=0.729$; Table 8.1). Furthermore, eagle feather moult tends to be continuous and irregular (Ginn & Melville, 1983), placing less importance on any particular feather or group of feathers with respect to mercury elimination.

White-tailed eagle feathers were obtained from juveniles, two to five year-olds and adults from the Isle of Rhum, and from adults from three confidential Inner Hebridean home range sites.

The regions of Scotland from which golden eagle feather samples were obtained are based on those defined by Dennis *et al.* (1984), as follows: the 'East Highland' region corresponds to area 'A'; 'Central Scotland' corresponds to area 'D'; 'South West Scotland' corresponds to area 'G'; 'West Scotland' combines areas 'C', 'E' and 'F', although the Isle of Mull has been included in the 'Inner Hebrides' region; area 'H' has been subdivided into 'Inner Hebrides', 'Outer Hebrides' (samples from both of these areas have been categorised as from either 'coastal' or 'inland' home range sites) and the 'Isle of Rhum' (Figure 1). Data on breeding success in the above regions, together with information on golden eagle diets have been abstracted from various sources as outlined in the Results section.

Samples from golden eagle prey species were obtained from a variety of sources: Manx shearwater *Puffinus puffinus*, red

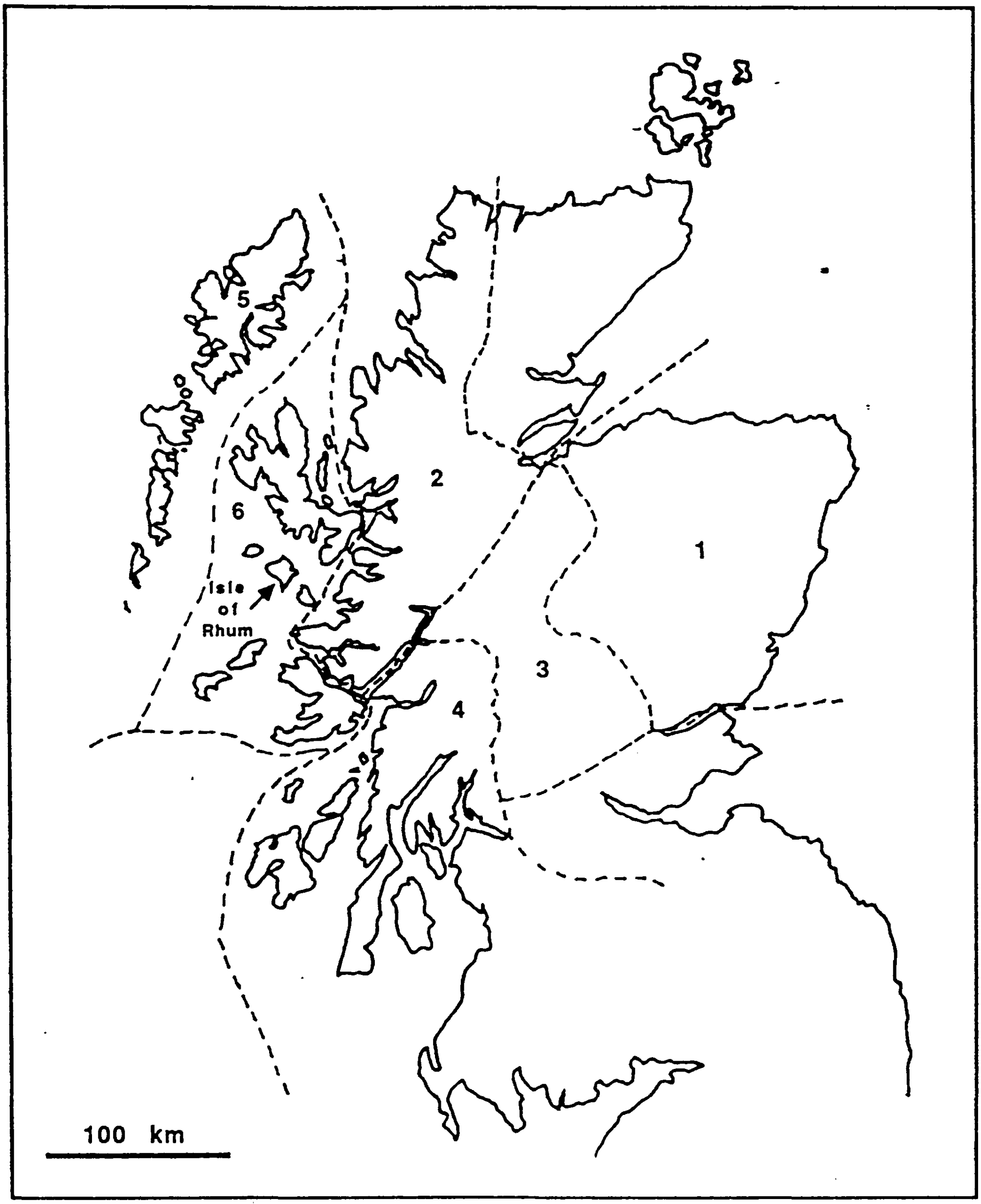

Fig. 8.1 Scottish regions from which golden eagle feather samples were obtained

Key: 1, East Highlands; 2, West Scotland; 3, Central Scotland; 4, South west Scotland; 5, Outer Hebrides; 6, Inner Hebrides.

TABLE 8.1: Comparison of total mercury concentration ($\mu g\ g^{-1}$ fresh weight) in flight (primaries and secondaries) and tail feathers with body feathers in golden and white-tailed eagles.

Flight/Tail feathers	Body feathers
2.6	2.2
1.6	1.2
0.4	0.3
0.3	1.7
2.0	1.2
1.6	0.9
1.2	1.5
2.4	2.3
5.1	3.3
5.7	4.1
1.8	4.4

one sample t-test, P=0.729.

grouse *Lagopus lagopus*, herring gull *Larus argentatus*, lesser black-backed gull *Larus fuscus* and hooded crow *Corvus corone cornix* feathers were obtained from the Isle of Rhum. Manx shearwater samples were collected from individual birds whilst other feather samples were made up of moulted feathers and as such represented an unknown number of individuals, although the number of individuals is likely to be similar to the number of feathers analysed. Carrion crow *Corvus corone corone* and rabbit *Oryctolagus cuniculus* muscle samples were obtained from freshly killed animals found on Scottish mainland roads; brown hare

Lepus capensis muscle samples were obtained from freshly killed animals found dead on roads from the Isle of Islay; brown rat *Rattus norvegicus* liver samples were obtained from animals trapped on the Isle of Rhum; Scottish lamb *Ovis* sp. muscle samples were obtained from local butchers. All internal tissues were oven-dried to constant weight at 50°C.

8.2.2 Mercury analysis

All samples (feathers and internal tissues) were analysed for total mercury as outlined in Chapter 3. All mercury concentrations are expressed on a fresh weight basis. Mercury concentration distribution patterns were tested for differences from a Gaussian distribution using Kolmogorov-Smirnov one sample tests. Since the distribution pattern for Inner Hebridean (coastal) birds was the only one amongst the golden eagle samples to deviate significantly from Gaussian ($P<0.05$), and since the distribution pattern of the nine region means did not differ significantly from Gaussian ($P=0.333$), 1-Way ANOVA and Student-Newman-Keuls (SNK) tests were employed to test for differences in the mercury levels of golden eagles from different regions. White-tailed eagle feather mercury concentrations were found not to deviate significantly from a Gaussian distribution (Kolmogorov-Smirnov one sample tests for all groups, $P>0.05$) and, again, 1-Way ANOVA SNK tests were used to assess differences between sites and age classes of white-tailed eagles. The word 'significant' has been used in the statistical context only, indicating a chance occurrence of less than 5%.

8.3 RESULTS

Total mercury concentrations in golden eagle body feathers are presented in Table 8.2 and Figure 8.2. Generally, mercury levels were found to increase from east to west with the highest levels found in the Western Isle birds. Mercury levels in birds from the Isle of Rhum were significantly higher than those from birds in all other areas (1-Way ANOVA, $P<0.0001$; SNK test, $P<0.05$). Similarly, mercury levels in eagles from coastal sites in the Outer Hebrides were significantly higher than those from other regions except those from inland Outer Hebridean sites (1-Way ANOVA, $P<0.0001$; SNK test, $P<0.05$). Mercury concentrations in feathers from birds from inland Outer Hebridean sites were significantly higher than those from birds from Western Scotland and the Inner Hebrides (coastal and inland: 1-Way ANOVA, $P<0.0001$; SNK test, $P<0.05$). Mercury levels in feathers from birds from the East Highlands, Central Scotland, South West Scotland, West Scotland and Inner Hebrides (both coastal and inland) were not significantly different from each other (1-Way ANOVA; SNK test, $P>0.05$).

Golden eagle breeding success data in the corresponding regions are presented in Table 8.3. Breeding success has been found to be consistently better in the East Highlands compared to South West Scotland, West Scotland and the Western Isles with breeding success in the Isle of Rhum considerably reduced compared to other regions (Corkhill, 1980; Dennis et al., 1984; Table 8.3). Eagle diet data are presented in Table 8.4. Generally, live, terrestrial prey species predominate in the diet of East Highland birds with sheep and red deer *Cervus elaphus* carrion being more important in the west. Seabirds form a major part of the diet of some eagles in the Western Isles,

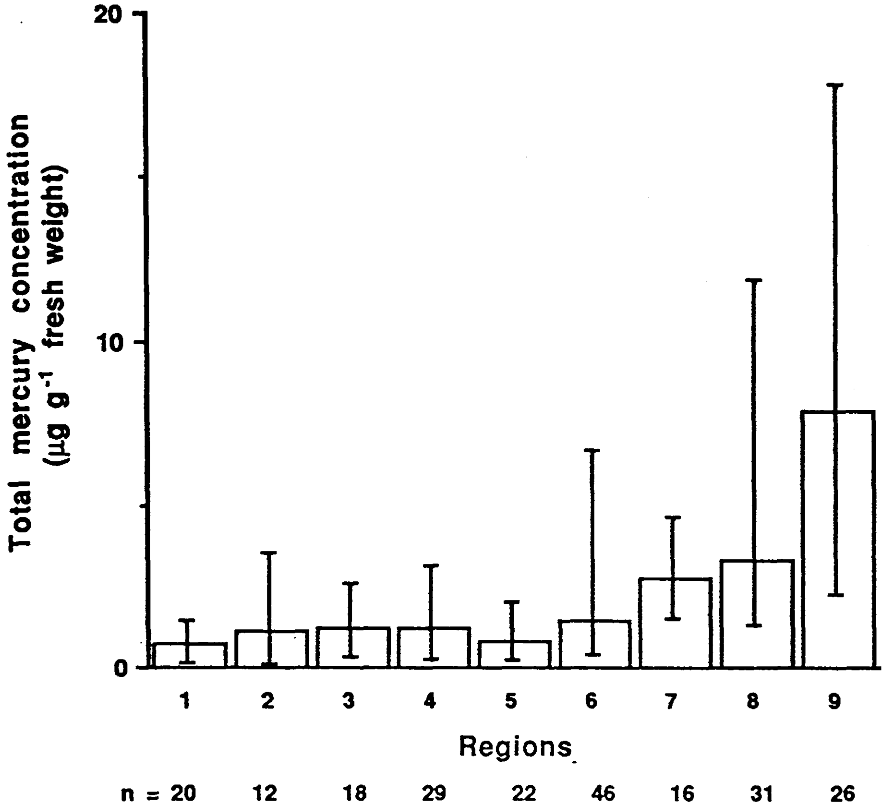

Fig. 8.2 Mercury levels in feathers from Scottish golden eagles.

Blocks represent mean values with ranges.

Key: 1, East Highlands; 2, Central Scotland; 3, South west Scotland; 4, West Scotland; 5, Inner Hebrides (inland); 6, Inner Hebrides (coastal), 7, Outer Hebrides (inland); 8, Outer Hebrides (coastal); 9, Rhum; n, sample size.

TABLE 8.2: Total mercury levels ($\mu g\ g^{-1}$ fresh weight) in Scottish golden eagle feathers. Sample sizes for each region are equivalent to number of analyses. See text for explanation of localities.

Location	No. of analyses (No. feathers)	Approx. no. home ranges	Mercury conc. Mean	S.D.	Median
			(range)		
East Highlands	20 (29)	5	0.75	0.41	0.70
			(0.20- 1.44)		
Central Scotland	12 (12)	6	1.16	1.24	0.69
			(0.07- 3.55)		
South West Scotland	18 (32)	6	1.17	0.67	0.96
			(0.35- 2.58)		
West Scotland	29 (45)	14	1.21	0.75	1.01
			(0.25- 3.12)		
Inner Hebrides					
Inland	22 (58)	4	0.83	0.42	0.69
			(0.25- 1.98)		
Coastal	46 (112)	12	1.41	1.35	0.87
			(0.44- 6.69)		
Outer Hebrides					
Inland	16 (20)	13	2.77	1.09	2.31
			(1.51- 4.57)		
Coastal	31 (47)	13	3.29	2.05	2.48
			(1.77-11.83)		
Rhum	26 (29)	4	7.89	4.93	5.90
			(2.23-17.73)		

notably those on the Isle of Rhum (Corkhill, 1980; Brown & Watson, 1964; Lockie et al., 1969; Lockie & Stephen, 1959; Marquiss et al., 1985; Table 8.4).

Mercury concentrations in some golden eagle prey species are presented in Table 8.5. The highest mercury levels were found in marine species, typically seabirds. Terrestrial prey

TABLE 8.3: Breeding success of golden eagles in the East Highlands, South West Scotland, West Scotland, the Hebridean Islands and Rhum, expressed as chicks reared per occupied territory.

Location	Pair-years	Chicks/Occ. territory	Source
East Highlands	30	0.80	Dennis et al. (1984)
Central Scotland	40	0.55	Dennis et al. (1984)
S-W Scotland	49	0.59	Dennis et al. (1984)
West Scotland	184	0.47	Dennis et al. (1984)
Hebridean Islands	77	0.56	Dennis et al. (1984)
Rhum	80	0.29	Corkhill (1980)

Closely similar patterns of breeding success between the above regions of Scotland have been reported in Brown (1969), Everett (1971), Lockie & Ratcliffe (1964), Marquiss et al. (1985), Sandeman (1957), Watson (1957) and in the annual reports of the Raptor Working Groups in Scottish Birds.

species exhibited uniformly low mercury concentrations by comparison with those of marine prey species (Table 8.5).

Total mercury concentrations in white-tailed eagle feathers from the Isle of Rhum and three confidential Western Isle home ranges are presented in Table 8.6 and Figure 8.3. Within Rhum birds, juveniles exhibited significantly lower mercury feather concentrations than both two to five year-olds and adults (nine year-olds: 1-Way ANOVA, $P<0.0001$; SNK test, $P<0.05$). There was no significant difference in mercury levels between two to five year-old and adult birds (SNK test, $P>0.05$). Rhum adult birds

TABLE 8.4: Diets of golden eagles in Scotland with the relative importance of each prey type within each region. +++= major prey; ++= regular prey of less importance; += rare prey items.

Prey	Rhum	Hebridean Islands	S-W Scotland	West Scotland	East Highlands
Red grouse	+	+	++	+	+++
Ptarmigan			+	+	+++
Rabbit		+++	++	+	+++
Mountain hare		+	+	+	+++
Sheep		+++	+++	+++	+
Red deer	+++	++	+++	+++	+
Voles					+
Carrion/Hooded crow	+	+	+	+	
Fox				+	
Feral goat	++	+	++	+	
Brown rat	++	++			
Fulmar	+++	++			
Manx shearwater	+++	+			
Larus gulls	+++	++			
Kittiwake	+				

Data abstacted from Corkhill (1980); Brown & Watson (1964); Lockie et al. (1969); Lockie & Stephen (1959); Marquiss et al. (1985).

had significantly higher feather mercury concentrations than all three confidential Western Isle home range sites, there being no significant difference in mercury levels between these latter three groups (1-Way ANOVA, $P<0.0001$; SNK test, $P<0.05$). Mercury concentration data for white-tailed eagles from other studies are presented in Table 8.6.

TABLE 8.5: Mercury concentrations ($\mu g\ g^{-1}$ fresh weight) in golden eagle prey species. Figures in brackets represent equivalent concentrations in liver tissue based on a 7:3:1 feather:liver:muscle mercury concentration ratio.

Species	Number sampled	Mean	S.D.	Range	Tissue analysed
A. MARINE PREY					
Manx shearwater *Puffinus puffinus*	78	4.67 (2.00)	1.93	1.40-10.48 (0.60- 4.49)	Body F's (Liv. eq.)
Herring gull[a] *Larus argentatus*	5[b]	2.76 (1.18)	1.26	1.67- 4.20 (0.72- 1.80)	1° F's (Liv. eq.)
Lesser b-backed gull[a] *Larus fuscus*	6[b]	3.04 (1.30)	1.43	1.25- 4.52 (0.54- 1.94)	1° F's (Liv. eq.)
B. TERRESTRIAL PREY					
Red grouse[a] *Lagopus lagopus*	12[b]	0.28 (0.12)	0.20	<0.01- 0.71 (<0.01- 0.30)	All F's (Liv. eq.)
Carrion crow *Corvus corone corone*	2	0.08 (0.24)	0.03	0.06- 0.10 (0.18- 0.30)	Muscle (Liv. eq.)
Rabbit *Oryctolagus cuniculus*	9	0.05 (0.15)	0.06	<0.01- 0.17 (<0.01- 0.51)	Muscle (Liv. eq.)
Brown hare *Lepus capensis*	5	0.04 (0.12)	0.01	0.03- 0.06 (0.09- 0.18)	Muscle (liv. eq.)
Brown rat *Rattus norvegicus*	14	0.08	0.04	0.03- 0.13	Liver
Lamb *Ovis* sp.	5	<0.01	----	----------	Muscle
C. INTERTIDAL-FEEDING PREY					
Hooded crow[a] *Corvus corone cornix*	21[b]	3.25 (1.39)	2.51	0.34-10.40 (0.15- 4.46)	1°/2° F's (Liv. eq.)

Manx shearwaters, red grouse, herring gulls, lesser black-backed gulls, hooded crows and brown rats from Rhum; brown hares from Islay; other species from mainland Scotland.

a- Furness (unpublished data); b- Number of feathers analysed, although the number of individuals these represent is probably very similar.

TABLE 8.6: Mercury levels (µg g^{-1} fresh (F) or dry (D) weight) in white-tailed eagles.

Location	Mean	(Range)		n	Tissue analysed	Source
Rhum (Ads.)	7.3	(1.9- 14.1)	F	21[a]	All feathers	This study
(2-5 ys.)	6.5	(1.5- 22.7)	F	19[a]		
(juvs.)	2.3	(0.1- 5.2)	F	7[a]		
Site 1	4.0	(2.5- 7.2)	F	66[a]	All feathers	This study
Site 2	3.9	(2.2- 6.0)	F	23[a]		
Site 3	2.4	(0.7- 7.9)	F	26[a]		
Sweden						
1832-1940	6.6	(2.7- 15.5)	F	13	T/F	Berg *et al.* (1966)
1941-1965	28.9	(4.9- 64.0)	F	14	1^{o} T/F	
South West Baltic	54.0	(---------)	D	1	Coverts	Falandysz *et al.* (1988)
	33.0	(---------)	D	1	Liver	
	18.0	(---------)	D	1	F/F	
	5.1	(---------)	D	1	Liver	
South West Baltic	30.0	(---------)	F	1	Liver	Falandysz (1984)
Poland	11.0	(---------)	F	1	Liver	Falandysz (1986)
	44.0	(---------)	F	1	Kidney	
East Germany						
1967-1976	0.8[b]	(---------)	F	23	Liver	Oehme (1981)
	5.8[b]	(---------)	F	22	Kidney	
1976-1978	90.8[b]	(---------)	F	10	Liver	
	115.5[b]	(---------)	F	10	Kidney	
East Germany	48.2	(---------)	F	1	Liver	Koeman *et al.* (1972)
	26.5	(---------)	F	1	Kidney	
Finland	17.9	(4.6- 27.1)	F	6	Liver	Henriksson *et al.* (1966)
	93.5	(48.6-123.1)	F	4	Kidney	
	18.6	(8.7- 28.5)	F	2	Feathers	
Norway	3.3[b]	(0.3- 16.0)	F	24	Liver	Norheim & Froslie (1978)
	3.5[b]	(0.3- 55.0)	F	24	Kidney	

a Number of feathers analysed; b Median value; T/F Tail feather; F/F Flight feather; 1^{o} Primary feather.

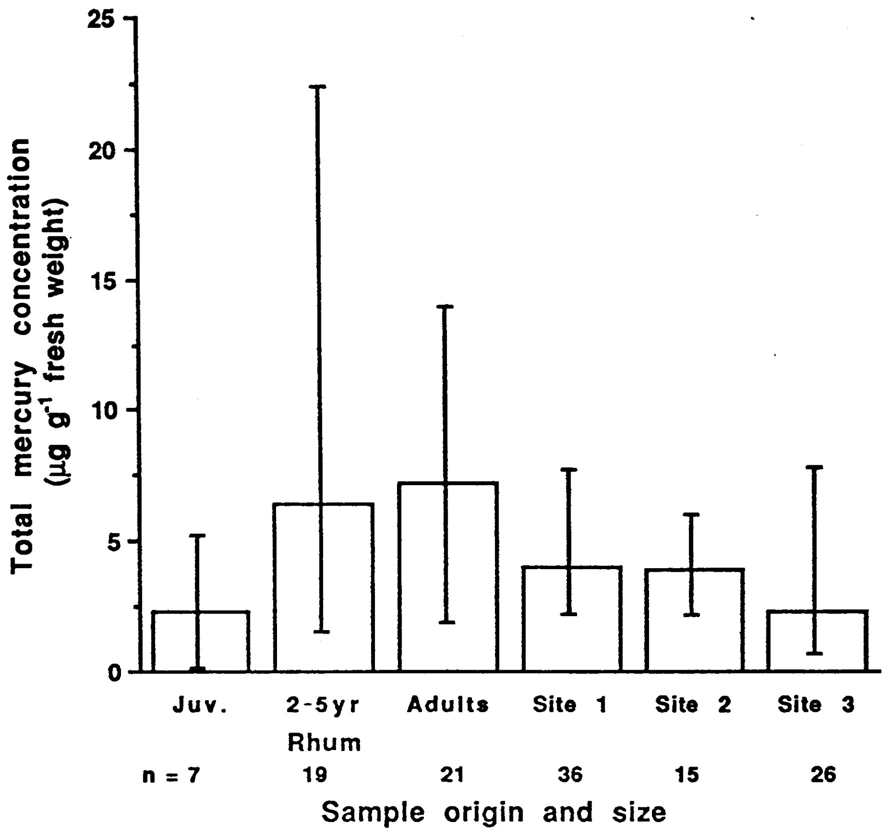

Fig. 8.3 Mercury levels in feathers from white-tailed eagles from Rhum and three confidential Inner Hebridean sites.
Blocks represent means with ranges; Juv., juveniles, 2-5yr, 2-5 year olds.

8.4 DISCUSSION

8.4.1 Golden eagles

The breeding success of Scottish golden eagles has been shown to vary in a consistent way from the East Highlands where productivity is relatively high, to Western Isles such as the Isle of Rhum where breeding success is considerably reduced (Brown, 1969; Corkhill, 1980; Dennis et al., 1984; Everett, 1971; Lockie & Ratcliffe, 1964; Marquiss et al., 1985; Sandeman, 1957; Watson, 1957; Table 8.3). Although changes in prey availability and land use, and the use of organochlorine pesticides, may lead to variations in golden eagle productivity in a given area (Lockie et al., 1969; Lockie & Ratcliffe, 1964; Marquiss et al., 1985; Watson et al., 1989), this general trend of high productivity in the east with progressively reduced productivity towards the west has remained over the years.

Golden eagles breeding in different areas of Scotland tend to have different diets, this largely reflecting the variation in prey availability between the areas. Generally, live prey form the bulk of the diet of eastern eagles with grouse, ptarmigan *Lagopus mutus*, rabbits and hares predominating (Brown & Watson, 1964). Towards the west of Scotland, sheep and red deer carrion become more important (Lockie et al., 1969). Eagles breeding in the Western Isles are faced with low densities of grouse and hares, extremely low numbers of ptarmigan and rely to a greater extent on carrion and rabbits (Lockie & Stephen, 1959). On the Isle of Rhum, this situation is particularly pronounced since sheep, ptarmigan and lagomorphs are absent; here, the eagles exploit the abundant seabird populations (Corkhill, 1980), a trend which has been reported from the neighbouring islands of Canna (Swann & Ramsay, 1978) and Eigg

(Hawker, 1975) and is likely to be true to some extent for other Western Isles.

Mercury concentrations tend to be higher in marine food chains, compared to terrestrial systems. This is clearly demonstrated by the mercury levels of eagle prey species presented in Table 8.5. By converting feather and muscle mercury concentrations into the equivalent liver mercury concentration using the 7:3:1 feather:liver:muscle mercury concentration ratio (see Chapter 9) mercury levels in different prey species can be compared, if only roughly. It can be seen that the seabirds analysed exhibit considerably higher mercury concentrations when compared to terrestrial birds and mammals (Table 8.5). The relatively high mercury concentrations in hooded crow feathers from Rhum are difficult to explain, but may be linked to the crows' habit of feeding upon local mussels <u>Mytilus edulis</u> (pers. obs.). Mercury levels in lamb, rats and lagomorphs are uniformly low, often below the limits of detection. It would seem likely that terrestrial prey species not analysed, such as ptarmigan and red deer, would also exhibit low mercury levels. It seems reasonable to conclude, therefore, that the relatively elevated mercury levels measured in Rhum golden eagles (max. 17.73 $\mu g\ g^{-1}$ fresh weight; Table 8.2) are a result of their dependence upon marine prey species whereas the relatively low mercury levels measured in mainland eagles (max. 3.55 $\mu g\ g^{-1}$ fresh weight; Table 8.2) reflect the uniformly low mercury burdens of their terrestrial prey. The age-accumulation of mercury in feathers can almost certainly be discounted as a potential complicating factor; Furness <u>et al.</u> (in press) and work on great skuas <u>Catharacta skua</u> (Chapter 4) have shown that feather mercury levels are independent of bird age, once adult status has been achieved.

It is interesting to note that 'coastal' Outer Hebridean and 'coastal' Inner Hebridean golden eagles tended to exhibit higher mercury levels (max. values 11.83 and 6.69 µg g^{-1} fresh weight, respectively; Table 8.2) than 'inland' Outer and Inner Hebridean golden eagles (max. values 4.57 and 1.98 µg g^{-1} fresh weight, respectively; Table 8.2). This presumably reflects a higher proportion of marine prey in the diets of the former 'coastal' eagles, although the availability of some terrestrial prey would tend to reduce mercury levels when compared to Rhum birds. This trend of relatively high mercury concentrations in raptors breeding in coastal areas has also been reported in British merlins and peregrines; merlin eggs from Orkney, Shetland, Mull and Lewis tended to have higher mercury levels compared to the rest of Britain, and peregrine eggs from coastal sites contained higher mercury concentrations compared to eggs from inland sites (Newton *et al.*, 1988; 1989).

Whether the relatively elevated mercury levels measured in Rhum golden eagles and their prey, compared to mercury concentrations in birds from other Scottish regions, are the cause of the reduced breeding success of these birds is more difficult to determine. As noted by Furness *et al.* (1989), the high mercury levels of Rhum golden eagles may correlate with low breeding success because both reflect the lack of lagomorph, ptarmigan and sheep, although within the golden eagle pairs nesting on Rhum, a significant negative correlation was found between seabird consumption and breeding success (Furness *et al.*, 1989). In studies of white leghorn chickens *Gallus* sp. experimentally fed methyl mercury, 10-20 µg g^{-1} (fresh weight) in the diet was found to impair egg production, hatchability and eggshell quality (Scott, 1977; Scott et al., 1975) whilst 3 µg g^{-1} (fresh weight) methyl mercury in the diet of mallards Anas platyrhynchos caused increased mortality of offspring, although adults suffered no obvious adverse effects (Heinz, 1974). The seabird prey of Rhum golden eagles may contain mercury at such concentrations (Table 8.5), although direct comparison with the above levels has been based on the use of the 7:3:1 feather:liver:muscle mercury concentration ratio (Chapter 9). It is likely, however, that the majority of the mercury present in the internal organs of these seabirds is in the methyl form; in a study of pelagic seabirds, Osborn et al. (1979), noted that the vast majority of the mercury in Manx shearwaters was in the methyl form, and Thompson & Furness (1989; Chapter 4) have suggested that seabirds which undergo a complete annual feather moult, such as shearwaters and gulls, are likely to contain a high proportion of methyl mercury.

A further problem in interpreting the potential harmful effects of mercury in Rhum golden eagles is that organochlorine residues may mask or even augment any effects of mercury. PCB's, known to bioaccumulate up marine food chains (Bourne, 1976), have been shown to be at high levels in golden eagle eggs from Rhum over recent years (Furness et al., 1989) and could contribute to the cause of the reduced productivity of these birds. However, Newton et al. (1988) found no evidence that organochlorines, unlike mercury, were now significantly and negatively correlated with productivity of merlins whilst Newton et al. (1989) reported a negative relationship between productivity and DDE (but not PCBs) in peregrines, a trend which mercury may have added to. It is clearly difficult to separate the effects of these various contaminants, but mercury levels in

Rhum golden eagles, in particular, would seem to warrant further investigation. Everett (1971) suggested that 0.5 young/pair are required to maintain a viable adult golden eagle population; clearly, the productivity of golden eagles on Rhum has been consistently less than this level and immigration of eagles from more productive regions would be necessary.

8.4.2 White-tailed eagles

The white-tailed eagle has been the subject of a reintroduction programme on the Isle of Rhum, following its extinction through persecution in Britain early this century (Love, 1980; Love & Ball, 1979; Love *et al.*, 1978). Juvenile white-tailed eagles, obtained from Norway between 1975 and 1985, were tethered on Rhum, fed local fish, seabirds, crows and goat and red deer meat and eventually released. Mean mercury levels in white-tailed eagle feathers from Rhum birds were found to increase between juveniles, two to fivey year-olds and adults, as has been demonstrated for other species (Hoffman & Curnow, 1979; Honda *et al.*, 1985; 1986). Furthermore, Rhum adult feather mercury levels were found to be significantly higher compared to adult birds from three confidential Inner Hebridean sites (Table 8.6; Figure 8.3). These latter three sites offer live terrestrial prey to the eagles which tend to exhibit low mercury concentrations (Table 8.5), and as with golden eagles, this may be the reason for the lower mercury concentrations away from Rhum. The relatively high mercury levels found in Rhum white-tailed eagle feathers (up to 23 $\mu g\ g^{-1}$ fresh weight in a two to five year-old bird; Table 8.6; Figure 8.3) are of note since in other parts of its European range, particularly those areas adjacent to the Baltic Sea, the white-tailed eagle has suffered reduced breeding success and population decline in recent decades. The extensive use of alkyl mercury seed dressings in Sweden was reported as being the cause of increased feather mercury levels in white-tailed eagles after about 1952 (Berg et al., 1966; Table 8.6). Elevated levels of organochlorines and mercury have been cited as being primarily responsible for the decline of the eagle (Koivusaari et al., 1976). More recently, however, Koivusaari et al. (1980) reported increased productivity in Finnish white-tailed eagles in association with decreasing DDE levels in eggs during the 1970's whilst Helander et al. (1982) noted a general decrease in mercury levels in the eggs of white-tailed eagles in Sweden during the 1970's, although both DDE and PCB's were negatively correlated with reproductive success.

Elevated mercury levels in white-tailed eagles found dead around the Baltic Sea have been suggested as being the cause of death. Henriksson et al. (1966) reported feather levels up to 28.5 $\mu g\ g^{-1}$ in Finnish eagles found dead whilst Falandysz et al. (1988) noted mercury concentrations up to 54 $\mu g\ g^{-1}$ dry weight in feathers of a female white-tailed eagle from the south west Baltic (Table 8.6). High mercury levels in internal tissues of other white-tailed eagles found dead around the Baltic have been considered as having been lethal, ranging from 11 $\mu g\ g^{-1}$ wet weight of liver tissue up to 123.1 $\mu g\ g^{-1}$ wet weight of kidney tissue (Falandysz, 1984; 1986; Koeman et al., 1972; Oehme, 1981; Table 8.6). Such elevated mercury levels may, however, be due to starvation and post mortem changes in tissue weight and composition and it is not clear how internal tissue mercury levels relate to those in feathers (Chapter 9). In Norway where mercury pollution, through seed dressing application, has been comparatively low, white-tailed eagle liver mercury levels have been reported as being generally less than the above values (up to 16 µg g^{-1} wet weight; Holt et al., 1979; Norheim & Froslie, 1978; Table 8.6). It would seem, therefore, that mercury levels in feathers of Rhum white-tailed eagles which take a greater proportion of marine prey compared to white-tailed eagles at other Scottish sites, are approaching those reported for Baltic eagles as having deleterious effects. Although it is difficult to draw any firm conclusions about the effects the measured mercury levels are having upon Rhum golden and white-tailed eagles, the possibility remains that the lack of live, terrestrial prey may be having an adverse effect on their productivity.

8.5 REFERENCES

Belisle, A.A., Reichel, W.L., Locke, L.N., Lamont, T.G., Mulhern, B.M., Prouty, R.M., DeWolf, R.B. & Cromartie, E. (1972). Residues of organochlorine pesticides, polychlorinated biphenyls and mercury, and autopsy data for bald eagles, 1969 and 1970. Pestic. Monit. J. 6, 133-138.

Berg, W., Johnels, A., Sjostrand, B. & Westermark, T. (1966). Mercury content in feathers of Swedish birds from the past 100 years. Oikos 17, 71-83.

Bourne, W.R.P. (1976). Seabirds and pollution. In Marine Pollution, Vol 6, Johnston, R. (ed.), Academic Press, London.

Brown, L.H. (1969). Status and breeding success of golden eagles in north-west Sutherland in 1967. Brit. Birds 62, 345-363.

Brown, L.H. & Watson, A. (1964). The golden eagle in relation to its food supply. Ibis 106, 78-100.

Corkhill, P. (1980). Golden eagles on Rhum. Scott. Birds 11, 33-43.

Cramp, S. (1973). Toxic chemicals and birds of prey. Brit. Birds 56, 124-139.

Dennis, R.H., Ellis, P.M., Broad, R.A. & Langslow, D.R. (1984). The status of the golden eagle in Britain. Brit. Birds 77, 592-607.

Everett, M.J. (1971). The golden eagle survey in Scotland in 1964-68. Brit. Birds 64, 49-56.

Falandysz, J. (1984). Metals and organochlorines in a female white-tailed eagle from Uznam Island, southwestern Baltic Sea. Environ. Conserv. 10, 262-263.

Falandysz, J. (1986). Metals and organochlorines in adult and immature males of white-tailed eagle. Environ. Conserv. 11, 69-70.

Falandysz, J., Jakuczun, B. & Mizera, T. (1988). Metals and organochlorines in four female white-tailed eagles. Mar. Pollut. Bull. 19, 521-526.

Furness, R.W., Johnston, J.L., Love, J.A. & Thompson, D.R. (1989). Pollutant burdens and reproductive success of golden eagles *Aquila chrysaetos* exploiting marine and terrestrial food webs in Scotland. In, Raptors in the Modern World. Proc. III World Conf. Birds of Prey and Owls. Meyburg, B.-U. & Chancellor, R.D. (eds.). WWGBP: Berlin, London, Paris.

Furness, R.W., Lewis, S.A. & Mills, J.A. (in press). Mercury levels in the plumage of red-billed gulls *Larus novaehollandiae scopulinus* of known age and sex. Environ. Pollut.

Fyfe, R.W., Risebrough, R.W. & Walker, W. (1976). Pollutant effects on the reproduction of the prairie falcons and merlins of the Canadian prairies. Can. Field-Nat. 90, 346-355.

Ginn, H.B. & Melville, D.S. (1983). Moult in Birds. British Trust for Ornithology, Tring.

Grier, J.W. (1974). Reproduction, organochlorines and mercury in Northwestern Ontario bald eagles. Can. Field-Nat. 88, 469-475.

Hawker, D.M. (1975). Golden eagle eating fulmars. Brit. Birds 68, 293.

Heinz, G. (1974). Effects of low dietary levels of methyl mercury on mallard reproduction. Bull. Environ. Contam. Toxicol. 11, 386-392.

Helander, B., Olsson, M. & Reutergardh, L. (1982). Residue levels of organochlorine and mercury compounds in unhatched eggs and the relationships to breeding success in white-tailed sea eagles Haliaeetus albicilla in Sweden. Holarct. Ecol. 5, 349-366.

Henny, C.J., Byrd, M.A., Jacobs, J.A., McLain, P.D., Todd, M.R. & Halla, B.F. (1977). Mid-Atlantic coast osprey population: present numbers, productivity, pollutant contamination and status. J. Wlidl. Manage. 41, 254-265.

Henriksson, K., Karppanen, E. & Helminen, M. (1966). High residue of mercury in Finnish white-tailed eagles. Ornis Fennica 43, 38-45.

Hoffman, R.D. & Curnow, R.D. (1979). Mercury in herons, egrets and their foods. J. Wildl. Manage. 43, 85-93.

Holt, G., Froslie, A. & Norheim, G. (1979). Mercury, DDE and PCB in the avian fauna in Norway 1965-1976. Acta Vet. Scand. Suppl. 70, 1-28.

Honda, K., Min, B.Y. & Tatsukawa, R. (1985). Heavy metal distribution in organs and tissues of the eastern great white egret Egretta alba modesta. Bull. Environ. Contam. Toxicol. 35, 781-789.

Honda, K., Min, B.Y. & Tatsukawa, R. (1986). Distribution of heavy metals and their age-related changes in the eastern great white egret, Egretta alba modesta, in Korea. Arch. Environ. Contam. Toxicol. 15, 185-197.

Jensen, S., Johnels, A.G., Olsson, M. & Westermark, T. (1972). The avifauna of Sweden as indicators of environmental contamination with mercury and chlorinated hydrocarbons. Proc. XVth. Intern. Ornith. Congr., Leiden. pp. 455-465.

Koeman, J.H., Hadderingh, R.H. & Bijleveld, M.F.I.J. (1972). Persistent pollutants in the white-tailed eagle (Haliaeetus albicilla) in the Federal Republic of Germany. Biol. Conserv. 4, 373-377.

Koeman, J.H., Vink, J.A.J. & de Goeij, J.J.M. (1969). Causes of mortality in birds of prey and owls in the Netherlands in the winter of 1968-1969. Ardea 57, 67-76.

Koivusaari, J. (1976). Chlorinated hydrocarbons and total mercury in the prey of the white-tailed eagle (Haliaeetus albicilla L.) in Quarken Straits of the Gulf of Bothnia, Finland. Bull. Environ. Contam. Toxicol. 15, 235-241.

Koivusaari, J., Nuuja, I., Palokangas, R. & Finnlund, M. (1980). Relationships between productivity, eggshell thickness and pollutant contents of addled eggs in the population of white-tailed eagles Haliaeetus albicilla L. in Finland during 1969-1978. Environ. Pollut. (A) 23, 41-52.

Krantz, W.C., Mulhern, B.M., Bagley, G.E., Sprunt, A., Ligas, F.J. & Robertson, W.B. (1970). Organochlorine and heavy metal residues in bald eagle eggs. Pestic. Monit. J. 4, 136-140.

Lockie, J.D. & Ratcliffe, D.A. (1964). Insecticides and Scottish golden eagles. Brit. Birds 57, 89-102.

Lockie, J.D., Ratcliffe, D.A. & Balharry, R. (1969). Breeding success and organo-chlorine residues in golden eagles in West Scotland. J. appl. Ecol. 6, 381-389.

Lockie, J.D. & Stephen, D. (1959). Eagles, lambs and land management on Lewis. J. Anim. Ecol. 28, 43-50.

Love, J.A. (1980). White-tailed eagle reintroduction on the Isle of Rhum. Scott. Birds 11, 65-73.

Love, J.A. & Ball, M.E. (1979). White-tailed sea eagle Haliaeetus albicilla reintroduction to the Isle of Rhum, Scotland, 1975-1977. Biol. Conserv. 16, 23-30.

Love, J.A., Ball, M.E. & Newton, I. (1978). White-tailed eagles in Britain and Norway. Brit. Birds 71, 475-481.

Marquiss, M., Ratcliffe, D.A. & Roxburgh, R. (1985). The numbers, breeding success and diet of golden eagles in southern Scotland in relation to changes in land use. Biol. Conserv. 34, 121-140.

Newton, I. (1974). Changes attributed to pesticides in the nesting success of the sparrowhawk in Britain. J. appl. Ecol. 11, 95-102.

Newton, I., Bogan, J.A. & Haas, M.B. (1989). Organochlorines and mercury in the eggs of British peregrines Falco peregrinus. Ibis 131, 355-376.

Newton, I. & Haas, M.B. (1988). Pollutants in merlin eggs and their effects on breeding. Brit. Birds 81, 258-269.

Norheim, G. & Froslie, A. (1978). The degree of methylation and organ distribution of mercury in some birds of prey in Norway. Acta Pharmacol. et Toxicol. 43, 196-204.

Odsjo, T. & Sondell, J. (1977). Populationsutveckling och hackningsresultat hos brun karrhok *Circus aeruginosus* i relation forekomsten av DDT, PCB och kvicksilver. *Var Fagelvarld* 36, 152-160. (English summary).

Oehme, G. (1981). Zur Quecksilberruckstandsbelastung tot aufgefundener Seeadler *Haliaeetus albicilla* in den Jahren 1967-1978. *Hercynia N. F., Leipzig* 4, 353-364. (English summary).

Osborn D., Harris, M.P. & Nicholson, J.K. (1979). Comparative tissue distribution of mercury, cadmium and zinc in three species of pelagic seabirds. *Comp. Biochem. Physiol.* 64C, 61-67.

Ratcliffe, D.A. (1965). The peregrine situation in Great Britain 1963-64. *Bird Study* 12, 66-82.

Ratcliffe, D.A. (1967). Decrease in eggshell weight in certain birds of prey. *Nature, Lond.* 215, 208-210.

Ratcliffe, D.A. (1970). Changes attributable to pesticides in egg breakage frequency and eggshell thickness in some British birds. *J. appl. Ecol.* 7, 67-107.

Ratcliffe, D.A. (1980). *The Peregrine Falcon.* T. & A.D. Poyser, Calton.

Reichel, W.L., Schmeling, S.K., Cromartie, E., Kaiser, T.E., Krynitsky, A.J., Lamont, T.G., Mulhern, B.M., Prouty, R.M., Stafford, C.J. & Swineford, D.M. (1984). Pesticide, PCB and lead residues and necropsy data for bald eagles from 32 states-1978-81. *Environ. Monit. Assess.* 4, 395-403.

Sandeman, P.W. (1957). The breeding success of golden eagles in the Southern Grampians. *Scott. Nat.* 69, 148-152.

Scott, M.L. (1977). Effects of PCB's, DDT and mercury compounds in chickens and Japanese quail. *Federation Proc.* 36, 1888-1893.

Scott, M.L., Zimmerman, J.R., Marinsky, S., Mullenhoff, P.A., Rumsey, G.L. & Rice, R.W. (1975). Effects of PCB's, DDT and mercury compounds upon egg production, hatchability and shell quality in chickens and Japanese quail. *Poultry Sci.* 54, 350-368.

Snyder, N.F.R., Snyder, H.A., Lincer, J.L. & Reynolds, R.T. (1973). Organochlorines, heavy metals and the biology of North American accipiters. *BioScience* 23, 300-305.

Swann, R.L. & Ramsay, A.D.K. (1978). Avian prey of large raptors on Canna, *Brit. Birds* 71, 46.

Thompson, D.R. & Furness, R.W. (1989). Differences in the chemical form of mercury stored in south Atlantic seabirds. *Environ. Pollut.* 60, 305-317.

Watson, A. (1957). The breeding success of golden eagles in the north-east Highlands. Scott. Nat. 69, 153-169.

Watson, A., Payne, S. & Rae, R. (1989). Golden eagles Aquila chrysaetos: land use and food in northeast Scotland. Ibis 131, 336-348.

Wiemeyer, S.N., Lamont, T.G., Bunck, C.M., Sindelar, C.R., Gramlich, F.J., Fraser, J.D. & Byrd, M.A. (1984). Organochlorine pesticide, polychlorobiphenyl and mercury residues in bald eagle eggs-1969-79-and their relationships to shell thinning and reproduction. Arch. Environ. Contam. Toxicol. 13, 529-549.

Wiemeyer, S.N., Spitzer, P.R., Krantz, W.C., Lamont, T.G. & Cromartie, E. (1975). Effects of environmental pollutants on Connecticut and Maryland ospreys. J. Wildl. Manage. 39, 124-139.

CHAPTER 9

The chemical form of mercury with respect to concentration ratios between tissues

9.1 INTRODUCTION

Birds have been widely used as monitors of a range of environments. Since many pollutants tend to accumulate up food chains, particularly in marine systems, top predators, such as seabirds, have been analysed for a variety of contaminants. Birds offer many advantages as monitors, not least of which is the possibility of using feathers to assess environmental mercury levels. For a recent review of the role of seabirds as monitors of metals in the marine environment see Walsh (in press).

Methyl mercury is deposited into the growing feather and binds strongly to disulphide linkages (Crewther et al., 1965) and is unaffected by a variety of rigorous treatments (Appelquist et al., 1984). By measuring the mercury concentration of a representative sample of body feathers (Furness et al., 1986), one is able to assess inter-species, geographical and historical mercury level differences in large numbers of live birds.

Although several studies have demonstrated positive correlations between feather mercury concentrations and those in internal tissues (Furness & Hutton, 1979; Hutton, 1981; Ohlendorf et al., 1985; Chapter 5), relating actual feather mercury concentrations to those of internal organs has proved more difficult. Recent studies have demonstrated that in some seabirds the mercury levels in internal organs can be extremely high (Muirhead & Furness, 1988) whilst the relative proportions of methyl (organic) and inorganic mercury vary in liver tissues of a range of seabirds in a species-dependent manner (Thompson & Furness, 1989; Chapter 4). Several authors have claimed that there is a ratio of 7:3:1 for mercury concentrations in feathers, liver tissue and muscle tissue, respectively, (Jensen et al., 1972; Johnels & Westermark, 1969; Westermark et al., 1975) and have used this to facilitate the conversion of mercury concentrations in one tissue, to those in another. This ratio has been used to convert levels in this way by Appelquist et al. (1985), Berg et al., (1966), Borg et al. (1970) and Buhler & Norheim (1981).

However, factors such as feather moult and the relative proprtions of the differing chemical forms of mercury in the liver tissue, for example, have tended to be overlooked in this respect. In this chapter, mercury concentration data, both methyl mercury and total mercury, are presented for internal tissues and feathers of a range of seabird species and the limitations of the use of the 7:3:1 conversion ratio are discussed.

9.2 MATERIALS AND METHODS

9.2.1 Sample collection, storage and preparation

Apparently healthy, adult birds were collected during the breeding season from the following locations: wandering albatross *Diomedea exulans*, yellow-nosed albatross *Diomedea chlororhynchos*, sooty albatross *Phoebetria fusca*, Atlantic petrel *Pterodroma incerta*, soft-plumaged petrel *Pterodroma mollis* and Tristan skua *Catharacta skua hamiltoni* from Gough Island as described by Muirhead & Furness (1988); northern fulmar *Fulmarus glacialis* from St. Kilda (June, 1983) and Foula (May, 1983) caught by hand at nests; great skua *Catharacta skua* from Foula as described in Chapter 5; guillemot *Uria aalge* from the north west of Scotland as described in Chapter 6.

Liver and muscle tissues were dissected out and stored at ca. -20^{o}C in mercury-free polythene bags prior to further treatment. They were subsequently dried to constant weight in an oven at 50°C, the water content being determined from change in weight. A sample of four to ten body feathers from each bird was dried at ambient laboratory temperature (ca. 22°C) and placed in mercury-free polythene bags prior to analysis. Wherever possible, tissue and feather samples were obtained from the same individual bird, but in some cases the number of feather samples analysed differs from the corresponding number of internal organs analysed (see Table 9.1).

9.2.2 Mercury analysis

Total and methyl mercury concentrations were determined as described in Chapter 3. Total mercury concentrations in liver tissues of wandering albatrosses, yellow-nosed albatrosses, sooty albatrosses, Atlantic petrels, soft-plumaged petrels and Tristan skuas are those presented in Muirhead & Furness (1988). Methyl mercury concentrations for the above species are the wet weight equivalents of those presented in Thompson & Furness (1989; Chapter 4). Mercury level data for great skuas are a sub-set of those data presented in Chapter 5 whilst guillemot mercury concentrations are those for the April and November (1988) collections, as presented in Chapter 6, and as such represent pre-moult and post-moult samples, respectively. Since all the mercury measured in the guillemots was found to be methyl mercury (Chapter 6), total mercury levels are presented, but for the purposes of calculating feather:liver mercury level ratios, have been treated as methyl mercury.

Mercury concentration ratios for mean feather concentration:mean liver total concentration, mean feather concentration:mean liver methyl concentration and mean feather concentration:mean muscle concentration were determined.

9.3 RESULTS

Liver total and methyl mercury concentrations, together with muscle and feather total mercury concentrations are presented in Table 9.1. In addition, feather:liver total, feather:liver methyl and feather:muscle mercury concentration ratios are presented in Table 9.1. The value of the mean feather mercury concentration:mean liver total mercury concentration ratio was found to range from 0.05 in sooty albatrosses to 2.6 in St. Kildan fulmars. The value of the mean feather mercury concentration:mean liver methyl mercury concentration ratio was always higher than when total mercury was considered, ranging from 1.7 in sooty albatrosses to 5.0 in 'post-moult' guillemots (Table 9.1). The value of the mean feather mercury concentration:mean muscle mercury concentration ratio was found to be generally somewhat higher than '7', ranging from 4.0 in 'pre-moult' guillemots to 15.3 in St. Kildan fulmars (Table 9.1).

9.4 DISCUSSION

The ability to be able to predict internal tissue mercury concentrations on the basis of feather mercury concentrations would obviously greatly enhance the value of feathers as a means by which mercury burdens of birds are assessed. Recent work has demonstrated that internal tissue mercury levels in some seabirds are both high (Muirhead & Furness, 1988) and comprise varying proportions of organic and inorganic mercury (Thompson & Furness, 1989; Chapter 4). In species which exhibit relatively high mercury concentrations in liver tissues, albatross species for example, it is clear that such high values are not related

TABLE 9.1: Methyl and total mercury concentrations in liver tissue and total (equivalent to methyl) mercury concentrations in muscle tissue and feathers (µg g^{-1} fresh weight) of a range of seabird species, together with feather:liver (total), feather:liver (methyl) and feather:muscle mercury level ratios.

Species	Liver T. n	Liver T. Mean (s.d.)	Liver M. n	Liver M. Mean (s.d.)	Muscle n	Muscle Mean (s.d.)	Feather n	Feather Mean (s.d.)	F:LT	F:LM	F:M
Wandering albatross	2	268.0 (----)	2	6.2 (---)	--	---	59	30.2 (15.6)	0.1	4.9	---
Y-nosed albatross	9	7.7 (5.1)	9	1.3 (1.6)	--	---	1	3.1 (---)	0.4	2.4	---
Sooty albatross	8	141.0 (48.0)	8	3.9 (4.9)	--	---	40	6.7 (4.2)	0.05	1.7	---
N. fulmar (Foula)	12	0.8 (0.2)	12	0.5 (0.2)	12	0.1 (0.1)	12	1.1 (0.3)	1.4	2.2	11.0
(St. K.)	19	1.8 (1.2)	19	1.1 (0.6)	19	0.3 (0.1)	19	4.6 (2.4)	2.6	4.2	15.3
Atlantic petrel	13	28.0 (11.0)	11	4.9 (2.9)	--	---	23	13.9 (3.6)	0.5	2.8	---
Soft-p petrel	18	21.0 (23.0)	8	3.9 (2.9)	--	---	21	10.3 (2.3)	0.5	2.6	---
Great skua	27	3.8 (2.0)	27	1.8 (0.7)	27	0.7 (0.4)	27	7.0 (4.9)	1.8	3.9	10.0
Tristan skua	13	7.4 (5.4)	13	3.7 (6.9)	--	---	32	8.1 (7.1)	1.1	2.2	---
Guillemot (Pre-m)	--	----	34	1.1 (0.3)	24	0.5 (0.2)	24	2.0 (0.6)	---	1.8	4.0
(Post-m)	--	----	20	0.3 (0.1)	20	0.1 (0.1)	20	1.5 (0.6)	---	5.0	15.0

n= Sample size; s.d.= Standard deviation.

to feather mercury concentrations by a 3:7 ratio (see Table 9.1). It would appear, therefore, that for any such conversion ratio to be applicable, the form of mercury in internal tissues should be considered.

If the species analysed in this study are considered, it can be seen that for the albatross species, Atlantic petrel, soft-plumaged petrel and the skua species, the feather:liver ratio is much closer to 2.33 (that is 7/3) when the respective methyl mercury concentrations are compared (mean value= 2.9, s.d.= 3.9, n=7, range= 1.7-4.9; Table 9.1). In contrast, values incorporating total mercury concentrations are consistently less than 2.3 (mean value= 0.6, s.d.= 3.9, n=7, range= 0.05-1.8; Table 9.1).

It is likely that in such species, the demethylation of ingested methyl mercury, resulting in the storage and accumulation of inorganic mercury, effectively serves to 'regulate' the flux of methyl mercury through the bird. The resultant high inorganic (total) mercury levels measured in these species cannot, therefore, be predicted by feather mercury concentrations, since they would be more likely to depend predominantly upon the rate of accumulation (and, hence, the age of the bird) rather than the levels of methyl mercury in internal tissues. Those studies which have cited the 7:3:1 conversion ratio made no mention of the relative proportions of the two forms of mercury in the species (Jensen et al., 1972; Johnels & Westermark, 1969; Westermark et al., 1975). Similarly, those studies which have applied the ratio to convert a given mercury concentration in one tissue to that in another took no account of the particular form of mercury being considered (Appelquist et al., 1985; Berg et al., 1966; Borg et al., 1970; Buhler & Norheim, 1981).

A further complicating factor with respect to relating liver and feather mercury levels, even if virtually all the mercury in the liver is in the methyl form, would appear to be the time of sampling, relative to the moulting process. Mercury concentrations of internal tissues have been shown to decrease markedly during feather moult and the growth of new feathers (for example, Braune & Gaskin, 1987; Honda et al., 1986; Chapter 6). In species such as the common guillemot, in which the mercury has been shown to be virtually all in the methyl form (see Chapter 6), there was still a considerable variation in the value of the feather:liver mercury concentration ratio, depending upon when the sample was obtained (Table 9.1). In the 'pre-moult' sample, liver mercury levels would be relatively high (since mercury would have been accumulated subsequent to the previous moult) when compared to the feather mercury levels and, hence, the feather:liver value was found to be relatively low (Table 9.1). Conversely, after moult the 'body pool' of mercury would have been greatly reduced via losses to new feathers, and the feather:liver value was found to be somewhat higher than that of the 'pre-moult' sample (Table 9.1).

Similarly, fulmars collected from St. Kilda had commenced moult whilst those sampled from Foula had not yet begun this process. It can be seen that the moulting (St. Kildan) birds had a relatively high feather:liver mercury concentration ratio value compared to those birds from Foula whose 'body pool' of mercury would have been relatively large prior to the onset of moult (Table 9.1).

The time of sampling, therefore, would be likely to be an important factor when relating feather mercury levels to those of internal tissues. Even in those species for which the complications of relatively large amounts of inorganic mercury can be discounted, that is in those species in which virtually all the mercury is present as methyl mercury, the moulting process can have a marked effect upon the value of the feather:liver mercury concentration ratio. Again, there seems to have been little consideration of this in other studies.

The value of feather:muscle mercury concentration ratios for species in this study showed pronounced deviations from that of 7:1 (Table 9.1). The use of such a conversion factor, relating these two tissues, would appear to be even less reliable than that relating feather and liver methyl mercury concentrations.

The choice of feather analysed would also be likely to effect the value of any ratio between internal tissue mercury levels and those in feathers. Although all feathers analysed in this study were body feathers, the use of primaries, secondaries and tail feathers which tend to be moulted and replaced first in many moult sequences and which tend to exhibit relatively high and variable mercury levels, would be more likely to give rise to large variations in any feather:liver/muscle ratio values and, hence, be less comparable on an inter-study basis. Body feather mercury levels tend to be less variable when compared to those of other feather types (Furness et al., 1986) and should be used in conversions of mercury levels to those in other tissues.

Generally, conversion factors relating mercury concentrations in different tissues would appear to be prone to variations caused by sampling time, differences in the chemical form of mercury present in different species and should only be used, therefore, as a rough means to gain an impression of mercury levels in various tissues. The limitations of this type of approach are clearly demonstrated if the mean liver total mercury concentration of wandering albatrosses is converted to what one might expect in feathers based on a 3:7 ratio. The value of 268.0 μg g^{-1} (Table 9.1) would be equivalent to 625 μg g^{-1} fresh weight of feather, while the mean feather mercury level was found to be only 30.2 μg g^{-1} fresh weight (Table 9.1) and the maximum feather mercury concentration measured to date in wandering albatrosses 87 μg g^{-1} fresh weight (Thompson, unpublished data).

9.5 REFERENCES

Appelquist, H., Asbirk, S. & Drabaek, I. (1984). Mercury monitoring: mercury stability in bird feathers. Mar. Pollut. Bull. 15, 22-24.

Appelquist, H., Drabaek, I. & Asbirk, S. (1985). Variation in mercury content of guillemot feathers over 150 years. Mar. Pollut. Bull. 16, 244-248.

Berg, W., Johnels, A., Sjostrand, B. & Westermark, T. (1966). Mercury content in feathers in Swedish birds from the past 100 years. Oikos 17, 71-83.

Borg, K., Erne, K., Hanko, E. & Wanntorp, H. (1970). Experimental secondary methyl mercury poisoning in the goshawk (Accipiter gentilis L.). Environ. Pollut. 1, 91-104.

Braune, B.M. & Gaskin, D.E. (1987). Mercury levels in Bonaparte's gulls (Larus philadelphia) during autumn molt in the Quoddy Region, New Brunswick, Canada. Arch. Environ. Contam. Toxicol. 16, 539-549.

Buhler, U. & Norheim, G. (1981). The mercury content in feathers of the sparrowhawk Accipiter nisus in Norway. Fauna norv. Ser. C, Cinclus 5, 43-46.

Crewther, W.G., Fraser, R.D.B., Lennox, F.G. & Lindley, H. (1965). The chemistry of keratins. Adv. Prot. Chem. 20, 191-346.

Furness, R.W. & Hutton, M. (1979). Pollutant levels in the great skua Catharacta skua. Environ. Pollut. 19, 261-268.

Furness, R.W., Muirhead, S.J. & Woodburn, M. (1986). Using bird feathers to measure mercury in the environment: relationships between mercury content and moult. Mar. Pollut. Bull. 17, 27-30.

Honda, K., Nasu, T. & Tatsukawa, R. (1986). Seasonal changes in mercury accumulation in the black-eared kite, Milvus migrans lineatus. Environ. Pollut. (A) 42, 325-334.

Hutton, M. (1981). Accumulation of heavy metals and selenium in three seabird species from the United Kingdom. Environ. Pollut. (A) 26, 129-145.

Jensen, S., Johnels, A.G., Olsson, M. & Westermark, T. (1972). The avifauna of Sweden as indicators of environmental contamination with mercury and chlorinated hydrocarbons. Proc. XVth. Intern. Ornith. Congr. Leiden, 1972. pp.455-465.

Johnels, A.G. & Westermark, T. (1969). Mercury contamination of the environment in Sweden. In, Chemical Fallout. Current Research on Persistent Pesticides. Millar, M.W. & Berg, G.G. (eds.). Thomas, Springfield. pp.221-239.

Muirhead, S.J. & Furness, R.W. (1988). Heavy metal concentrations in the tissues of seabirds from Gough

Island, south Atlantic Ocean. Mar. Pollut. Bull. 19, 278-283.

Ohlendorf, H.M., Anderson, D.W., Boellstorff, D.E. & Mulhern, B.M. (1985). Tissue distribution of trace elements and DDE in brown pelicans. Bull. Environ. Contam. Toxicol. 35, 183-192.

Thompson, D.R. & Furness, R.W. (1989). The chemical form of mercury stored in south Atlantic seabirds. Environ. Pollut. 60, 305-317.

Walsh, P.M. (in press). The use of seabirds as monitors of heavy metals in the marine environment. In, Heavy Metals in the Marine Environment. Furness, R.W. & Rainbow, P.S. (eds.). CRC Press, Boca Raton, Florida.

Westermark, T., Odsjo, T. & Johnels, A.G. (1975). Mercury content of bird feathers before and after Swedish ban on alkyl mercury in agriculture. Ambio 4, 87-92.

CHAPTER 10

Discussion

There is clearly much information to be gained regarding dynamics of mercury within marine ecosystems by using seabirds as monitor species. Furthermore, by virtue of the fact that mercury is chemically stable, once bound to the feather keratin molecule, and that there is a relatively large number of preserved bird study skins available, seabirds provide the most appropriate means of assessing temporal variations in mercury levels in many marine ecosystems.

Fundamental to the study of mercury, and heavy metals generally, is the impact man's activities, through industrial and agricultural discharges, have had upon levels of this metal within the biosphere. The assessment of historical changes in mercury concentrations in physical and biological samples has provided conflicting results, due partly to the choice of species or tissue analysed and the relatively small number of samples. Although feathers overcome these problems, contamination with inorganic mercury through preservation processes, has proved problematical. The extraction technique developed in this study represents a method by which meaningful and reliable results can be obtained. Such an approach provides scope for further work of this kind, enabling temporal trends in mercury concentrations in other species and locations to be assessed in order to complement studies of historical changes in sea water, ice and snow mercury concentrations. Indeed, the use of stable biological samples to investigate changes in the levels of other metals, most notably lead, is an area worthy of further appraisal.

The results from Chapter 7 would tend to indicate that mercury levels in some species of British seabirds have generally increased, by up to a factor of three in some species, over the last 150 years. This leads to the question of whether there is any evidence to suggest that such an increase is causing any discernable deleterious effects in the species concerned. From the findings of this work, the answer would have to be 'no' with the possible exception of the eagles from the west of Scotland. The results of Chapter 4, in particular, suggest that seabirds which exhibit the highest avian mercury levels yet reported, are able to deal with the mercury in such a way as to convert as much ingested methyl mercury into an inorganic storage form as is necessary, and excrete the remainder via the feathers. Such an adaptive detoxification process seems to be characteristic of particular species and it could be, therefore, that an increase in mercury in a species not normally exposed to elevated mercury levels may cause some deleterious effect. There is no evidence to suggest that Manx shearwaters Puffinus puffinus and puffins Fratercula arctica, the two species showing the most marked increases in feather mercury levels in this work, are suffering as a result of their higher mercury burdens. It could be concluded, therefore, that even with an increase in mercury exposure over the last 150 years, the mercury levels of the majority of seabirds are well within the limits of tolerance. In more heavily contaminated, localised areas where clear-cut anthropogenic mercury emissions have had a pronounced effect, this situation may not prevail, and examples of breeding failure and death through mercury poisoning have been noted.

One possible exception to the above picture, may involve those golden eagles Aquila chrysaetos and white-tailed eagles Haliaeetus albicilla which do not have access to high densities of live, terrestrial prey, and which feed to a large extent upon marine species (see Chapter 8). The reduced breeding success of golden eagles which fall into this category and which exhibit high mercury concentrations may simply reflect a correlation with a diet containing a relatively large proportion of seabirds, rather than a genuine effect of metals. However, raptors suffering reduced breeding success and/or population decline represent an area of study requiring further assessment.

The availablity of a sample of great skuas Catharacta skua of known age provided a rare opportunity to investigate age-related trends in mercury levels, accumulation and storage (Chapter 5). The results obtained would suggest that straight forward accumulation of mercury, as noted in many species of marine fish and mammal, is not necessarily the only pattern observed in higher marine organisms. In this respect, the dietary specialisation of the great skua may have effectively masked any positive trend in mercury level with age. Further work to investigate age-related trends in mercury dynamics in birds is required to produce a more complete picture.

In choosing species with which to study such patterns, note should be taken of the form of mercury in internal tissues. As found in the guillemots Uria aalge in this work (Chapter 6), some species contain mercury, of which virtually all is methyl (organic) mercury. Such species, generally those with complete annual feather moults and which are exposed to relatively low levels of mercury, would tend to be unsuitable for studies of age-accumulation of mercury in birds. If the patterns of mercury dynamics suggested in Chapter 4 are applied to such frquently-moulting species with relatively low mercury concentrations, it could be argued that ingested methyl mercury would be almost completely lost via the feathers; the lack of inorganic mercury, formed by demethylation, would indicate that losses via the plumage are sufficient to account for the amount of mercury ingested, and that the biotransformation of ingested methyl mercury is unnecessary. The importance of the egg with respect to mercury loss, and the incorporation of such losses with those via the feathers to create a 'mercury budget' would be a valuable way to assess the dynamics of mercury. The fact that seabirds have different strategies for dealing with ingested mercury, provides great potential for further work to investigate uptake, biotransformation, storage and elimination via the egg(s)/feathers in a variety of species.

SUMMARY

1. A review of the major heavy metals in marine vertebrates was undertaken. Metal levels, trends in tissue distribution patterns, detoxification mechanisms and geographical variations within this group were assessed.

2. A method for the extraction of organic mercury from feathers and internal tissues was developed. The efficiency of the method was tested using standard mercury solutions and reference materials and found to be 90.04% efficient. Matrix effects were not significant and inorganic mercury was not extracted.

3. The relative proportions of inorganic and organic mercury were determined in liver tissues of a range of south Atlantic seabirds and found to vary in a species-dependent manner.

4. Despite extremely high total mercury levels in some species, only a small percentage (as little as 2.6% in wandering albatrosses) was in the methyl form. Those species with relatively low mercury levels tended to have a greater proportion of mercury in the methyl form. Within several species, generally those with high total mercury concentrations and slow moult cycles, methyl mercury, expressed as a percentage of the total mercury level, showed significant decreases with increasing total mercury concentration. For all species combined, there was a significant negative trend between mean percentage methyl mercury and mean total mercury concentration.

5. The effect of age upon mercury concentration, accumulation and storage was investigated in feather and internal tissue samples of great skuas of known age.

6. Feather mercury concentrations were not influenced by age in adults or chicks. A significant negative trend was found between age and liver total mercury concentration in adult birds, but it was thought that this was a chance finding. Dietary

specialisation could be an important determinant of mercury levels in this species.

7. Great skua feather mercury levels were found to correlate well with those of internal tissues, suggesting that a bird with a high mercury level one year would be likely to exhibit a high mercury level in the following year.

8. Seasonal variation in mercury concentrations in common guillemots was studied. Mercury levels in internal tissues decreased over the period April-November whilst those in body feathers remained fairly constant.

9. There were no differences in seasonal mercury losses between male and female guillemots and the egg was thought not to represent an important eliminatory pathway for mercury in this species. Mobilisation of mercury, in association with reproductive processes, could account for the observed decrease in mercury concentration (and content) in internal tissues over the egg-laying period. Feathers were suggested as being the major eliminatory pathway for mercury.

10. The mercury content in feathers of a range of seabirds was found to be virtually all in the methyl (organic) form.

11. The organic mercury extraction technique was used to assess historical changes in mercury levels in feathers of some British seabirds. Contemporary feather mercury levels were compared with those in feather samples obtained from museum study skins.

12. Generally, mercury levels in seabirds from comparable geographical locations were found to have increased over the last 150 years. This increase was most notable in Manx shearwaters and puffins from the south and west of Britain and Ireland, and less pronounced in species from the north and east of Britain. A decrease in the mercury burdens of fulmars from

Shetland and Orkney since early this century was thought to be associated with a change in the population structure and diet at that locality.

13. The levels of mercury in feathers from Scottish golden and white-tailed eagles were measured. Golden eagles from the Western Isles, particularly Rhum, exhibited significantly higher mercury concentrations than those in eagles from the mainland, especially the east highlands. This trend was due, in part, to prey availability, with eagles in the Western Isles feeding to a greater extent on seabirds, with terrestrial prey species predominantly in the diet of the eastern birds.

14. The possibility that reduced breeding success in the western birds could be the result of elevated mercury burdens was discussed and the relatively high mercury levels in western birds of both eagle species was assessed with respect to deleterious effects.

15. The validity and use of mercury concentration conversion ratios for tissue comparisons was briefly discussed. Tissue methyl mercury levels would seem to be a more appropriate measure to use in such comparisons, total mercury levels, in some species, deviating considerably from the predicted ratios.

APPENDIX I

Appendix I. Historical body feather samples: capture details, methyl mercury concentrations (µg g^{-1} fresh weight) and museum obtained from (RSM=Royal Scottish Museum, Edinburgh; H'cock=Hancock Museum, Newcastle upon Tyne; BM(Tr.)=British Museum (Natural History), Tring). All adult birds unless stated. summ=summer.

Species	Capture Date	Locality	Hg Conc.	Museum
Wandering albatross	23.11.1955	Gough Island	27.05	BM (Tr.)
	16.04.1956	Gough Island	26.40	BM (Tr.)
Yellow-nosed albatross	19.03.1956	Gough Island	3.24	BM (Tr.)
	19.03.1956	Gough Island	3.63	BM (Tr.)
Sooty albatross	02.12.1955	Gough Island	11.65	BM (Tr.)
	24.03.1956	Gough Island	13.18	BM (Tr.)
Fulmar	06.06.1884	St. Kilda	2.05	BM (Tr.)
	20.05.1905	Shetland	1.50	RSM
	20.05.1905	Shetland	3.65	RSM
	16.03.1908	Orkney	5.25	RSM
	16.03.1908	Orkney	5.54	RSM
	16.03.1908	Orkney	4.81	RSM
	16.05.1908	Orkney	4.64	RSM
	02.06.1908	Orkney	4.82	RSM
	02.07.1908	Orkney	3.09	RSM
	26.02.1909	Lewis	3.83	BM (Tr.)
	30.07.1909	St. Kilda	6.71	BM (Tr.)
	11.04.1910	Orkney	6.32	RSM
	23.07.1910	North Rona	3.82	BM (Tr.)
	23.03.1911	Unst	3.84	RSM
	27.04.1911	Fair Isle	1.62	RSM
(juv.)	07.09.1911	St. Kilda	3.18	RSM
	09.09.1911	St. Kilda	4.72	RSM
	21.09.1911	St. Kilda	6.83	RSM
	21.09.1911	St. Kilda	4.64	RSM
	--.06.1912	Fair Isle	4.13	RSM
	05.06.1912	Fair Isle	2.37	RSM
	10.08.1912	Orkney	5.99	RSM
	19.08.1912	Orkney	4.23	BM (Tr.)
	19.08.1912	Orkney	10.74	BM (Tr.)
	19.08.1912	Orkney	5.61	BM (Tr.)
	19.08.1912	Orkney	3.94	BM (Tr.)
	19.08.1912	Orkney	2.83	BM (Tr.)
	23.01.1913	Shetland	4.00	BM (Tr.)
	03.03.1913	Scalloway	3.49	BM (Tr.)
	20.07.1913	Orkney	2.02	RSM
	20.07.1913	Orkney	1.27	RSM
	--.05.1914	North Scotland	2.58	BM (Tr.)
	--.05.1923	St. Kilda	1.85	RSM
	--.04.1925	St. Kilda	4.98	RSM
	25.02.1931	Fair Isle	3.74	BM (Tr.)
	01.01.1935	Dornoch Firth	1.82	RSM
	24.08.1939	Noss	6.91	BM (Tr.)

Appendix I continued

Manx shearwater	summ. 1854	Shetland	1.72	RSM
	--.--.1859	Shetland	1.50	H'cock
	--.--.1859	Shetland	2.45	H'cock
	24.05.1866	Rathlin	0.34	BM (Tr.)
	24.05.1866	Ireland	1.07	BM (Tr.)
	01.04.1867	Northumberland	0.66	H'cock
	--.06.1867	Co. Antrim	0.59	RSM
	31.03.1871	Scillies	0.43	BM (Tr.)
	12.06.1884	St. Kilda	0.41	BM (Tr.)
	23.09.1887	North Berwick	1.04	RSM
	23.11.1887	North Berwick	0.77	RSM
	11.04.1892	Mayo	0.08	BM (Tr.)
	22.04.1892	South Wales	1.57	BM (Tr.)
	22.04.1892	South Wales	2.21	BM (Tr.)
	17.09.1908	Orkney	0.42	RSM
	04.06.1909	Rhum	2.77	RSM
	04.06.1909	Rhum	1.50	RSM
	01.06.1910	Eigg	1.13	RSM
	21.06.1912	Scillies	1.21	BM (Tr.)
	21.06.1912	Skokholm	1.17	BM (Tr.)
	25.09.1912	Orkney	0.78	RSM
	25.09.1912	Orkney	0.24	RSM
	25.05.1929	Orkney	1.24	RSM
	25.05.1929	Orkney	2.07	RSM
	06.08.1930	Skokholm	1.32	RSM
	06.08.1930	Skokholm	2.00	RSM
	03.06.1937	Skomer	1.45	RSM
	04.06.1937	Skomer	2.19	H'cock

Appendix I continued

Gannet		--.05.1866	Bass Rock	2.48	BM (Tr.)
	(juv.)	--.10.1870	Northumberland	0.94	H'cock
	(juv.)	21.08.1872	Bass Rock	0.83	RSM
	(juv.)	--.07.1873	Bass Rock	1.59	BM (Tr.)
		--.07.1873	Bass Rock	6.00	BM (Tr.)
		--.11.1873	Sunderland	3.18	RSM
		04.09.1875	Bass Rock	10.00	BM (Tr.)
		--.05.1876	Northumberland	3.50	H'cock
		--.09.1876	Loch Fyne	6.01	BM (Tr.)
		--.06.1878	St. Kilda	2.48	BM (Tr.)
		--.--.1879	St. Kilda	3.65	BM (Tr.)
		--.07.1888	Ailsa Craig	5.38	RSM
		27.08.1890	Sutherland	8.71	RSM
		05.08.1895	Bass Rock	4.21	BM (Tr.)
		--.09.1895	Bass Rock	4.29	BM (Tr.)
		--.09.1895	Bass Rock	3.81	BM (Tr.)
	(juv.)	--.09.1895	Bass Rock	1.21	BM (Tr.)
	(juv.)	04.09.1895	Bass Rock	2.72	BM (Tr.)
	(juv.)	13.09.1895	Bass Rock	2.10	BM (Tr.)
		13.09.1895	Bass Rock	6.72	BM (Tr.)
		13.09.1895	Bass Rock	4.10	RSM
		--.09.1895	Bass Rock	1.77	BM (Tr.)
		--.09.1895	Bass Rock	8.09	BM (Tr.)
		--.08.1896	Bass Rock	9.21	BM (Tr.)
		--.09.1896	Bass Rock	10.62	BM (Tr.)
		--.09.1896	Bass Rock	6.74	BM (Tr.)
		10.09.1896	Bass Rock	8.30	BM (Tr.)
		26.08.1897	Bass Rock	4.55	BM (Tr.)
		28.08.1897	Bass Rock	7.30	BM (Tr.)
		10.09.1897	Bass Rock	6.14	BM (Tr.)
		--.09.1905	Bass Rock	3.81	BM (Tr.)
		--.06.1907	Orkney	10.63	RSM
		01.10.1912	Beaulyfirth	6.82	RSM
		06.09.1913	Orkney	6.65	RSM
	(juv.)	12.10.1914	Yorkshire	0.97	BM (Tr.)
		12.05.1915	Ross-shire	5.32	BM (Tr.)
		21.09.1920	Northumberland	6.03	H'cock
	(juv.)	06.11.1923	Orkney	1.06	RSM
	(juv.)	19.08.1927	Firth of Forth	1.47	RSM
	(juv.)	27.08.1931	Bamburgh	1.74	H'cock
	(juv.)	05.06.1932	Northumberland	4.04	H'cock
	(juv.)	14.09.1933	Northumberland	1.03	H'cock
		14.04.1936	Northumberland	4.22	H'cock
		24.07.1936	Northumberland	4.34	H'cock
	(juv.)	29.08.1939	Bass Rock	1.64	BM (Tr.)
		--.08.1951	Bass Rock	9.07	H'cock
White-tailed eagle		--.--.1896	Scotland	4.13	BM (Tr.)
		--.--.1911	Astrakahn, USSR	4.73	H'cock
		--.--.1911	Astrakahn, USSR	8.63	H'cock
Golden eagle		07.07.1908	Argyllshire	0.31	BM (Tr.)
		24.11.1911	Ross-shire	1.37	BM (Tr.)

Appendix I continued

Great skua	--.--.1835	Shetland	3.39	H'cock
	--.--.1835	Shetland	4.29	H'cock
	10.06.1873	Faeroe	12.25	RSM
	26.06.1873	Faeroe	4.12	BM (Tr.)
	22.07.1873	Faeroe	5.95	BM (Tr.)
	28.08.1873	Faeroe	6.22	BM (Tr.)
	--.08.1877	Faeroe	12.12	BM (Tr.)
	12.06.1879	Faeroe	6.27	BM (Tr.)
	06.07.1879	Faeroe	9.65	BM (Tr.)
	26.05.1884	Faeroe	9.00	BM (Tr.)
	26.09.1884	Faeroe	5.46	BM (Tr.)
	04.08.1907	South Iceland	3.67	BM (Tr.)
	04.08.1907	South Iceland	2.48	BM (Tr.)
	31.08.1907	Unst	2.41	BM (Tr.)
	30.08.1908	Aberdeen	3.24	BM (Tr.)
	11.08.1910	North Iceland	3.54	BM (Tr.)
	30.07.1911	North Iceland	3.88	H'cock
	02.08.1911	North Iceland	4.06	RSM
	30.09.1911	Shetland	4.65	BM (Tr.)
	21.10.1912	North Iceland	4.95	RSM
	20.06.1914	Unst	10.62	BM (Tr.)
	10.10.1934	Shetland	12.97	RSM
	20.06.1935	Shetland	4.46	RSM
	15.10.1935	Shetland	4.66	RSM
	11.08.1938	Orkney	9.74	BM (Tr.)
	28.08.1938	Orkney	4.18	BM (Tr.)
	11.08.1939	Orkney	13.57	BM (Tr.)
	17.08.1939	Shetland	3.75	BM (Tr.)
	26.08.1939	Shetland	6.12	BM (Tr.)
	27.08.1939	Shetland	7.34	RSM
	10.07.1949	Foula	5.95	RSM
	10.07.1949	Foula	16.91	RSM
Herring gull	summ. 1854	Orkney	1.28	BM (Tr.)
	--.05.1856	Eastbourne	7.11	BM (Tr.)
	--.06.1860	Orkney	3.76	RSM
	--.03.1874	Sunderland	0.34	BM (Tr.)
	--.03.1876	Wick	2.35	BM (Tr.)
	17.02.1893	Wales	1.38	BM (Tr.)
	28.01.1902	Ireland	2.24	BM (Tr.)
	28.06.1903	Wales	1.08	BM (Tr.)
	05.07.1912	Caithness	9.47	BM (Tr.)
	19.08.1912	Cromarty Firth	1.04	BM (Tr.)
	04.06.1913	Fair Isle	1.28	RSM
	02.03.1914	Inverness	0.68	BM (Tr.)
	07.02.1915	Cornwall	2.29	BM (Tr.)
	05.04.1915	Cromarty Firth	3.02	BM (Tr.)
	27.06.1916	Inverness	2.71	RSM
	27.07.1916	Argyll	2.29	BM (Tr.)
	04.01.1917	Ireland	7.72	BM (Tr.)
	22.07.1948	Skye	2.34	RSM

Appendix I continued

Lesser black-backed gull	pre- 1849	Orkney	1.68	BM (Tr.)
	summ. 1861	Orkney	9.50	RSM
	25.04.1862	Orkney	1.89	BM (Tr.)
	--.--.1870	North Berwick	5.19	BM (Tr.)
	25.05.1870	Loch Lomond	2.91	BM (Tr.)
	--.06.1870	Orkney	3.64	BM (Tr.)
	03.09.1873	Faeroe	3.34	BM (Tr.)
	--.07.1876	Loch Lomond	5.23	RSM
	29.08.1883	Romney Marsh	4.66	BM (Tr.)
	07.06.1886	Durham	1.78	H'cock
	19.05.1891	Northumberland	0.43	H'cock
	21.05.1892	Boreland	3.75	RSM
	03.06.1894	Oban	2.22	BM (Tr.)
	--.--.1895	Cambridge	2.94	BM (Tr.)
	14.08.1895	Orkney	3.67	BM (Tr.)
	06.06.1900	Forres	17.94	BM (Tr.)
	--.05.1905	Loch Katrine	8.88	BM (Tr.)
	06.07.1909	Silverdale	4.81	RSM
	09.07.1909	Silverdale	4.72	RSM
	09.07.1909	Silverdale	3.83	RSM
	29.06.1912	Northumberland	4.70	BM (Tr.)
	20.05.1913	Fair Isle	2.01	RSM
	31.05.1913	Fair Isle	12.38	RSM
	01.07.1913	Loch Trlig	4.18	RSM
	03.09.1913	Northumberland	3.03	BM (Tr.)
	04.09.1913	Northumberland	15.20	BM (Tr.)
	05.09.1913	Northumberland	8.45	BM (Tr.)
	06.09.1913	Northumberland	3.49	BM (Tr.)
	19.09.1913	Orkney	7.36	BM (Tr.)
	17.04.1914	Fair Isle	3.63	RSM
	07.05.1914	Caithness	4.38	BM (Tr.)
	07.05.1914	Fair Isle	10.08	RSM
	12.05.1914	Caithness	2.15	BM (Tr.)
	20.07.1914	Caithness	2.49	BM (Tr.)
	02.09.1914	Fair Isle	4.86	RSM
(juv.)	12.09.1914	Fair Isle	3.42	RSM
	14.09.1914	Fair Isle	2.38	RSM
	19.06.1915	Lancashire	2.43	BM (Tr.)
	30.06.1916	Inverness	8.80	RSM
	27.04.1920	Northumberland	2.64	H'cock
	--.--.1923	Faeroe	2.23	H'cock
	04.08.1924	Sunderland	2.43	RSM
	26.04.1925	Suffolk	1.61	BM (Tr.)
	02.05.1934	Pitlochry	3.12	RSM

Great black-backed gull	04.12.1818	Shetland	5.11	BM (Tr.)
	15.06.1860	Orkney	3.40	RSM
	03.01.1870	Orkney	5.06	BM (Tr.)
	16.06.1871	Orkney	9.34	BM (Tr.)
	14.07.1871	Orkney	6.84	BM (Tr.)
	summ. 1872	Orkney	4.81	BM (Tr.)
	17.06.1872	Sutherland	8.17	BM (Tr.)
	14.02.1877	Holy Isle	2.15	BM (Tr.)
	--.05.1891	Ireland	4.52	BM (Tr.)
	07.09.1891	Douna Nook	4.36	BM (Tr.)
	29.02.1892	Mayo	2.41	BM (Tr.)
	12.03.1892	Suffolk	4.04	BM (Tr.)
	17.06.1892	Sutherland	8.59	BM (Tr.)
	17.06.1892	Sutherland	15.04	BM (Tr.)
	09.06.1909	Shetland	12.11	BM (Tr.)
	25.08.1913	Ross-shire	7.83	BM (Tr.)
	01.04.1913	Beauly	4.98	BM (Tr.)
	16.09.1920	Wigtonshire	4.83	BM (Tr.)
Guillemot	--.--.1839	Northumberland	1.30	H'cock
	--.--.1850	Northumberland	4.12	H'cock
(juv.)	--.--.1864	Iceland	1.68	H'cock
	summ. 1866	Orkney	2.47	BM (Tr.)
	--.--.1869	Orkney	1.59	BM (Tr.)
	--.03.1874	Sunderland	1.31	BM (Tr.)
	--.02.1885	Northumberland	0.66	H'cock
	--.--.1887	Flamborough	2.42	BM (Tr.)
	--.--.1887	Flamborough	2.33	BM (Tr.)
	--.--.1887	Flamborough	2.57	BM (Tr.)
	--.--.1891	Mayo	1.18	BM (Tr.)
	--.--.1891	Mayo	1.63	BM (Tr.)
	--.--.1892	Mayo	0.84	BM (Tr.)
	--.--.1892	Mayo	1.78	BM (Tr.)
	--.--.1892	Mayo	0.58	BM (Tr.)
	--.06.1892	Mayo	3.68	BM (Tr.)
	--.06.1892	Mayo	0.47	BM (Tr.)
	14.08.1893	Orkney	1.63	BM (Tr.)
	--.--.1895	Scarborough	1.17	BM (Tr.)
	--.06.1904	Achill Isles	1.00	BM (Tr.)
	--.--.1909	Ross	1.75	BM (Tr.)
	--.--.1912	Dornoch	1.53	BM (Tr.)
	--.--.1912	Ross	1.42	BM (Tr.)
	--.--.1912	Ross	3.34	BM (Tr.)
	22.06.1912	Shetland	4.40	BM (Tr.)
	--.--.1913	Orkney	1.77	BM (Tr.)
	--.04.1913	Dornoch	2.00	BM (Tr.)
	--.05.1913	Wigton	2.24	BM (Tr.)
	--.--.1915	Ross	1.75	BM (Tr.)
	--.06.1916	Ross	1.08	BM (Tr.)
	--.--.1920	Handa	0.99	BM (Tr.)
	--.06.1920	Dornoch	1.10	BM (Tr.)
	13.09.1920	Northumberland	1.70	H'cock
	27.07.1924	Shetland	2.02	BM (Tr.)
	27.07.1924	Shetland	1.79	BM (Tr.)
	30.07.1924	Canna	2.34	BM (Tr.)
	16.05.1925	Treshnish Isles	1.25	BM (Tr.)
	--.07.1925	Barra	1.24	BM (Tr.)

Appendix I continued

Black guillemot	09.06.1833	Norway	0.58	H'cock
	13.06.1833	Norway	2.40	H'cock
Puffin	--.07.1842	Scarborough	0.37	BM (Tr.)
	--.--.1856	-----------	2.00	H'cock
	--.--.1866	Orkney	0.18	BM (Tr.)
	24.04.1866	Northumberland	0.52	BM (Tr.)
	--.02.1870	Devon	1.62	BM (Tr.)
	--.--.1876	Hastings	0.91	BM (Tr.)
	summ. 1887	Flamborough	0.80	BM (Tr.)
	summ. 1887	Flamborough	0.39	BM (Tr.)
	--.--.1887	Flamborough	0.27	BM (Tr.)
	10.04.1891	South Wales	1.72	BM (Tr.)
	10.04.1891	South Wales	1.57	BM (Tr.)
	10.04.1891	South Wales	0.23	BM (Tr.)
	01.07.1891	Mayo	2.13	BM (Tr.)
	22.07.1891	Mayo	3.68	BM (Tr.)
	22.07.1891	Mayo	0.67	BM (Tr.)
	22.07.1891	Mayo	1.88	BM (Tr.)
	06.04.1892	Mayo	1.42	BM (Tr.)
	11.04.1892	Mayo	0.71	BM (Tr.)
	24.04.1892	Dublin	0.18	BM (Tr.)
	04.05.1892	Mayo	1.40	BM (Tr.)
	04.05.1892	Mayo	1.60	BM (Tr.)
	11.05.1892	Mayo	0.37	BM (Tr.)
	--.06.1892	Mayo	0.34	BM (Tr.)
	03.06.1892	Mayo	2.11	BM (Tr.)
	08.06.1892	Mayo	2.00	BM (Tr.)
	08.06.1892	Mayo	2.88	BM (Tr.)
	14.07.1892	Mayo	1.64	BM (Tr.)
	01.08.1892	Mayo	1.12	BM (Tr.)
	03.08.1892	Mayo	1.99	BM (Tr.)
	13.08.1892	Mayo	1.77	BM (Tr.)
	22.06.1894	Isle of Man	2.44	BM (Tr.)
	22.06.1894	Isle of Man	2.38	BM (Tr.)
	20.06.1895	South Wales	1.87	BM (Tr.)
	20.06.1895	South Wales	2.39	BM (Tr.)
	20.06.1895	South Wales	2.17	BM (Tr.)
	23.06.1895	South Wales	1.83	BM (Tr.)
	29.01.1899	Kent	1.73	BM (Tr.)
	30.06.1903	South Wales	2.48	BM (Tr.)
	27.06.1904	West Ireland	0.79	BM (Tr.)
	17.07.1906	South Wales	2.54	BM (Tr.)
	17.07.1906	South Wales	1.68	BM (Tr.)
	28.05.1910	Galloway	0.80	BM (Tr.)
	08.05.1912	Orkney	3.24	BM (Tr.)
	14.05.1912	Orkney	1.32	BM (Tr.)
	06.08.1912	Ross-shire	2.63	BM (Tr.)
	--.05.1913	Cornwall	1.31	BM (Tr.)
	01.05.1913	Galloway	1.95	BM (Tr.)
	10.05.1913	Wigton	1.92	BM (Tr.)
	22.12.1913	Caithness	1.35	BM (Tr.)
	27.05.1914	Caithness	3.53	BM (Tr.)
	27.05.1914	Caithness	0.52	BM (Tr.)
	--.06.1916	Saltee	1.73	BM (Tr.)
	29.08.1917	Northumberland	1.51	BM (Tr.)
	28.11.1921	Northumberland	1.13	H'cock