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THE ACCUMULATION, STORAGE AND ELIMINATION OF METALS AND
ORGANOCHLORINES IN THE GREAT SKUA Catharacta skua skua AND METAL
ACCUMULATION IN ATLANTIC PROCELLARIIFORMES

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A THESIS submitted for the degree of
DOCTOR OF PHILOSOPHY in the FACULTY
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S.J. Muirhead

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ABBREVIATIONS

PLEASE NOTE:- Due to the limitations of the word-processing system used to produce this thesis, it has not been possible to print the character ' μ '. Because of this, the abbreviation ug has been used throughout the thesis to represent micrograms.

ABSTRACT

The concentrations of metals and organochlorines (DDE and polychlorinated biphenyls) were measured in tissues of seabirds from the North and South Atlantic in order to examine possible differences between north and south populations. The seabirds were collected from the islands of Foula (Shetland), St. Kilda (Outer Hebrides) and Gough (Tristan da Cunha), the species investigated being the Great skua Catharacta skua skua and C.s. hamiltoni and several North and South Atlantic Procellariiformes.

The North Atlantic Great Skua C.s. skua was of special interest for two reasons as it is a top marine predator and the birds were of known age. Great Skua tissues and feathers were analysed in order to compare the inter-organ distribution of the essential metals copper, zinc, and the essential metalloid selenium, with two chemically related metals, mercury and cadmium, which have no known physiological function. Eggs, liver, muscle and body fat were analysed for organochlorines.

Concentrations of metals were determined in the liver and kidney of South and North Atlantic Procellariiformes and Great Skuas to indicate levels of potential pollutants and to compare concentrations in pelagic seabirds north-east Atlantic with the South Atlantic.

The metals cadmium, copper, and zinc were determined by atomic absorption spectrophotometry (AAS); mercury by cold-flame AAS and mercury/hydride/AAS; selenium by instrumental neutron activation analysis and organochlorines by electron-capture gas chromatography.

In the individual tissues of the Great Skua correlations were found between DDE and PCB's for both whole tissue and lipid concentrations. DDE levels were found to have declined in the eggs and tissues of the Great Skua between 1971 and 1983, but this was not found for PCB concentrations.

The South Atlantic Procellariiformes accumulate high concentrations of the potentially toxic metals cadmium and mercury, the highest levels for cadmium being found in the kidney and for mercury in the liver (up to $148\mu\text{g g}^{-1}$ wet weight cadmium in the kidney and up to $271\mu\text{g g}^{-1}$ wet weight mercury in the Wandering Albatross Diomedea exulans). North Atlantic Procellariiformes contained lower concentrations of cadmium in the kidney (up to $25\mu\text{g g}^{-1}$ Cadmium wet weight in the Fulmar Fulmarus glacialis) which may be a consequence of diet, those birds taking a higher proportion of squid in their diet (several of the South Atlantic species) having higher cadmium concentrations than birds feeding mainly on other food sources (all of the North Atlantic birds). Squid may form a potential source of metals for the Procellariiformes as cephalopods are known to accumulate metals in the digestive gland.

Many of the seabirds showed correlations between kidney cadmium and zinc concentrations, and liver and kidney cadmium concentrations. Accumulation of zinc and cadmium together suggests the existence of a possible detoxification mechanism involving zinc and metallothionein, but the correlation does not exist for all birds accumulating high cadmium concentrations. The normal distribution of some of the data suggests that there may be metabolic regulation of cadmium.

The North Atlantic Great Skua shows strong relationships between most of the metals and between renal and liver cadmium concentrations. However, no correlation between age and accumulation of any of the metals was shown. Correlations of selenium and mercury concentrations in the liver indicate, as with zinc and cadmium, a possible protective role by selenium.

Levels of PCB's and DDE in muscle and body fat all correlate with each other and vary greatly between individuals, suggesting individual

variation in excretion rates, feeding habits or distribution in winter.

Mercury levels in primary feathers indicate the concentration of mercury in the bloodstream at the time of feather formation, reflecting in turn either environmental levels at the time of feather formation or the mobilisation of tissue mercury and its excretion via the feather. Mercury concentrations in the primary feathers of several species decline from primary one to primary ten, with the levels being higher in South Atlantic seabirds. No significant differences were found in mercury concentrations between present day and museum samples of feathers of the Great Skua.

Great skuas from the South Atlantic have significantly higher renal cadmium concentrations than North Atlantic Great Skuas. This can probably be attributed to dietary differences, the birds from the S. Atlantic feeding entirely on seabirds with elevated cadmium levels and the Great Skuas of the North Atlantic feeding primarily on fish containing less than $1 \mu\text{g g}^{-1}$ wet weight of cadmium. No such difference was found for mercury and there were no marked differences in mercury concentrations in the prey species.

The North Atlantic Great Skuas and Procellariiformes feeding on seabirds, fish and marine invertebrates at the ocean surface, which is often enriched with metals and organochlorines, provide possible indicators of offshore pollution in the north-east Atlantic. However, levels of possible pollutants, though elevated, are relatively low compared to those of the South Atlantic Procellariiformes. This is despite the fact that the South Atlantic birds, the feeding habits of which have been little researched, are less likely to have contact with anthropogenic sources of metals.

CHAPTER 1

INTRODUCTION

Much of the work concerned with monitoring the levels of organochlorines and metals in the environment has been concerned with human health, and many studies on top marine predators were initiated because of concern for the species themselves. This was because many birds and marine mammals were shown to concentrate contaminants to a much higher level than invertebrates. The hypothesis was therefore put forward that these animals, as top predators may be especially vulnerable to various contaminants, and this concern was added to as a result of 'wrecks', such as that on the Irish Sea coast in 1969 (Parslow and Jefferies, 1972), and strandings of cetaceans. Marine top predators are therefore a potentially threatened part of the natural ecosystem and are consequently of interest to science and conservation alike.

In carrying out studies on pelagic seabirds many problems are encountered. Frequently there are difficulties in obtaining specimens, which may be in different nutritional or physiological states. Various organs have in the past been used which differentially accumulate a variety of contaminants. For example metals are most often associated with liver, kidney and bone, whereas organochlorines are usually concentrated in the fatty tissue. Often sample sizes have been small, with samples, frequently of birds found dead, coming from a wide range of geographical areas. In samples where the birds have been found dead, there may after death have been some redistribution of metals between the various organs producing anomalous results.

Seabird eggs were first analysed for hydrocarbon pesticides and their residues in 1963 (Moore and Tatton, 1965), and the analysis of eggs continued throughout the sixties, receiving impetus from the work of Ratcliffe (1967), who isolated DDT as the cause of eggshell

thinning. Work on PCB's (polychlorinated biphenyls) was further increased when elevated levels of both PCB's and heavy metals were found in the livers of 9 auks which died in the seabird wreck around the Irish Sea in 1969 (Parslow and Jefferies, 1973).

A considerable amount of work has been carried out on the levels of organochlorines in seabirds (Prestt et al., 1970; Bourne and Bogan, 1972), but for many species the number of birds or eggs analysed has been small. There is often considerable variation between individuals in contaminant concentrations. Thus the number of firm conclusions drawn from organochlorine studies in the field has been small due to the egg/tissue/location problems and the difficulty of applying results from laboratory dosing studies to the field situation, where environmental variables also play a role.

Metals and organochlorines form some of the most persistent toxic substances in the environment and are therefore more easily accumulated by organisms from their food. Organochlorines and methylmercury, especially, are readily lipid-soluble and are often biomagnified through the food chain. The metals cadmium and inorganic mercury may act antagonistically towards both zinc and copper due to the chemical similarity of the four metals. Their persistence and ability to accumulate in tissues, together with their toxicity has given rise to much concern over effects on marine animals. Pelagic seabirds are at or close to the top of the marine food chain and may in polluted situations accumulate toxic doses of contaminants, and for this reason they form a suitable study group. They also appear to accumulate elevated concentrations of metals naturally but there may be a fine balance controlling the tolerance of the birds to these metals, a balance which may be disturbed if anthropogenic input of metals to the environment increases.

The sample of Great Skuas Catharacta skua skua from the Shetland Islands forms a potentially interesting study group. The sample was large (up to 47 birds) and the birds were known to contain high concentrations of metals and organochlorines (Furness and Hutton, 1979). More importantly the birds were of known age and therefore provided a unique opportunity to study the possible accumulation of metals and organochlorines in a seabird over time.

However, the evidence for mercury and cadmium accumulation in seabirds shows that there is much variation between individuals (Fimreite, 1974; Furness and Hutton, 1979; Osborn et al., 1979). Concentrations of metals were also found to vary widely depending on the element, geographical location and season (Osborn, 1979). The levels of the essential metals zinc and copper are of interest as the copper status in animals is known to be depressed in the presence of elevated concentrations of zinc or cadmium (Bremner, 1978; cited in Denton et al., 1980), and cadmium may affect zinc metabolism (Bremner, 1978). Copper concentrations are usually in tens of mg kg^{-1} wet weight and zinc levels are usually much higher often over 100mg kg^{-1} in the kidney. Zinc concentrations have also been found to correlate with cadmium concentrations in the kidney (Osborn et al., 1979).

The soft tissues selected for the study of metal concentrations were the muscle, liver and kidney, as in many cases the liver has been found to be the main concentrating organ for mercury and the kidney for cadmium (Stoneburner and Harrison, 1981).

In geographical terms the distribution pattern of most of the contaminants studied appears to be similar, with the most highly contaminated specimens coming from estuaries and coastal waters. However even in birds from remote areas elevated levels of PCB's, DDE and metals have been found (Bull et al., 1977). In order to examine accumulation of the metals through the food chain, as many items as

possible from the Great Skuas' diet including fish and petrels were analysed for heavy metals.

High concentrations of mercury have been found in the liver and kidneys of pelagic seabirds and the proportion of this mercury present as methyl-mercury appears to be highly variable (Osborn et al., 1979; Norheim and Froslic, 1978). In several species, including man, mercury levels have been closely correlated with selenium concentrations in the liver and kidney, and this relationship has also been found in the Great Skua (Furness and Hutton, 1979). Mercury concentrations in the Great Skua were also related to age. The concentrations of selenium were found to exceed those of mercury in the liver and kidney (Furness and Hutton, 1979). These aspects, due to a larger sample size, were expanded upon in this study to give more conclusive results.

Organochlorines were examined to give an indication of tissue variations, and relationships between the organochlorines PCB and DDE. As organochlorines are extremely persistent, levels were examined in relation to age. Due to the solubility of organochlorines in lipids fatty tissue was included in this study. Organochlorines have been analysed in skuas for just over a decade and therefore trends over this time to the present day were examined. Both PCB's and DDE in the last decade have been subject to various bans and usage restrictions, such that concentrations may be declining in the environment, as found in the eggs of Shags and Norwegian seabirds (Coulson et al., 1972; Barrett et al., 1985).

The North Atlantic, because of its close proximity to the industrial regions of Europe and the eastern seaboard of North America, might be expected, through the discharges of industrial and domestic wastes into the ocean, to be more polluted than the South

Atlantic. From the island of Gough a number of samples of the Great Skua Catharacta skua hamiltoni were obtained, allowing a direct comparison between North and South Atlantic populations of skuas. The diets of the two populations were known, at least in part, allowing examination of the accumulation of metals through the food chain.

Procellariiformes form a major part of the pelagic avifauna and are taxonomically closely related. Metal concentrations in South Atlantic Procellariiformes were examined to compare with levels in North Atlantic Procellariiformes, to identify any differences in metal accumulations between the two oceans and between species, as the birds have different feeding habits. The fourteen species of South Atlantic Procellariiformes were collected from Gough Island which may be expected to be relatively pollution free.

Antarctic birds have been shown to accumulate elevated concentrations of mercury and cadmium in the liver and kidney (Anderlini et al., 1972; Norheim and Frosli, 1978; Schneider et al., 1985), but sample sizes have often been very small. For most of the species in this study the sample size is greater than 10. In the tissues of the Procellariiformes and skuas it was hoped to discover whether tissues containing high zinc concentrations also had elevated concentrations of mercury and cadmium as these two metals are known to interfere with zinc metabolism (Bremner, 1978). The levels of the metals were also examined to see if concentrations in the tissues were related to the physiological accumulation of zinc. As cadmium, zinc and mercury are in many ways chemically similar and often occur naturally together, the work was designed to look for any of the above correlations between metal concentrations that may be of biological significance. Another aim was to look for any sexual differences in the accumulation of the metals. Body composition and hence contaminant burden can vary significantly between the sexes in birds and mammals

at different times of the year, because of the different sexual roles during breeding. Females may, for example, get rid of fat soluble contaminants into the eggs.

The main problem of studying seabirds in order to examine metal concentrations in the environment is that individuals may range over large areas during the year. They are, however often more suitable than invertebrates or fish as monitors because day to day and seasonal variation in food intake is relatively small. If the maximum age attained by the species is unknown, longevity may present problems as contaminants may be accumulated from different sources with time. Since sampling can usually only be done during the breeding season, seasonal physiological changes in metal concentrations due to breeding, moult and migration cannot be readily identified. Nevertheless this study of levels in Procellariiformes may provide a baseline study of metal concentrations in the South Atlantic, which may assist in identifying pollutants in the future.

Feathers formed the final part of the study as these provide an alternative route for removal of metals besides eggs and faeces (Teijing, 1967). Stickel et al., (1977) found that in contaminated Mallards Anas platyrhynchos the loss of methyl-mercury from the tissue to the growing feather was particularly important. The analysis of feathers also provides a means of monitoring mercury concentrations in birds without killing them and concentrations of mercury in the liver and the feather have been found to be related in the Great Skua (Furness and Hutton, 1979).

Primary feathers have most often been used and the mercury content in the feather has been related directly to the diet of the bird when the feather was formed (Berg et al., 1966; Johnels et al., 1968), and this aspect will be examined in relation to Great Skua feathers. Since

feathers are durable due to their keratin structure (Crewther et al., 1965), present day mercury concentrations in feathers can be compared to concentrations in feathers from museum specimens. In Sweden, concentrations of mercury in the feathers of terrestrial birds were found to increase after the introduction of alkyl-mercury seed dressings in 1940, and in the Osprey Pandion haliaetus and Great-crested Grebe Podiceps cristatus levels increased after 1900 coinciding with the introduction of chlor-alkali production plants (Berg et al., 1966; Johnels and Westermarck, 1969). In this study concentrations were examined in North Atlantic Great Skuas from 1873 to 1983 in order to determine any changes that may have occurred in environmental mercury concentrations, because of anthropogenic inputs into the oceans over that time. Feathers of the closely related populations of the South Atlantic Great Skua were examined to compare South and North Atlantic concentrations of mercury in the skuas.

CHAPTER 2

ACCUMULATION OF ORGANOCHLORINES AND METALS IN SEABIRDS AND THEIR ENVIRONMENT

2.1 INTRODUCTION

A wide range of pollutants enter the marine environment, displaying a broad spectrum of effects, from the highly visual ones such as floating plastics, wood debris and foam, to the very subtle and insidious effects of bioaccumulation of metals and chlorinated hydrocarbons. It is the effects of the latter two topics and their effects on seabirds which are reviewed here.

2.2 METALS

Virtually all metals are found in the marine environment, some in moderate concentrations e.g. magnesium and calcium, and others in very low concentrations, e.g. gold and silver. Almost all metals are accumulated in one or more components of the marine food chain, and are the most persistent substances in the environment. They can not be destroyed or transmuted, although they can be combined in various compounds and complexes. Certain metals can combine with organic substances to form highly toxic metallo-organic complexes, e.g. methylmercuric chloride, and some of these reactions can be carried out by bacteria. Some metals, e.g. copper, mercury and silver, are highly toxic to organisms whereas calcium, magnesium, and sodium are relatively innocuous. Indeed metals such as sodium, magnesium, zinc, iron, calcium and even copper are an essential part of nutrition. However, certain organisms have a high affinity for particular elements, unrelated to physiological requirements. For example vanadium reaches high concentrations in tunicates (Macara et al., 1979), cadmium is concentrated in Halobates species (Cheng et al., 1976, Bull et al., 1977), and zinc in oysters (cited in Bryan, 1984).

The mechanisms and causes of this accumulation have not been fully elucidated but there is little evidence of harm to the organisms concerned. In addition to inter-specific variations in the toxic effects of metals, the various life stages and different individual organisms within a species may be affected differently by high metal concentrations.

In excess, even essential metals are toxic and can therefore be considered with non-essential metals in identifying the possible deleterious modes of action of metals in living systems. These may be:

- i) binding at centres where metals are not normally bound,
- ii) substitution of essential elements particularly at the active site of enzymes,
- iii) binding which changes the conformation and reactivity of enzymes,
- iv) replacement of groups such as phosphate by the formation of very insoluble metal phosphates,
- v) alteration of membrane permeability by combination of metals with various groups in proteins,
- vi) replacement of elements with electrochemical roles (Bryan, 1984).

The toxicity of metals to organisms has been placed in the following order (Waldichuk, 1977), though it may vary slightly between species: Hg>Ag>Cu>Zn>Ni>Pb>Cd>As>Cr>Sn>Fe>Mn>Al>Be>Li. However the concentration and form of each element in seawater might be an important factor to consider in its toxicity. In addition to this, many of the metals can be bioaccumulated, thus drastically changing concentrations available to the organism from the environment. For example, cadmium is concentrated 80,000-180,000 times relative to seawater levels in macro-invertebrates such as the Pacific Oyster Crassostrea virginica and 180-730 times in the Pacific Halibut Hippoglossus stenolepis. The bioaccumulation of metals through the

food chain can provide potential problems for top marine predators including man.

This study and review is primarily concerned with two essential metals, two non-essential metals and an essential metalloid copper, zinc, mercury, cadmium and selenium respectively. At the present time it appears that, outside coastal areas, lead has exhibited the greatest increase in concentration in oceanic areas (Waldichuk, 1977); this is clearly attributable to man through the emission into the atmosphere of tetraethyl lead from motor vehicles. As the natural concentrations of trace metals in the sea are generally low, the possibilities of contamination with other potentially toxic metals, from man's activities are high. However, in the marine situation the utilisation of the ocean for diluting and disposing of wastes may mean that the greater abundance of metals such as zinc and copper will prove to be a greater hazard than the more toxic metals such as mercury and silver.

Contamination of the marine environment may come from a variety of sources, including mine tailings run-off into rivers and hence into the ocean, various industrial processes, electricity power stations which burn coal and oil, sewage disposal, especially the dumping of sludges, contamination from marine anti-fouling paints, and discharge into the atmosphere. Since the influences of most of these outputs is likely to be limited mainly to coastal waters the relative importance of atmospheric sources probably increases with distance from land. For example up to 50% of the cadmium input into south Californian coastal waters is from atmospheric sources and up to 90% of the cadmium input may remain in the water column (Cheng *et al.*, 1976).

2.2.2 Cadmium and Zinc

The concentration of heavy metals in the ocean surface varies considerably due to the non-uniform input of metals into the sea, and

their distribution is affected by various factors including biological transport. The oceans act as a pseudo-sink in the biogeochemical cycle of metals, with dry and wet deposition the principal modes of input (Nurnberg et al., 1983). Cadmium concentrations in the open ocean are 0.015-0.118 ppb (Bruland et al., 1978). The concentration of cadmium near the surface is lowered probably because of uptake by phytoplankton as levels are closely correlated with phosphate concentrations (Nurnberg et al., 1983). From the surface to a depth of 1000m there is an increase in cadmium concentration and the same is found with copper. Copper concentrations in ocean waters range between 0.24 and 0.92 ppb and for zinc 0.007 to 0.04 ppb (Bruland et al., 1979). The results obtained by Bruland and Nurnberg are consistent with the idea that in addition to nutrients, heavy metals are absorbed by planktonic organisms in the photic zone and transferred to deeper water when the dead organisms and faeces sink. The metals in sediments are not necessarily inert. Depending on conditions, remobilisation may occur, sometimes followed by a return of the dissolved metals to overlying water (Summer, 1981). In a transect between the open North Atlantic and the German Bight the hydrographical front is accompanied by an increase in inorganic nutrients (phosphate, silicate), and dissolved trace elements such as cadmium and copper, which suggests that the trace metals are mobilised from partly reduced sediments and vertically mixed into surface waters (Kremling, 1983).

Organisms in the ocean may absorb metals directly from solution in seawater across the general body surface, gills or the wall of the gut. Availability of metals from food is influenced by the dietary matrix. The accumulation of metals in abnormal concentrations in tissues is of concern, as higher vertebrates and man may be exposed through the food chain to potentially toxic levels. In examining the

higher vertebrates in the food chain, a knowledge of the bioaccumulation of various metals in the lower trophic levels is required. However, much of this information is unavailable. Phytoplankton have been found to be extremely efficient at concentrating cadmium from the dissolved phase (Hardy et al., 1984; Jennings and Rainbow, 1979). Cadmium accumulation increases with increasing concentration of the metal in the water, and is dependent on light energy. The cadmium apparently accumulates within the cells as the result of an energy dependent process (Jennings and Rainbow, 1979).

Marine organisms, particularly zooplankton, molluscs and other filter feeders concentrate cadmium by a factor of 10^3 or 10^4 . In metal contaminated seawater, bivalves concentrate metals to a greater extent in the presence of algae than in seawater alone suggesting that both direct absorption across the gills and dietary input are occurring. Crabs concentrate cadmium in their renal and digestive system. The prawn Palaemon elegans is able to regulate the two essential metals, copper and zinc, up to concentrations of 100ug l^{-1} . In contrast cadmium is not regulated at any concentration and the body concentration is proportional to the external concentration (Jennings and Rainbow, 1982). In Gastropods and the euphausiid Meganyctiphanes norvegica the concentration of some metals is governed by the size of the organism, values decreasing with increasing size (J.R. Rainbow pers comm). Metal levels may vary with season depending on gonad development and spawning (Bryan, 1984).

In marine and freshwater fish concentrations of cadmium are usually very low, approximately 0.03ug g^{-1} (Topping, 1973). However in a comparative study on Plaice Pleuronectes platessa and rays it was found that cadmium was not as readily accumulated as other metals such as zinc and mercury (Pentreath, 1977). Fish can accumulate cadmium

from water passing over the gills and from food, the former appearing to be a limited method due to the high toxicity of the cadmium ion. Accumulation from food is not very rapid, as plaice and rays took up 5 and 17% of dietary cadmium in food respectively (Pentreath, 1977). In the natural situation there is some evidence of accumulation from food as in the Severn estuary an increase in cadmium concentration was correlated with an increase in the crustacean component of the diet (cited by Pentreath, 1977). There is evidence for the regulation of copper and zinc in the Plaice (Pentreath, 1976).

In decapods cadmium concentrations may reach 13mg kg^{-1} dry weight and may vary depending on the geographical location (Davies et al., 1981). Cephalopods are an important component of the diet of many pelagic seabirds, but unfortunately few data are available on their metal levels, especially for open ocean species. The oceanic squid Ommastrephes bartrami and Symplectoteuthis oualensis contained 287ug g^{-1} dry weight and 782ug g^{-1} dry weight of cadmium respectively (Martin and Flegal, 1975).

The concentrations of metal that will kill an aquatic organism are dependent on the metal, the species and the chemical form of the metal. Furthermore, complex interactions are known to affect the toxicity of heavy metals, for example the ingestion of zinc ameliorating the toxicological properties of administered cadmium (Flick et al., 1971). The accumulation and distribution pattern in tissues is influenced by several factors other than total metal intake, including levels of calcium phosphate and Vitamin D, status of the diet, intensity and timing of exposure and seasonality (Johnson et al., 1978; Di Guilio, 1984).

The distribution of cadmium between tissues in birds and mammals follows a common pattern, with the highest concentration in the kidney

followed by liver, bone, brain and muscle in descending order. Low concentrations in the brain may be due to the inability of cadmium ions to cross the membranes between the brain and blood, the so called 'blood-brain barrier' (Osborn, 1979). Cadmium is similarly excluded from seabird eggs, although these do contain mercury (Parslow and Jefferies, 1971), and this could also be explained by the inability of cadmium to cross complex tissue-tissue surfaces.

Many metals, orally ingested, accumulate primarily in renal and hepatic tissue and the gradual elimination of the metals from the organism may take place through the bile, e.g most organometals, or through the kidney e.g inorganic mercury, cadmium and zinc. For cadmium it appears that marine mammals and birds are physiologically similar to humans, in that levels are very low in young animals and increase with age, e.g in voles, (Johnson et al., 1978), Great Skua (Furness and Hutton, 1979), deer (Elinder, 1980), Laughing Gull Larus atricilla (Hulse et al., 1980), Sooty Terns Sterna fuscata (Stoneburner et al., 1980), and Oystercatchers Haematopus ostralegus (Hutton 1981). The Herring Gull Larus argentatus did not accumulate cadmium with age (Hutton, 1981; Nicholson 1981). It appears that marine mammals and pelagic seabirds are able to accumulate and tolerate high concentrations of cadmium which would often be regarded as toxic in other animals (Jernelov 1972; Osborn et al., 1979; Nicholson et al., 1981). Sea otters Enhydra lutris accumulate up to 500ug g⁻¹ dry wt Cd in the kidney; a corresponding amount in man would cause severe kidney damage. The highest values in pelagic seabirds found so far are 480ug g⁻¹ Cd dry wt in the Northern Fulmar Fulmarus glacialis and 336ug g⁻¹ Cd dry wt in the Great Skua (Furness and Hutton, 1979; Osborn et al., 1979).

Cadmium levels are higher in the kidney than the liver for most species where data are available, including Royal and Sandwich Terns,

Sterna maxima and S. sandvicensis (Maedgen et al., 1975), Manx Shearwaters Puffinus puffinus, Puffins Fratercula arctica, Razorbills Alca torda and petrels (Bull et al., 1977), Laughing Gulls (Hulse et al., 1980), Herring Gulls, Great Skuas, Oystercatchers (Hutton, 1981) and Sooty Terns (Stoneburner et al., 1981).

Copper concentrations show less variation than those of cadmium, both between and within species. Published liver concentrations of copper include 18-19ppm dry weight in Brown Pelicans Pelicanus occidentalis (Connors et al., 1972), 13-28ppm in Common Terns Sternus hirundo (Connors et al., 1975), an average of 17ppm in Lesser Black-backed Gulls Larus fuscus (Lande, 1977), 19-53ppm in Puffins (Parslow et al., 1972) and 17-21ppm in three species of petrel (Anderlini et al., 1972). In contrast the mean concentration of copper in the Common Eider Somateria mollissima was 367ppm dry weight (Lande, 1977).

Zinc concentrations are more variable; 98-151ppm dry weight in Puffins, 117-170ppm in Manx Shearwaters, 225-688ppm in Northern Fulmars (Osborn et al., 1979), 104-148ppm in Greater Scaup Aythya marila and Surf Scoters Melanitta perspicillata (Vermeer and Peakall, 1979) and averaged 131-176ppm dry weight in three species of petrel (Anderlini et al., 1972). Zinc levels in the liver and kidney do not show a uniform pattern. Higher levels have been reported in kidney compared to liver in the Herring Gull and Great Skua (Hutton, 1981), Herring Gull (Nicholson, 1981), and for the liver compared to kidney in the Knot Calidris canutus (Evans and Moon, 1981) and Oystercatcher (Hutton, 1981). Similar levels in the two tissues have been reported for the Common Tern (Connors et al., 1975). A more comprehensive study of zinc levels in bird tissues found the highest levels of zinc in the pancreas, probably due to the presence of metallo-enzymes requiring

zinc (Osborn et al., 1979). In the Herring Gull the pancreas contained the lowest levels of zinc, as compared to other tissues (Nicholson, 1981), indicating that there is considerable variation in zinc concentrations between species.

There are, therefore, large differences in the concentration and inter-tissue distribution of metals between species. Such differences are difficult to explain although they probably reflect unknown differences in metal metabolism or in the level of exposure. In a study of Antarctic and North American seabirds it was found that there were no significant interspecific or geographical variations in copper and zinc concentrations among four populations of petrels (Anderlini et al., 1972). Distribution of individual levels about the mean for each tissue was narrower for essential than for non-essential elements. Such a relationship is indicative of the metabolic regulation of essential elements (Anderlini et al., 1972; Nicholson, 1981; Di Guillo, 1984).

The concentrations of cadmium and mercury were found to be higher in Ashy Petrels Oceanodroma homochroa (kidney 200-300ppm dry weight) from the industrialised coast of California than in birds from Antarctica. Bourne (1976) concluded that individual birds were becoming contaminated through feeding near areas of local pollution around the British coast. Bull et al. (1977) suggested that it was debatable as to whether cadmium should be regarded as a pollutant to seabirds and that the high levels of cadmium found in tissues should be regarded as of natural rather than industrial origin, especially as high cadmium residues have been found in a marine insect Halobates, which is widely distributed in tropical regions of the Atlantic and Pacific, far from sources of industrial cadmium (Bull et al., 1977; Cheng et al., 1976). High concentrations of cadmium have been found in the tissues of Emperor and Adelie Penguins, Aptenodytes forsteri and

Pygoscelis adeliae and McCormick's Skua Catharacta maccormicki from Antarctica (kidney $86\mu\text{g g}^{-1}$, $324\mu\text{g g}^{-1}$ and $224\mu\text{g g}^{-1}$ dry weight respectively) (Schneider, 1985). Osborn (1979) found that Puffins from the island of St Kilda, which winter in the North Atlantic, have higher tissue cadmium levels than Puffins from the Isle of May, which winter in the North Sea.

In Great Skuas (Furness and Hutton, 1979), Fulmars, Manx Shearwaters, Puffins (Osborn et al., 1979) and Herring Gulls (Nicholson, 1981) strong positive correlations have been found between the concentrations of zinc and cadmium in the kidney, and liver cadmium concentration was positively correlated with kidney cadmium concentration. It was suggested by Osborn et al. (1979) that such correlations might arise because zinc and cadmium can be bound in the renal and hepatic tissue by metallothionein (a protein rich in zinc and cadmium, first isolated by Margoshes and Vallee (1957)). Half to two-thirds of the total body-burden of cadmium accumulates in liver and kidneys of humans and rats (Nomiya, 1980), and 75-80% of the cadmium accumulating in these tissues is bound by metallothioneins (Webb, 1975). Metallothioneins have been isolated from the kidneys of Fulmars (Osborn, 1979) and Great Skuas (Hutton, 1981).

Cadmium is a highly toxic element (Webb, 1975) though uptake from food may only be in the order of 20% in mice and 1.5-29% in humans (Nomiya, 1980). The first manifestations of chronic exposure to cadmium are symptoms of kidney malfunction such as proteinuria and morphological changes of the proximal tubules (Friberg et al., 1974). Metallothionein is considered to have a protective role against cadmium toxicity and its synthesis may also be induced by mercury. The rapid incorporation of these metals in this form stimulated the view that the role of the protein was detoxification of heavy metals

(Bremner, 1975). However, metallothioneins which contain no cadmium or mercury have been isolated and characterized from liver of horses, sheep, calves and humans (Bremner, 1978) and the binding of cadmium and mercury may be the result of the chemical similarities between these metals and zinc (Bremner, 1975).

The concentrations of cadmium in pelagic seabirds reach such high levels that they might be expected to cause kidney damage, and in St. Kilda seabirds structural lesions of a nephrotoxic type, patch necrosis of proximal tubules and glomerular damage were found (Nicholson and Osborn, 1983). Such damage was seen in dosed birds (Starlings *Sturnus vulgaris*) thus supporting the idea that the lesions were metal-induced rather than caused by some other factor (Nicholson and Osborn, 1983). Both dosed birds and seabirds had elevated zinc concentrations in the kidney and a metallothionein-like cadmium and zinc-binding protein was present in the tissues (Osborn, 1979). No overt or external signs of toxicity or changes in condition of the birds were observed in any of the wild seabirds and this may be for a number of reasons:- 1) the kidney has a large spare capacity (i.e. not all the nephrons need to operate continuously), 2) the regenerative capacity of the kidneys is very high, and 3) birds may be able to survive for a long time with non-functional tubules, since they have some capacity to deposit insoluble uric acid in their viscera (Nicholson and Osborn, 1983).

Metallothionein may ameliorate the toxic effects of cadmium toxicity but the possible role of metallothionein as a zinc store must be clarified before any conclusions can be drawn (Osborn, 1978).

2.2.2 Mercury and Selenium

Mercury is a very toxic metal and attention has been drawn to it as a pollutant through Minamata disease in humans, caused by the

consumption of fish and shellfish containing methyl-mercuric chloride. In addition, the use of alkyl-mercury seed-dressings has been shown to be harmful, causing the deaths of birds in Sweden (Westermarck, 1975).

Mercury in nature has seven stable isotopes and is found in seawater mainly as HgCl_3^- and HgCl_2^{4-} with a residence time of 4.2×10^4 years (Keckes and Miettinen, 1970). By analysis of the Greenland icesheet it has been shown that the mercury burden has increased in the last few decades. This has been partly attributed to evaporation of mercury following agricultural activity and partly due to emissions resulting from some industrial processes and the burning of fossil fuels (Jernelov, 1975).

Due to the great affinity of mercury and organomercurials for sulphur (SH) groups and the common occurrence of traces of proteinaceous material in natural waters it can be assumed that mercury is usually bound to matrix-like suspended matter. Only a fraction of the total mercury is found free in solution, except at the points of discharge (Johnels et al., 1969). The cycling of mercury in nature is facilitated by the volatile character of its metallic and methylated forms and by the solubility of mercuric chloride in aqueous medium.

Organisms are able to bioconcentrate mercury but the ecological significance of this is unknown. In phytoplankton mercury accumulates mostly by surface adsorption but relatively little is known about the bioaccumulation and biochemical transformation of mercury in higher marine organisms (Keckes and Miettinen, 1970).

The biological effect of mercury is strongly dependant on its concentration, chemical form and water temperature (Cember et al., 1978). In addition, effects differ greatly between species and may for a given organism vary seasonally. The biological toxicity of inorganic mercury compounds appears to be proportional to their ability to yield

active inorganic mercuric ions which probably react with thiol groups in the protein and enzyme systems, forming mercury mercaptide. After incorporation into organisms a typical organomercuric compound of type $R-Hg^+X$ (R = organic radical, X = dissociable anion) may undergo biotransformation, yielding inorganic mercury, Hg^{2+} , or other Hg compound and a changed organic radical R' . The first type of reaction occurs, for instance, with phenyl mercury and methoxy-ethyl mercury. The alkyl mercury compounds, however, are strongly lipophilic and once introduced into the body exist unchanged for a long time. In high enough doses they may cause severe functional and histopathological changes to the central nervous system which may be irreversible. Mercury may also cause teratogenic and foetotoxic effects (Luten et al., 1980).

Mercury enters organisms by absorption through free surfaces such as skin or gills, by intake of water or food or, in terrestrial organisms, by inhalation of mercury vapour. Various zooplankters (copepods, nauplii larvae of polychaetes) tested with a series of homologous alkyl-mercuric chlorides showed a clearly decreasing survival rate with increasing number of cations. It appears that the alkyl-mercury compounds are concentrated more easily by organisms is than inorganic compounds. The clam Venus saponica has been shown to accumulate 70ppm dry weight of alkyl-mercury within four days as opposed to a concentration of 30-40ppm increase after 10 days of exposure to inorganic mercury (Hardy et al., 1984).

Fish are apparently able to accumulate mercury compounds to a greater extent than many other aquatic organisms, both directly from seawater and indirectly through the food chain. Marine fish average 25-155ppb mercury wet weight in their tissues, but in polluted environments and certain species much higher values have been

recorded. An enrichment factor of 5000 relative to seawater has been reported for fish (Seraptis, 1983), the mercury in fish being almost entirely in the form of methyl-mercury (Lofroth, 1973).

In some sharks there appears to be a relationship between mercury concentrations in liver and muscle tissue and body length (i.e age) (Boush and Thieleke, 1983). The same effect is seen in Pike Esox lucius in central Sweden (Johnels et al., 1969) and in Antimora rostrata, a deep sea fish (Barber et al., 1972). The relatively high mercury contents of marine fish that inhabit the open ocean appear to be due to natural processes rather than as a result of pollution and comparisons between recently-caught and museum specimens of A. rostrata have shown no increase in mercury concentrations since the 1880's (Barber et al., 1984). In more coastal waters such as the Baltic, however, an increase in the level of mercury has been seen since the 1930's and 40's (Lofroth, 1973) and this might be expected to show up in the food chains associated with such areas.

A strong correlation has been found between mercury and selenium in fish such as tuna Thunnus obseus and T. albacares (Ganther et al., 1974) and Marlin Makeria indica (Mackay et al., 1975), and marine mammals (Koeman et al., 1973). It is believed that the selenium has a protective role against the toxicity of inorganic and organic mercury (Beijer and Jernelov, 1978). In some marine mammals high concentrations of mercury and selenium have been found in the liver tissue, and concentrations tend to increase with age. In Common Seals Phoca vitulina, mercury concentration was found to increase with age in the liver but not in brain tissue, once a ceiling of 12-18 months was reached. Some seals had liver mercury levels up to 100mg kg⁻¹ fresh weight.

Koeman et al. (1973) found high mercury levels in livers of marine mammals and these levels were usually balanced in a 1:1 molecular

ratio by selenium, suggesting selenium is involved in the demethylation and detoxification of mercury. Ven de Ven et al. (1979) showed that in seals fed methyl mercury, mercury concentrations increased in tissues but only the liver and kidney showed an increase in selenium concentrations, though the molar ratio was greater than 1:1. A 1:1 molar ratio was found in humans in organs which accumulate and retain mercury (thyroid, pituitary and kidney) (Kosta et al., 1978).

Many fish species (e.g Herring Clupea harengus, Plaice, Mackerel Scomber scombrus, Pike, Pike-perch Stizostedion lucioperca and Swordfish Xiphais gladius) show mercury:selenium ratios different from the 1:1 ratio often found in those mammals that might feed on them (Freeman, 1978), thus implying that the 1:1 relationship is established in the tissues of the mammal.

Selenium is an essential element in small quantities but is toxic at higher concentrations. It is an intrinsic component of glutathione peroxidase, an antioxidase enzyme which may provide protection to neuronal tissues against methyl-mercury toxicity (Chang, 1982). The 1:1 molar ratio of mercury and selenium in various organisms suggests a direct mercury-selenium link. This coaccumulation could be thought of as a result of compensation by the organism for the depletion of the physiologically essential levels of selenium as mercury is accumulated and linked to selenium already present in normal homeostatic regulation.

In the Great Skua, concentrations of selenium exceed those of mercury in the liver and kidney tissues but the levels were found to be related and increase markedly with age. Concentrations of cadmium and selenium were also found to be related in the kidney and it was suggested that selenium may play a role in the detoxification of

mercury and cadmium (Furness and Hutton, 1979). A positive linear relationship in mercury concentrations in the liver with age was found in Sooty Terns (Stoneburner et al., 1980).

In most bird species analysed for mercury, concentrations are highest in the liver (Fimreite et al., 1970; Turner et al., 1970; Vermeer and Armstrong, 1972; Dale et al., 1973; Osborn, 1979; Hutton, 1981; Parslow et al., 1982; Lindsay and Dimmick, 1983.) Concentrations of mercury in the liver of birds around the British coast varies from 0.7ppm in a young Guillemot Uria aalge to 122ppm in a Red-breasted Merganser Mergus serrator (Dale et al., 1973). Lindsay and Dimmick (1983) found the highest levels of mercury in the liver and lowest in body fat of Wood Duck Aix sponsa. Median mercury levels increase from the brain (0.09-0.53ppm wet weight) to breast muscle (0.17-0.98ppm) to liver (0.53-16.52ppm) and feathers (1.10-7.26ppm) in Great Blue Herons Ardea herodias (Hoffman and Curnow, 1979).

Results from various studies show that the levels of mercury and cadmium in the liver and kidney are dependent on diet, with the highest concentrations being found in fish- and bird-eating species (Fimreite et al., 1970; Hutton, 1981; Parslow et al., 1982; Lindberg and Odjso, 1983). For example, Peregrine Falcons Falco peregrinus from northern Fennoscandia had significantly higher levels of mercury in the liver (adults mean 17.6ppm dry weight) than falcons from southern Sweden (mean=9.95ppm). This was associated with a higher proportion of aquatic birds in the diet of the northern falcons. Migrant waders were the most mercury contaminated of the prey species, and terrestrial birds such as Willow Grouse Lagopus lagopus and Wood Pigeon Columba palumbus contained low levels (Lindberg and Odjso, 1983). It was estimated that, on average, the pectoral muscle of northern prey would contain 0.203ppm Hg as compared to a value of 0.066ppm in southern Sweden.

In a study of 184 fish-eating and aquatic birds in northwestern Ontario, Canada, Fimreite (1974) found a clear difference between species from different trophic levels. Highest mercury concentrations appeared in scavengers e.g Turkey Vulture Cathartes aura, and typical fish-eating birds. They were lowest in Mallards and Pintails Anas acuta, whose diet is 90% plant material. For all the adult birds the mercury concentrations in the breast muscle averaged 32% of that in the liver and it was therefore concluded that mercury levels in muscle tissue may be predicted on the basis of those found in the liver and vice-versa (Fimreite, 1974). Parslow (1977) also concluded that, despite seasonal physiological changes such as moult and egg-laying, the avian liver appeared to provide a useful and valid reflection of body levels, and hence the degree to which any individual bird has been exposed to mercury through its diet.

Fimreite (1974) found a significantly higher proportion of total mercury as methyl-mercury in breast muscle than liver, though there was some species variation. The microflora of the gut, especially in the herbivorous species, may have converted organic mercury to the methyl form, as this is well documented in microorganisms (Jensen and Jernelov, 1969). Osborn (1979) suggested that the two to three times greater concentrations of mercury in the tissue of St. Kilda Puffins as compared to the Isle of May Puffins may have been a consequence of differences in diet. However in contrast to Fimreite (1974) most of the mercury in the liver was present as methyl-mercury.

Routes of removal of metals from the bird include excretion in faeces and incorporation into feathers and eggs. Mercury levels in primary feathers have been found to correlate with levels in other tissues, for example in the Great Blue Heron (Hoffman and Curnow, 1979). However, the pattern of feather replacement and moult must be

understood in order to select and analyse the correct feathers. A marked correlation was found between the mercury content of primaries and the moulting process in Sparrowhawks Accipiter nisus and in the Goshawk Accipiter gentilis a high percentage of the total mercury was present as methyl-mercury which, is always excreted more slowly than other mercury compounds (Buhler and Norheim, 1982). Since this compound can pass through various tissue barriers, it may be excreted partly via the egg in the female. Heavy metal burdens may therefore be reduced in female birds via the production of eggs. Proteins in the eggs are derived from adult blood serum proteins and Jabuskowski (1970) demonstrated that mercury in avian blood is bound to these blood serum proteins.

The analysis of feathers provides a means of monitoring mercury levels in birds without killing them, since concentrations in the feathers and the liver may be related (Furness and Hutton, 1979). The concentrations of mercury in bird's feathers can be used to give an indication of mercury contamination in the environment both in present day and historical terms (Berg et al., 1966; Lindberg and Mearns, 1982; Lindberg and Odjso, 1983; Appelquist et al., 1985). In most studies the feathers chosen for study have mainly been remiges, normally primaries. Metal content of feathers may vary between different parts of the individual feather (Goede and de Bruin, 1984) and between different parts of the plumage (Buhler and Norheim, 1982; Doi and Fukuyamo, 1983). Where primaries have been used to monitor mercury levels in the environment the concentration of mercury has been shown to decrease from earlier moulted feathers to late moulted feathers as in the Osprey, (Johnels et al., 1969), Peruvian Booby Sula variegata (Gochfield, 1980), Sparrowhawk (Buhler and Norheim, 1982), Peregrine Falcon (Lindberg and Odjso, 1983), Black Guillemot Cepphus grylle and Guillemot (Appelquist et al., 1984).

The use of feathers for monitoring mercury levels in the environment was developed in Sweden to illustrate the increase in the concentration of mercury in avian species after the introduction of alkyl-mercury seed dressings. In 1958 birds were found dead with 4-200ug g⁻¹ dry weight mercury in the liver and kidney tissues, with peaks in mortality coinciding with autumn and spring sowings (Johnels and Westermark, 1969). Johnels et al., (1972) demonstrated that levels in feathers from birds of prey from 1860 to 1870 were less than a tenth of levels in 1964 and 1965. Feathers reflect the blood levels of mercury at the time of feather formation and this is believed to reflect the dietary intake (Johnels and Westermark, 1969; Westermark et al., 1975; Lindberg and Mearns, 1982; Lindberg and Odjso, 1983; Delbaeke et al., 1984). In the Osprey and the Great-crested Grebe which reflect mercury levels in the aquatic environment, a rise in the mercury content of the birds was seen after 1900 due to the introduction of chlor-alkali production plants around 1900. Berg et al., (1966) recorded that in each of the terrestrial species investigated during 1840 to 1940 mercury levels were fairly constant and differences were due to the trophic level of the species. An increase in the mercury content of the bird's feathers was seen after the introduction of alkyl-mercury seed dressing. Since the banning of these compounds a drop in the mercury concentrations of feathers has been seen (Westermark, 1975).

Both sea and freshwater birds feeding substantially on aquatic organisms provide relevant samples for the monitoring of mercury in the aquatic environment. Since birds concentrate mercury compounds from their food and a substantial knowledge of the moult, feeding and migration of the birds is often known, bird feathers should be considered as suitable for monitoring mercury concentrations in any

marine area (Appelquist et al., 1985). Due to the stability of keratin in the feathers, museum specimens can be used to ascertain changes in avian mercury concentrations over the course of time. The highest mercury levels are found in the plumage and the relationship between feathers, liver and muscle is approximately 7:3:1 (Buhler and Norheim, 1982). Though Appelquist et al. (1985) advocate the use of feathers for monitoring mercury in the environment, they suggest that because of the great variation between individual seabirds, chronological series based on seabird feathers should be evaluated together with a time series based on sediment cores.

In a study of selenium levels in waders of the Dutch Waddensee, concentrations in the kidney and preen gland were found to increase rapidly over the winter. This could be monitored by analysing the selenium content of the feathers, since these became contaminated with secretions from the preen gland when the birds preened (Goede and de Bruin, 1984). Thus selenium in the environment may also be monitored, albeit indirectly, by the use of feathers.

2.3

ORGANOCHLORINES

Since the turn of the century the manufacture and use of synthetic chemicals has become widespread, such that by the 1970's about 70,000 man-made chemicals were on the market. The chlorinated hydrocarbons or organochlorines include pesticides such as DDT and the polychlorinated biphenyls (PCB's). PCB's were first produced industrially in 1929 and have been used in a wide variety of applications including uses as heat transfer liquids, condenser dielectrics and hydraulic fluids. They are prepared industrially by the chlorination of biphenyl, a reaction which yields a wide range of compounds differing in the number and position of chlorine substituents on the biphenyl molecule. PCB's are produced as distillation fractions of the refined reaction

products and each fraction contains a number of compounds (Gooch and Hamdy, 1983). There are special problems in analysing PCB's and in interpreting their environmental significance, as they consist not of one discrete compound, but of several and the pattern may vary from sample to sample (Addison, 1976).

PCB's exhibit a number of unique properties, such as chemical inertness, resistance to acid and alkali, thermal stability, low water solubility and high solubility in organic solvents. Large quantities have readily escaped into the environment due to their diversity of uses; they are also very persistent because of their stability and hydrophobic nature (Gooch and Hamdy, 1983).

PCB's can be accumulated in aquatic and terrestrial organisms including man (Geyer et al., 1984). For this reason, voluntary restrictions on the use of PCB's came into force in 1970 in the USA, and in 1979 the United States Environmental Protection Agency (EPA) banned their manufacture in the United States. Production of PCB's in Japan and West Germany stopped in 1976 and 1983 respectively. However several European countries and Russia still manufacture PCB's (Geyer et al., 1984).

The DDT (p,p'-DDT, 2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane) group of insecticides was introduced in the mid-1940's. They were rapidly found to be effective in preventing insects making undue inroads into agriculture and in breaking the vector chain for diseases carried by insects to man and domestic animals. Widespread application to fields, forests and marshland introduced the pesticides directly to the environment over large areas, and waste disposal or leakage from manufacturing plants introduced materials directly to waterways (Stickel, 1973).

Many of the pesticides have a persistency of only a few months,

but DDT, dieldrin, aldrin, lindane, endosulfan and heptachlor are more persistent. Despite a few warning signs it was not until the late 1950's that increasing numbers of reports of dead birds found near sprayed fields and the build up of high concentrations in soils, stream sediments and wildlife, led to a realization of the toxic effects of the organochlorine pesticides (Stickel, 1973).

The organochlorine pesticides are stored and accumulated in tissues of a wide variety of invertebrates and vertebrates, including marine species. Both organochlorine pesticides and PCB's are strongly lipophilic and therefore accumulate in the lipid tissue of animals, which if mobilised in times of stress, can result in toxic effects to the animal. There is also a measurable increase in concentration of organochlorines with ascending trophic level in the food chain, and animals well away from sites of organochlorine usage contained concentrations of the compounds above the level of detection (Portmann, 1975).

On entering the marine environment the organochlorine is most likely to be absorbed into particulate material, either inorganic or organic, or dissolved in lipid such as surface film or animal fat (Portmann, 1975). Of the synthetic organic compounds present in the North Atlantic, PCB's may be the most abundant. In seawater and all components of the biota, PCB's are found throughout the ocean at levels consistently exceeding those of other chlorinated hydrocarbons (Bourne and Bogan, 1972; Harvey et al., 1973; 1974).

This abundance stems from the high industrial utility of PCB's, a utility due to their unique properties (cited by Sproul et al., 1975). In the past many of the industrial and commercial uses of PCB's resulted in their exposure to the environment. Since 1971 with voluntary restrictions on the use of PCB's, levels in the atmosphere over the North Atlantic and in surface waters and mixed plankton

appear to have declined (Waldichuk, 1977). The PCB predominantly found in seawater is most similar to Arochlor 1254. In plankton in British waters levels of 40-230ppm (lipid) have been measured (Portmann, 1975). Off the West coast of Scotland and in the North Atlantic plankton samples, DDT concentrations ranged from 3-100ug g⁻¹ wet weight, with the highest value coming from near a sewage outfall (Portmann, 1975). In planktonic Sargassum from the open Atlantic a concentration of 0.2-0.5ug g⁻¹ DDT was found and in zooplankton, a concentration of 0.01-9.5 ug g⁻¹ fresh weight (Portmann, 1975).

In the open ocean, gilled organisms do not exhibit biomagnification of chlorinated hydrocarbons. The residue levels appear to be determined by physiochemical equilibrium relationships with the surrounding water (Hickey, 1975). Cod Gadus morrhua and Herring in the Atlantic have been found to contain 0.003-0.05mg kg⁻¹ DDT and 0.03-0.33mg kg⁻¹ DDT respectively (Portmann, 1975). In a study on fish in the United States, PCB's were found to be the major contaminant and in two-thirds of the samples the PCB residues were higher than those of total DDT (Hickey, 1975).

In general the concentrations of organochlorines are lower in invertebrates than in fish and such differences are reflected in their predators, for example Gray's Whales Mesoplodon grayi feeding on invertebrates contained lower residues than Sperm Whales Physeter catodon feeding on fish (Portmann, 1975).

The relationship between the concentration of a contaminant in an organism and the environment may deviate considerably from a direct proportionality, as accumulation may depend on such factors as the ability to store or excrete the contaminant, the lipid-water partition coefficient and the amount of lipid in the organism (Bryan, 1979). Size and age are also important factors to consider when comparing

levels of contamination in organisms from different areas.

For pesticides, there is no evidence for increasing concentration with trophic level since pesticide levels tend to be related to the lipid pool of the organism and many top predators have large fat deposits (Portmann, 1975). Portmann (1975) concluded that if DDT concentrations are taken on a lipid basis as opposed to fresh mass the increase from plankton to predator is within one order of magnitude rather than five orders of magnitude. Addison (1976) suggested that a trophic level and age effect may apply in larger organisms not capable of direct uptake from the water. In small organisms the influence of partitioning from water to body lipids is more likely to apply where the uptake from the water appears to be the most significant factor.

Species vary greatly in their susceptibility to the toxic effects of organochlorines. The Brown Shrimp Crangon crangon has a LC50 of 0.003-0.1ppm for DDT and 0.3->10ppm for PCB's, the range reflecting the degree of chlorination of the PCB. For Plaice the LC50 for DDT is 0.3-1ppm and >10ppm for PCB's.

The chlorinated hydrocarbons have received particular attention because of the ecological damage which came to light through the use of DDT, i.e the reproductive failure in birds due to eggshell thinning and breakage, inhibition of photosynthesis, direct toxicity to fish, reproductive failure in fish and the destruction of useful insects in streams (Addison, 1976). The PCB's have also been a focal point of attention due to their inadvertent release into the environment through leakage, breakage of containers and emissions from combustion. In a large-scale leakage of PCB's from heat exchangers in Japan, contaminated rice-oil led to death in severe cases and a chloracne type skin eruption in milder cases amongst the human consumers. PCB's were also found to be highly toxic to marine crustaceans, when accidental discharge of this material into Escambia

Bay, Florida, led to a large scale mortality of shrimps (Waldichuk, 1977).

Biomagnification can occur in seabirds according to Hickey (1975). Organochlorine pesticides, being strongly lipophilic, accumulate in the fat of birds after a relatively small exposure to DDE, the primary breakdown product of DDT. The long-lived lipid soluble PCB's present at low levels in the food of seabirds can be concentrated many fold in their tissues. PCB's and DDT are distributed throughout the world's oceans (Bourne and Bogan, 1972), being found in the tissues of Antarctic seabirds (Riseborough, 1974; Lukowski, 1978) and pelagic seabirds (Fisher, 1973; Johnston, 1973) seemingly far from possible sources of contamination. However levels of HCB, DDE and PCB are much higher in the Northern Fulmar than the Southern Fulmar Fulmarus glacialis (Norheim, 1984). Wilson's Petrel Oceanites oceanicus contained 2.2ug g^{-1} and 11.0ug g^{-1} lipid weight of DDT and PCB respectively (Peakall, 1975).

Weber (1983) found PCB and DDT in the pectoral muscle and eggs of the equatorial Brown Booby Sula leucogaster and also found a trophic effect, since concentrations in Rock Lobsters Palinurus echinatus and Land Crabs Grapsus grapsus were lower than in reef fish, which also had higher concentrations than open sea fish. In that study the PCB levels were always higher than those of DDT and its metabolites in all the samples taken, and aerosol transport was suggested as the reason for the presence of the organochlorines. The trend of PCB's occurring in greater quantities than DDE (although the ratio varies considerably) is reversed in the Pacific, where pesticides usually occur in greater quantities (Bourne and Bogan, 1972). This was not the case for the Black-footed Albatross Diomedea nigripes (DDE 18.2ug g^{-1} wet weight, PCB 22.3ug g^{-1}) and the Laysan Albatross Diomedea

immutabilis (3.7ug g^{-1} DDT wet weight, PCB 8.2ug g^{-1}). The greater residues in the Black-footed Albatross are thought to be related to its more scavenging habits (Fisher, 1973).

The findings of Tatton and Ruzicka (1967) suggested that increased residues may be found in Antarctic skuas compared to penguins due to their scavenging habits. From nine species sampled in the Antarctic the McCormick's Skua contained the highest residues of DDT and its metabolites (Lukowski, 1978). The adipose tissue of the Wandering Albatross, the Giant Petrel Macronectes giganteus and the Brown Skua C. skua lonnbergi also contained the highest residues of the nine Antarctic species, and dietary residues are probably the source of the accumulation (Lukowski, 1978). These species feed on other birds, large fish and the remains of large vertebrates, while those feeding on small fish and krill Euphausia sp. i.e Cape Pigeon Daption capense, Antarctic Petrel Thalassoica antarctica, Southern Fulmar, Southern Black-backed Gull Larus dominicanus, Antarctic Tern Sterna vittata and Blue-eyed Shag Phalacrocorax atriceps contained much lower residues of organochlorines (Lukowski, 1978). PCB levels in the southern hemisphere are about 1-2 orders of magnitude lower than in the northern hemisphere, but DDE concentrations are only slightly lower (Lukowski, 1978).

A study of levels of organochlorines in eggs of eight species of South African seabird, (reflecting and paralleling organochlorines in the parent bird, Stickel, 1973) feeding in different areas and on different food types, showed that there was an inverse relationship between residue levels and the extent to which a species fed in the marine environment (de Kock and Randall, 1984). The marine environment was less polluted than the estuarine regions. The levels found in the eggs of the seabirds sampled were below those expected to cause egg-shell thinning (de Kock and Randall, 1984).

A relationship between trophic level in the food chain and organochlorine content also appears to exist in the North Atlantic. Glaucous Gulls Larus hyperboreus feeding on eggs of the Little Auk Plautus alle fish, fish offal, carrion and Northern Fulmars in Spitzbergen contained higher organochlorine residues than the Little Auk. The Little Auk feeds mainly on crustaceans (Norheim, 1984). One Glaucous Gull in a survey on organochlorines in the North Atlantic seabirds in 1972 (Bourne and Bogan, 1972) was found dying from convulsions and found to contain very high residues (PCB liver=311 $\mu\text{g g}^{-1}$, muscle=88 $\mu\text{g g}^{-1}$ fresh weight). This bird weighed less than the other Glaucous Gulls caught at Bear Island suggesting that the possible utilisation of fat reserves resulted in the mobilisation of toxic amounts of residues into target organs (Bourne and Bogan, 1972).

Although many of the larger auks and Gannets Sula bassana were found to contain high concentrations of residues during bird-kills in 1969 and 1972 respectively (Parslow and Jefferies, 1972), the more pelagic seabirds in northern Britain were found to contain the highest body burdens of organochlorines. Those pelagic seabirds found on isolated breeding colonies, including the Fulmar, British Storm Petrel Hydrobates pelagicus, Kittiwakes Rissa tridactyla, skuas and gulls contained relatively high organochlorine levels (Bourne and Bogan, 1972). The Kittiwake had a consistently higher PCB/DDE ratio than other species which may be the result of its distribution in winter or metabolic differences (Bourne and Bogan, 1972). The lowest ratio found was for two species of shearwater returned from winter quarters in the South Atlantic where PCB's may still be relatively scarce compounds (Bourne and Bogan, 1972).

In a survey of Icelandic birds, Sproul et al. (1975) found that PCB levels in Sandeels Ammodytes sp. and Herring, two mid-water fish

preyed on by many seabirds, were an order of magnitude or more below levels found in breast muscle and eggs of Icelandic seabirds. Biomagnification was said to have occurred, and it was most pronounced in the Great Skua, a bird at the apex of the food chain. Fulmars fed on by Great Skuas in summer carried PCB levels an order of magnitude lower than the skua. The birds with less than 1.0ug g^{-1} fresh weight in the breast muscle were species that feed by diving, particularly alcids and also Shags Phalacrocorax aristotelis and Comorants Phalacrocorax carbo. The species with mean PCB concentrations between 1.0ug g^{-1} and 10ug g^{-1} in the breast muscle were either species of gull or pelagic seabirds which feed on the sea surface. It is known that surface waters are enriched with PCB's relative to sub-surface waters and plankton, an important component of petrel, Kittiwake and Fulmar diets, may also be enriched. Larus gulls are more complicated in that they tend to have a more varied diet, preying on eggs, fish and general scavenging thereby obtaining higher residues. Anomalies also appear in the general pattern. For example, the Lesser Black-backed Gull accumulated higher residue loads than would be expected by its position in the food chain. However, it winters off Iberia and the north-west coast of Africa and may pick up PCB's in these locations. The Great Skuas combine various traits favouring it as a possible accumulator of PCB's. It preys on other seabirds and feeds at the ocean surface. Levels of PCB's in the tissues were consistently above 10ug g^{-1} fresh weight (Bourne and Bogan, 1972; Sproul et al., 1975; Furness and Hutton, 1979).

The results found by several workers in other areas reflect those of Bourne and Bogan (1972), illustrating the ubiquitous distribution of PCB's in birds that have come from the east coast of North America (Hays and Riseborough, 1972), from the Irish Sea (Prestt et al., 1970), from the Dutch coast of the North Sea (Koeman et al., 1978) and

from the Baltic (Jensen et al., 1969; Helander, 1982). Generally low concentrations have been reported for Arctic sites (Bjerk and Holt, 1971; Bourne and Bogan, 1972), Norway and Scotland (Parslow et al., 1972). Seabirds contain higher concentrations near industrialised areas. Over the entire North Atlantic PCB:DDE ratios increase from west to east declining again only in the Baltic Sea (Sproul et al., 1975). Along the east coast of North America DDE levels approach those of PCB's. In moving eastwards away from industrialised areas out into the North Atlantic, DDE levels decline faster than PCB's, giving an increased PCB:DDE ratio (Passiverta et al., 1981). The source of PCB and DDE may be difficult to assess; more PCB may come from Europe, or North America may be the major source of DDE (Sproul et al., 1975).

Despite voluntary restrictions on the use of PCB's and the banning of DDT in the 1970's, by 1974 there was little evidence of a decline in the levels of residues. However Coulson et al. (1972) found a decline in levels in north-east England for Shag eggs and Barrett et al. (1985) suggested that there was a trend towards declining organochlorine levels in Herring Gulls and Guillemots in Norway.

It is clear that seabirds are accumulating toxic chemicals and it is the pelagic species and top predators which are accumulating the largest amounts. Many of these species, however, such as Fulmar, Great Skua and Kittiwake, have seen a large increase in numbers since the turn of the century. If pollutant levels continue to increase then predatory species such as the Glaucous Gull and the Great Skua (Bourne and Bogan, 1972, Furness and Hutton, 1981) may eventually become susceptible to toxic effects as found in Peregrines feeding on other seabirds. The Peregrine has recovered less successfully in coastal areas, (PCB in eggs=4.6 $\mu\text{g g}^{-1}$ wet weight) than on inland sites (PCB in eggs=1.3 $\mu\text{g g}^{-1}$ wet weight) (Parslow, 1973).

The ratio of PCB to DDE shows large variations between species and with age (Passiverta et al., 1981; Newton and Bogan, 1978). There are also significant correlations between different chlorinated hydrocarbons and fat content. The organochlorine concentrations in the bird's body depends on the past history of the bird. Gannets found dead and in poor condition in Lancashire had high levels of organochlorines in the liver, and these high concentrations may have built up subsequent to the mobilisation of fat (Parslow and Jefferies, 1973). The PCB's may therefore have had a sub-lethal effect on the birds when other stress factors were operating upon them. Levels in liver averaged 200ppm wet weight, nearly twice as high as levels in Guillemot livers in the 1969 wreck (Parslow et al., 1969). The Gannets were thus carrying a body load of 25-39mg as compared to 3.5-5.5ng PCB in Guillemots. This may be related to diet as Gannets feed on larger fish and it has been shown in Cod that liver residues of DDT were related to the weight of the fish (Stenersen and Kvalag, 1972). Organochlorines are lipophilic and when birds such as the Gannets suffer starvation, reserves of fatty tissue are utilised as an energy source. The adipose tissue is the the main site of organochlorine accumulation, and as the birds metabolise fat organochlorines are relocated to other organs, especially the liver and brain. Redistribution to the latter can have severe effects on the central nervous system which may contribute to the death of the bird.

The most toxic effects of organochlorines have been evidenced through the reproductive failure of fish-eating birds and terrestrial birds of prey. This failure has been associated with the presence of very high concentrations of DDT, dieldrin and PCB's. In the Baltic region serious reproductive failure and even direct death of Ospreys and Sea-eagles Haliaeetus albicilla was attributed to organochlorines (Helander et al., 1982).

In many cases the failure of birds to reproduce over successive years was attributed to egg-shell thinning, thought to be caused by DDE. Ratcliffe (1967) first reported thinner shells in raptor eggs and suggested that this effect was linked to organochlorine insecticides, since the increase in egg-shell thinning incidence coincided with the introduction of these insecticides. Shell thickness also declined in Britain in the Grey Heron Ardea cinerea (Prestt, 1970) and the Kestrel Falco tinnunculus, Merlin Falco columbaris, Hobby Falco subbuteo, Osprey, Rook Corvus frugilegus, Carrion Crow Corvus corone and Shag (Ratcliffe, 1970).

One of the most susceptible species appears to be the Brown Pelican, eggs from Anacapa Island, California showing up to a 50% decrease in thickness. DDT production had commenced in 1944 in the region of Anacapa Island and the wastes of the Montrose company were discharged into the sewer systems, ultimately leading to the sea. By 1942 first analyses showed the presence of DDT in the sediments off the coast. The DDT concentrations steadily increased until 1969 when production and waste disposal were controlled. However between 1969-1972 egg-shell thinning was recognized in the Brown Pelican colony on Anacapa Island (Keith et al., 1970). In South Carolina, Brown Pelican eggs were 14-17% thinner in the years 1967-1973 than they had been prior to 1947. After the 1970 ban on the use of DDT the residues of p,p'-DDE, p p'-DDT, p'-TDE and dieldrin significantly declined from 1969 to 1973. PCB residues in the Pelican eggs peaked in 1972 and declined in 1973, and the South Carolina population of Pelicans has increased rapidly since then (Blus et al. 1977).

The kinetic processes of absorption, metabolism, storage and output of a pollutant vary considerably depending on both the chemical and the species involved. Addison et al. (1974), for example, showed

that in four Swedish populations of Razorbills Alca torda normal reproductive rates were maintained despite levels of DDE in the eggs of 600-1600mg kg⁻¹ lipid weight (60-160mg kg⁻¹ fresh weight). The shell-thickness of the Razorbills was found to show a decrease of 12% as compared to eggs from the years 1861-1940. The critical levels in Peregrine Falcon eggs were found to be about 15-20mg kg⁻¹ wet weight (Peakall, 1975) and 12mg kg⁻¹ in Ospreys in Connecticut and Maryland, United States (Wiemayer et al., 1975). Grey Herons, nesting in Troy heronry, Lincolnshire, between 1966 and 1968 laid eggs with shells 20% thinner than those from the years 1931 to 1935 (Prestt, 1969). In addition 35-40% of the birds accidentally destroyed their eggs which contained on average 6ppm DDE, 3ppm dieldrin and 6ppm PCB's.

Field studies have therefore shown that organochlorines influence the thickness of eggshells, the species usually most affected being those with the highest levels of organochlorine residues in their tissues.

The modes of action of organochlorines are probably not independent of one another and may cause a decline in egg production, aberrant incubation, mortality of breeding adults, egg-shell deficiencies and mortality or aberrant behaviour of recently hatched young (Peakall and Peakall, 1973). Often spatial and temporal associations have been noted between shell thickness and decreases and organochlorine insecticide usage, and relationships have frequently been observed between a decrease in shell thickness and levels of p p'-DDE in the parent bird or egg. Since the ban on the usage of DDT and dieldrin, residues have declined in birds of prey. For example the poor reproduction of Golden Eagles Aquila chrysaetos in the west coast of Scotland was correlated with the amounts of organochlorine residues ingested with their food (Lockie and Ratcliffe, 1964), and it was suggested that dieldrin was the primary cause. The use of dieldrin in

sheep dips was banned in 1966 and residues in Golden Eagle eggs subsequently declined from a mean of 0.86ppm from 1963-5 to 0.34ppm in the period 1966-1968. The breeding success (number of young fledged) between 1963-1965 was only 31% but rose to 69% between 1966 and 1968 (Lockie, 1969).

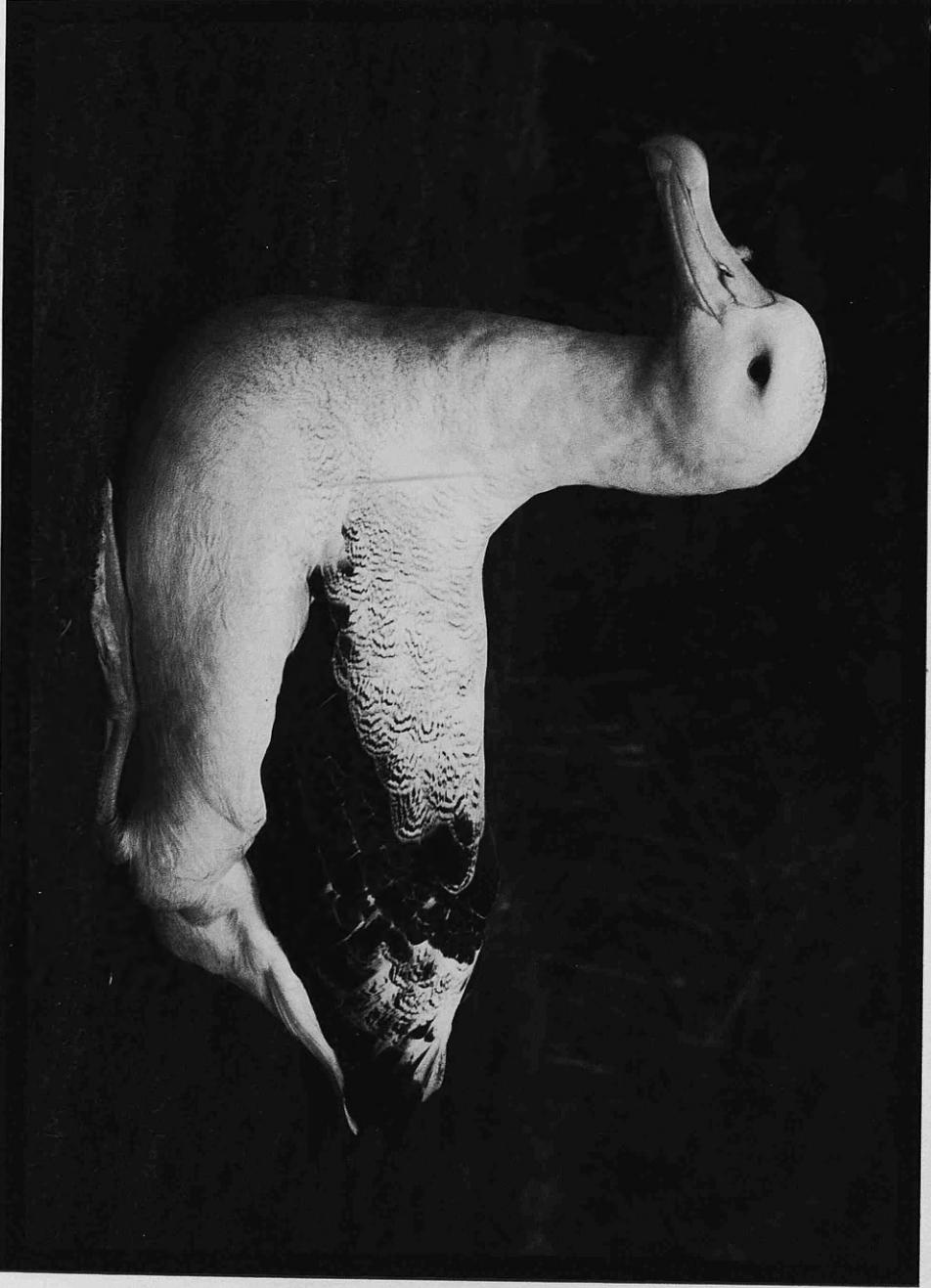
Shell-thinning apparently may be caused by:- 1) a general impairment of calcium metabolism, 2) a reduction in available carbonate in the shell gland through inhibition of carbonic anhydrase (Peakall 1970), 3) a deleterious effect on both the thyroids and adrenals and 4) an alteration in organic matter being incorporated into the developing shells. Each of these detrimental changes is probably potentially capable of disrupting shell structure, but each factor is liable to be influenced by variables such as species, bird condition and environmental conditions (Cooke, 1973).

PCB's, have been shown to have strong effects on the reproduction of the domestic hen, causing low hatching success, high embryo mortality and deformities of the embryo but most of the evidence suggests that they are not involved in egg-shell thinning (Tumasonsis, 1973, Peakall, 1975). However, the reproduction of Mallards and Bobwhites Colinus virginianus were not affected by a diet containing 20-50mg kg⁻¹ Arochlor 1254 in a two year controlled study (Peakall, 1975). PCB's have been implicated as a partial cause of seabird mortality (Koeman et al., 1973; Parslow and Jefferies, 1973); but their exact role in reproduction is uncertain (Blus et al., 1971; Furness and Hutton, 1979).

Although the effects of PCB's and DDE may be difficult to separate in the field, Peakall and Peakall (1973) gave circumstantial and experimental evidence of PCB's involved in bird mortality incidents and reduced breeding success. Laboratory experiments have shown PCB

components to cause reduced immunological responses (cited by Harris and Osborn, 1981), reduced weight (Bunyan and Stanley, 1982) and changed hormone levels (Parslow and Jefferies, 1976) in various species. All these effects might reduce survival or breeding success in the wild.

Plate 1 Wandering Albatross Diomedea exulans



CHAPTER 3

THE ECOLOGY OF THE STUDY SPECIES

This chapter is mainly based on published work as follows:

Fisher, J. 1952; Strange, I.J. 1982; Williams, A.J. and M. Imber 1982; Furness, R.W. 1983; Imber, M. 1984.

3.1 PROCELLARIIFORMES

The Procellariiformes are a group of small to large tube-nosed seabirds represented by four families, the Diomedidae, the Procellariidae, the Hydrobatidae and the Pelecanoididae. The group is strictly marine, only coming ashore to breed.

Characteristics of the group include a large salt secreting gland, a well developed olfactory organ compared to most other birds, and most species possess a musty body odour. All the families except the Pelecanoididae store large quantities of an oily fluid in the proventriculus at certain times of the year. This fluid is believed to be a dietary residue allowing adults to forage at long distances from the colony and feed the young on a very nutritious and partially digested liquid food. The liquid may also be used in some species as a method of defence against territorial intruders and predators, by both adults and young.

3.1.1 Diomedidae: Albatrosses

The albatrosses are the largest flying seabirds, relying on dynamic soaring flight. The body tends to be short and broad but the wings are long and narrow, reaching a wingspan of 3.35m in the larger species. The nostrils open into nasal tubes located on either side of the culmen and the heavy bill has a horny sheath divided into conspicuous plates. The smaller members of the family (mollymawks) have a dark mantle and wings and a short rounded tail. The large Wandering and Royal Albatrosses (Diomedea exulans and D. epomophora)

are mostly white as adults. The albatrosses rely on their strong wings for 'effortless' gliding flight, needing only to make minor adjustments at the wrist and the elbow to change the effective wing area. Albatrosses cannot take off from water unless they are headed into the wind and the lift-off still requires much flapping of the wings and paddling along the surface. On land they walk clumsily but tend to have a more upright stance than other Procellariiformes. Their moult is a gradual process and in the larger species individual wing feathers may not be replaced annually.

In the southern hemisphere albatrosses build their nest, a truncated cone of seaweed, grass and mud, on an exposed hillside. The single white egg is incubated by both parents and the young remain in the nest for many months before fledging. The chicks repel intruders and predators by ejecting squirts of stomach oil and partly digested food.

3.1.1.1 Diomedea exulans: Wandering Albatross

The Wandering Albatross (Plate 1) is one of the largest albatrosses and has mainly white adult plumage, a short tail and a massive pale-coloured bill. The sexes show some differences, for example the female is slightly smaller. The immature plumage is very distinctive, being brown on the body and upperwing but with a white face and underwing. As the birds mature they pass through various stages during which the bird's plumage gradually whitens. The eye is brown and eyelids are greenish-white to blue or pink, and the feet are coloured from pink through to mauve.

In a strong wind the Wandering Albatross flies in long sweeping glides on fully outstretched wings. In calm weather the albatross tends to rest more often on the sea's surface and flapping of the wings in flight is more prolonged.

This albatross is semi-colonial, nesting in small groups with nests 18-23m apart. The nest, made of mud and tussock grass, is 0.3-0.9m high. The Wandering Albatross has a 13 month breeding cycle and therefore breeds biannually if successful, for if the egg or chick is lost early in the season the pair will reneest the following year. The birds arrive on the nest site in November-December and the single white egg is laid mid-December to early January. The chicks hatch early-to mid-March and are brooded for the first 4-5 weeks. The birds fledge and depart from the nest after an average of 278 days in the nest.

The Wandering Albatross feeds mainly on squid and fish usually caught at night, and the birds will follow ships and take galley refuse. These albatrosses are highly pelagic, migratory and dispersive in antarctic and sub-antarctic waters, but rarely near pack-ice. Their pelagic distribution is mainly between 30⁰S and 60⁰S i.e. within the west-wind zone. They are rarely found north of the equator. Their migration may be circumpolar but little is known of the summer ranges of the pre-breeders. The birds breed on Tristan da Cunha, Gough Island, South Georgia, Marion Island, Prince Edward Islands, Crozet Islands, Kerguelen, Antipodes Island, Campbell Island (few), Auckland Islands, Macquarie Island and occasionally Amsterdam Island.

3.1.1.2 Diomedea chlororhynchos: Yellow-nosed Albatross

The Yellow-nosed Albatross is the smallest, most slender and longest tailed of the mollymawks. The adult has a white head and largely white underwings, a slender black bill with a yellow culminicorn and pinkish tip, and pinkish blue legs and feet. The juvenile has an entirely black bill, a paler mantle and tail, and more extensive dark margins on the underwing. In flight they flap the wings more than the Wandering Albatross. Their food consists of cephalopods, fish and shrimps. They may also scavenge behind fishing boats,

particularly off Namibia.

The birds arrive at the nest sites from August to September and though nests are solitary on Tristan, Inaccessible, and Gough Islands, on Nightingale and Prince Edward Islands the birds nest in groups of several hundred pairs. The nest is 30-60cm high, made of mud and placed on a ledge, cliff, slope, plateau or in a boggy flat valley. The single egg is laid in early September (Nightingale Island) or early October elsewhere. The chick hatches after an incubation period of 78 days and is brooded for a 2-3 week period. The fledged chicks leave the nest in late March to mid April after approximately 130 days in the nest. The adults leave the islands in late March and the chicks from mid-April to mid-May.

The birds are largely pelagic in subtropical and warmer subantarctic waters. They occur at sea in the South Atlantic and Indian Oceans between 20⁰S and 50⁰S and are numerous at sea near the Iles Kerguelen. In the Pacific they reach as far as New Zealand but there are no records of their occurrence on the coast of South America.

3.1.1.3 Phoebetria fusca: Sooty Albatross

The adult of the Sooty Albatross has a brownish-grey body, long slender wings, wedge-shaped tail and black bill. The feet are pale grey and an incomplete ring of white feathers partially surrounds the dark eyes. The juvenile resembles the adult but has dark rather than white shafts on the wing and tail quills. This albatross is one of the more inquisitive species and follows ships closely. They feed on squid, fish, crustaceans and carrion, including remains of prions, diving petrels and penguins, presumably found floating at sea.

The Sooty Albatross breeds on Prince Edward, Marion and Crozet Islands and on the Tristan da Cunha Group, Gough, Amsterdam and Saint-Paul Islands. They are loosely colonial, usually nesting in small

groups among heavy vegetation including tussock clumps on steep coastal cliffs. The low conical nests (15cm high) are composed of mud, grass and moss. They arrive at the breeding sites in mid-July on Marion Island, (up to one-month earlier on the Tristan da Cunha group and Gough Island) occupying nests in late August. The single pale grayish-white egg is laid in late September (Tristan da Cunha group) and early November (Marion Island). The incubation period is about 62 days in length and the chicks fledge at 5 months of age, departing from the islands by late June.

The species is highly pelagic in temperate and subantarctic waters between 30⁰ and 50⁰S in the Atlantic and Indian Oceans.

3.1.2 Procellariidae: Fulmars, Prions, Petrels and Shearwaters

This group of small to large sized seabirds is the most diverse of the Procellariiformes and may be divided into four sub-groups based on anatomical and ecological differences; fulmarine petrels, petrels, gadfly-petrels and shearwaters. Their wings tend to be long and narrow and they tend to fly on stiff wings. The shearwaters also use their wings for underwater propulsion. The bill is usually heavy but it is more slender in shearwaters, broad in prions, and with a hooked tip. The legs are set far back, the bird crouching on tarsi when on land. The birds all have a peculiar musky odour and the sexes have similar plumage characteristics, the male usually being larger than the female.

This group occurs in all the world's oceans and all species are essentially pelagic. They are most abundant in cool or cold waters, rich in plankton and mainly clear of floating ice. The birds nest on sea-cliff slopes or mountains and tend to avoid open-ground. Most of the hole-nesters only return to their nests at night while the open-nesters are diurnal. The Procellariidae are very susceptible to ground

predators, and local declines of some species have been caused by human interference. They are both migratory and dispersive and most species have a gradual moult.

The main food species taken are fish, cephalopods and crustaceans (often as plankton), but they also take offal and carrion. Food is obtained in several ways: 1) flight-feeding, mainly swooping to the surface and pattering, employed by a minority (e.g. Pterodroma species), 2) plunge-diving (shearwaters and allies), 3) surface-feeding, mainly by seizing and filtering prey (prions and fulmars) and 4) surface-diving and underwater pursuit (shearwaters and their allies). They are usually gregarious at sea, though some species are typically solitary.

All procellariids lay a single, relatively large white egg in a variety of colonial nest-sites. Both parents share incubation of the egg and feed the chick by regurgitation, initially of stomach oil and later on invertebrates and small fish. The downy young remain in the nest for two or more months undergoing two moults before fledging. They and the adults repel predators and intruders by squirting stomach oil and undigested food from an open bill.

3.1.2.1 Fulmarine Petrels:- Fulmarus glacialis: Northern Fulmar

The Fulmar is a strong billed petrel 45-50cm in size with similar plumage in the two sexes, though the males tend to be larger. The adult may be either a light or dark morph, though a range of different shades of grey is found between the two morphs. The lightest birds have a white head, neck, upper back and underparts and grey back, tail and wings. In the dark morph all the underparts are grey as well. The bill at the tip is usually yellow but otherwise ranges in colour from olive-green to blue-grey.

The variation in timing of the moult has been little studied. The adult post-breeding moult is a complete moult, normally starting after

departure from the colony. The primaries are lost and replaced in rapid succession but the outer ones grow slowly and do not reach their full length until late February. The body moult begins before the wings and continues at least until mid-February, with feathers of two successive generations present for most of the year. Tail feathers are renewed simultaneously with the outer primaries. The flight action in all winds is strong, with bursts of stiff wing strokes alternating with gliding.

At the larger breeding colonies the Fulmar is essentially gregarious, but with an expanding population small groups are found elsewhere, even nesting slightly inland. In the early 19th century the only breeding site for Fulmars in Britain was the island of St Kilda. In 1878 Fulmars colonized the island of Foula and since then a rapid increase has been seen in their numbers, not only in Shetland but also in mainland Britain. The colonization of Britain is believed to have been by Icelandic birds (Fisher, 1952) and the increase has been connected to the increase in the size of the fishing industry, though this has not been confirmed.

The Fulmar is attracted to waste food provided by man e.g. fish offal from trawlers and carrion, but the main components of its diet are crustaceans, cephalopods and fish mostly caught by surface-seizing whilst floating or swimming. They also occasionally feed by pursuit-plunging reaching depths of 4m using their legs and half-opened wings. They range far from the breeding site for food both at night and during the day.

The Northern Fulmar covers the entire marine sector from polar pack-ice through arctic, subarctic and Gulf Stream waters to about 50°N , moving in winter as far south as $40-42^{\circ}\text{N}$. They are mostly found on fishing banks, areas of upwelling, current rips and offshore reefs.

The Fulmar is both a migratory and dispersive species. In temperate and subarctic latitudes, breeding adults are present at sea within the feeding range (up to 320km) of colonies for most of the year. In the high Arctic birds are mainly absent from the frozen seas from November to February. British ringed birds after fledging reach as far south as the Bay of Biscay though most move west or northeast. The major all year round feeding concentrations are found on the Grand Banks off Newfoundland (probably Canadian and Greenland birds) and in the Varanger Fjord-Barents sea area (Spitzbergen and Soviet islands birds), which are both regions of high productivity.

Fulmars usually breed on narrow ledges on sea cliffs or inland crags and grass and earth slopes. The birds are colonial, though the colonies are not dense. The nest is a shallow depression in the ground and the white oval egg is laid in mid-May (outside the Arctic laying is usually later, up to mid-June). The incubation period lasts 52-53 days and the semi-altricial and nidicolous chick is fed by both parents on regurgitated liquid fish offal and plankton. Both the young and the adults defend themselves against intruders by spitting oil. The birds fledge at about 46 days of age and first breed when 6-12 years old.

3.1.2.2 Pachyptila spp: Prions

Prions, also known as whalebirds, are bluish-grey petrels with white underparts and underwings, and prominent black tipping on the wedge-shaped tail and undertail coverts. The various species are so similar on the wing that the shape of the bill and head pattern are usually the only features diagnostic of the species in the field. In large species the sides of the bill have fine palatal lamellae which are used for straining crustacean food from the water. Prions are remarkable for buoyant erratic flight, 'hydroplane' feeding and highly social flocking.

3.1.2.3 Pachyptila vittata: Broad-billed Prion

The Broad-billed Prion is a large, richly pigmented prion with a culmen less than twice as long as it is broad at the base and perceptibly bowed at the sides. They are very gregarious and feed mainly on copepods. Feeding is largely by hydroplaning.

They breed on the Tristan da Cunha group, Gough Island, Ile Saint-Paul and New Zealand subantarctic islands, nesting in burrows on a variety of coastal sites wherever suitable soil and cover are available. Two or more pairs may occupy the same burrows, though in different nesting chambers within the burrow. They arrive in early July on the Tristan da Cunha group, October on Marion Island and September on Iles Crozet. The single white egg is laid in August in the Tristan da Cunha group and hatches after an incubation period of 56 days (needs confirmation). The chicks fledge and depart after 50-60 days. They are subject to heavy predation by skuas and gulls which may dig out the burrows, and Giant Fulmars take adults. The prion is pelagic in the subantarctic zone ranging throughout the southern Antarctic Ocean and round New Zealand.

3.1.2.4 Gadfly Petrels

The gadfly petrels are small to medium sized, highly pelagic birds which superficially resemble shearwaters, but their wings are shorter in relation to body length than those of fulmars and shearwaters. They have a strongly hooked bill which is short and stout with prominent nostrils. They flap and glide like shearwaters but tend to be more erratic, holding their wings bent at the wrist rather than stiffly extended. Gadfly petrels feed largely on squid but in Antarctic waters crustaceans are probably an important part of the diet. They seldom alight on water, do not dive and tend to avoid ships.

3.1.2.5 Pterodroma incerta: Atlantic Petrel

The Atlantic Petrel is regarded to be a dark-headed Atlantic Ocean race of the White-headed Petrel. The throat, upper breast, underwing and undertail coverts of this gadfly petrel are brown while the rest of the underparts are white or faintly tinged grey. The bill is black and the feet are flesh coloured with brown colouration of the outer toes and webs.

The Atlantic Petrel breeds on the Tristan da Cunha group and Gough Island, arriving February to mid-March, and they lay one white egg between mid-June and mid-July. The hatching and fledging dates are unknown. They breed colonially, burrowing in soft soil on exposed ridges.

Little is known of their feeding habits but squid probably forms an important part of their diet. They are found in the warmer parts of subantarctic waters, ranging over the South Atlantic and Western Indian Oceans as far north as 50°S outside the breeding season.

3.1.2.6 Pterodroma brevirostris: Kerguelen Petrel

The Kerguelen Petrel is a medium-sized (34cm) gadfly petrel that has a glossy silvery sheen to fresh plumage. The coverts of the underwing and along the leading edge of the upperwing have narrow white edges. It is a solitary species though small flocks may form on the water. It beats its wings rapidly to gain height but then 'floats' distinctively in a strong wind. In calm weather its flight is more 'batlike'. The Kerguelen Petrel feeds mainly on cephalopods and to a lesser extent crustaceans.

It breeds colonially on Marion, Crozet, Kerguelen and Gough Islands and possibly in the Tristan da Cunha group. The burrows are dug in soft, deep, and usually wet soil, and the 1.5-1.8m burrow is often branched and curving. A drainage channel leads away from the nest, which is a truncated cone of twigs of Acaena. The adults

probably arrive at most sites in August but on Iles Crozet they are present all year. The single white egg is laid mid-September to early October and hatches in late November after an incubation period of 47-51 days. Both sexes incubate and feed the young. The birds fledge after two months in the nest.

The Kerguelen Petrel outside the breeding season ranges over subantarctic and antarctic waters north of the pack ice.

3.1.2.7 Pterodroma mollis: Soft-plumaged Petrel

The Soft-plumaged Petrel is also a medium-sized (36cm) gadfly petrel with distinctive dark underwings and white face. The upper surface from the crown to the tail is grey with darker markings about the eyes. The dark wing coverts produce an open 'M' on the spread wings. Occasionally individuals have all grey underparts. The bill is black. The Soft-plumaged Petrel is generally shy and solitary, flying with fast wingbeats and gliding frequently but it does not 'float' like the Kerguelen Petrel. It feeds mainly on cephalopods and fish.

The Soft-plumaged Petrel breeds on the Tristan da Cunha group, Gough, Marion, Crozet (Ile de la Possession only), and probably the Antipodes islands. They breed colonially on steep slopes along the perimeters of oceanic islands. Dry grass and Acaena stems line the nest which may occupy one of two chambers in a long burrow, each chamber occupied by a pair of petrels. The birds start to arrive at the breeding colonies at the beginning of August but most arrive in September. The single white egg is laid in early November though the date of hatching is unknown and the birds apparently fledge in May.

The petrel is found mainly in subtropical and subantarctic waters but occasionally enters the Antarctic zone during the summer. This petrel also breeds in the North Atlantic on the Maderia Islands, Ithas Desertas and Cape Verde Islands.

3.1.2.8 Shearwaters

The shearwaters are long-billed, medium to large petrels with long narrow wings and short rounded tails. In flight the smaller shearwaters alternate short bursts of rapid flapping with long stiff-winged banking glides low over the water surface. Shearwaters feed while they are swimming on the surface or by making shallow dives and they take squid, small fish, crustaceans and occasionally floating offal.

3.1.2.9 Puffinus gravis: Great Shearwater

The Great Shearwater is a large (46-51cm) brown-backed shearwater with a sooty brown headcap and white underparts and underwings, and a white bar at the base of the tail. Some blotching with brown on the underparts and underwings is also found. The bill is strong with inconspicuous tubed nostrils. The legs and feet are pale flesh to bright pink in colour with browner colouration on the tarsus and toes. Their flight action is urgent and powerful with rapid beats of stiff wings interspersed with glides and banking. The birds moult while in their winter quarters in the North Atlantic from the end of May to mid-August. The primaries are moulted in rapid sequence such that take-off may be hindered occasionally but they are never flightless.

The Great Shearwater has only three main breeding sites, Nightingale and Inaccessible Islands in the Tristan da Cunha group and Gough Island, although recently small numbers have been found breeding on the Falkland Islands. It is estimated that 2 million pairs nest on Nightingale Island, 150,000 pairs on Inaccessible Island and 600,000 pairs on Gough Island.

The main food items taken are fish and cephalopods, by pursuit-plunging, pursuit-diving and surface-seizing, the shearwater surfacing to swallow prey. It is mainly a daytime feeder and is often gregarious when food is abundant. The shearwater also scavenges offal

from fishing boats and in its northern locations takes Capelin (Mallotus villosus). They are often found near whales and porpoises which may drive fish to the surface. Sandeels and crustaceans have also been recorded in their diet.

The birds arrive at the nesting sites from August to September, laying the single white oval egg in early November. The chicks hatch after an incubation period of 53-57 days and fledge at about 105 days (late April-early May) and leave the island during May. The shearwaters migrate into the North Atlantic passing the horn of Brazil, arriving along the North Atlantic coast of North America in May and early June. Fewer birds migrate to the east Atlantic. The birds are present off Newfoundland and the Grand Banks all through the northern summer. Some birds spread eastwards towards Europe in July and August. The rapid return passage starts in August and most breeders have returned to their breeding colonies by mid-September.

3.1.2.10 Puffinus assimilis: Little Shearwater

The Little Shearwater is a small black and white shearwater with slaty blue-black upperparts and white cheeks, throat and underwings. The bill is a dull grey-blue and the feet are blue with pinkish webs. The Little Shearwater flies fast with very rapid fluttering wingbeats and keeps low over the water surface. It both swims and dives, often congregating in large flocks while feeding. It feeds mainly on fish and cephalopods caught by surface-seizing and by pursuit plunging and diving.

The Little Shearwater breeds on Tristan Island, Gough Island, possibly Ile Saint-Paul, on many islands off southern Australia and New Zealand (many subspecies), Rapa Island and possibly islands off the coast of Chile. Other subspecies occur in the eastern North Atlantic.

The birds nest in burrows dug in steep tussock grass banks in ravines near the sea.

3.1.3 Hydrobatidae: Storm Petrels

The Storm Petrels are very small pelagic petrels and fall into two main groups representing the main radiations, each originating in different hemispheres though they overlap in the tropics 1) southern species (Oceanites, Garrodia, Pelagodroma, Fregetta and Nesofregetta) and 2) northern species (Hydrobates, Halocryptena and Oceanodroma).

The petrels' principal foods are planktonic crustaceans, molluscs, small fish, and oily and fatty substances. Some species habitually follow ships taking scraps and natural prey in their wake. They are mainly flight-feeders taking prey at the surface while hovering, fluttering and pattering the surface. They rarely alight on the water and on land usually shuffle on their tarsi. They may be gregarious or solitary at sea but are colonial when breeding. The nest sites are either in rocky crevices or short burrows and the adults are most active at the breeding colonies at night, communicating mainly vocally. The breeding stages of incubation and chick rearing are prolonged except in the subarctic, where breeding is more strictly seasonal. The young are cared for and fed by incomplete regurgitation by both parents. The chicks are brooded continuously for the first 5-7 days after hatching and then visited nightly for feeding, the frequency of feeding dropping towards fledging which takes place at 59-73 days. Most petrels reach maturity between four and five years old.

3.1.3.1 Fregetta grallaria: White-bellied Storm Petrel

The White-bellied Storm Petrel is sooty-black in colour with a white rump, underwings and belly. The bill, legs and feet are entirely black. The flight is rapid, erratic and butterfly-like, the petrel

also springing from side to side over the surface on outspread motionless wings, using both feet as 'springboards'.

The White-bellied Storm Petrel breeds on South Georgia, South Orkney, South Shetland, Bouvet, Crozet, Kerguelen, Auckland, Bounty, Antipodes and Gough islands. It is a loosely colonial species nesting in well hidden crevices in stable boulder scree or in rock and lava slopes near the sea. On Gough Island the nest is found in a short burrow and consists of leaves and stems of decaying tussock grass or other vegetation. Both sexes incubate the single white egg which is laid in December-January and the male takes the first incubation shift, each shift usually lasting three days. The incubation period is 38-44 days long and the chicks fledge after 65-71 days in the nest.

These petrels feed on small cephalopods, crustaceans and fish picked up from the surface, and small pebbles and pumice are also found in the stomach. This species is highly pelagic, frequenting antarctic and subantarctic waters in the breeding season and the central tropics in winter.

3.1.3.2 Garrodia nereis: Grey-backed Storm Petrel

The Grey-backed Storm Petrel is a small (17cm) ashy-grey petrel with white belly and underwings. The breast, head, primaries, the leading edge of the underwing and the terminal band on the tail are sooty black. The rump and the base of the tail are light grey and both the bill and feet are black. The petrel skips and bounces from side to side very low over the water, with wings extended, while it is feeding. It hovers buoyantly over food, which comprises small cephalopods and other molluscs.

The Grey-backed Storm Petrel breeds on Falkland, South Georgia, Crozet, Kerguelen, Macquarie, Auckland, Antipodes, Chatham, and Gough islands. The birds are loosely colonial and excavate either small scrapes or short burrows in the bases of Tussock Grass and Acaena

clumps or other low vegetation near the sea. The adults arrive in late October to early November, laying a single egg in mid-November to mid-December. Relatively little is known of the breeding biology of this species.

It is a highly pelagic species in the subantarctic zone but its overall range, especially in the Indian Ocean, is poorly known.

3.1.3.3 Pelagodroma marina: White-faced Storm Petrel

The White-faced Storm Petrel is of a similar size to Leach's Petrel (Oceanodroma leucorhoa) (20-21cm). The adult's crown is dark grey, shading to a brown grey on the back and upperwing coverts. The rump is light gray and the head has a distinctive pattern, with a black subocular eyestrip and white on the forehead superciliary and cheek merging into the white underparts. The bill and long legs are black and the feet have yellow webs. The flight is erratic but stronger than other storm petrels. In flight it dangles its long legs as it 'dances' from right to left in a pendulum motion and jumps over the waves. It feeds by lowering the legs and splashing into the water with the body to pick up surface plankton, the diet consisting of planktonic crustaceans and, to a lesser extent, squid.

The White-faced Storm Petrel breeds on temperate and subtropical islands in the North and South Atlantic Oceans, including the Tristan da Cunha group, Gough Island and islands off Australia and New Zealand. It nests colonially, breeding during the summer in burrows lined with vegetation. As with many petrels they are nocturnal in their visits to the breeding colonies.

In the breeding season the petrel frequents the area covered by the subtropical convergence and in winter it is highly pelagic. Pelagodroma marina from Gough Island and the Tristan da Cunha group winter within the tropical South Atlantic, dispersing west to South

America and east almost to Africa. Their limited northward dispersal is recorded by scattered records at sea between Ascension Island and Angola (north to 6.5⁰S).

3.1.3.4 Oceanodroma leucorhoa: Leach's Storm Petrel

Leach's Storm Petrel is 19-22cm in size and is blackish-brown above and browner below, with a white rump and forked tail. The sexes are similar and the bill, legs and feet are all black. It has a distinctive leaping and darting flight with constant changes of speed and direction. It does not, however patten the surface like other storm petrels. It is less markedly pelagic than other species and is usually found singly or in small groups.

It inhabits cool or cold waters fringing the subarctic or in lower latitudes, areas of oceanic convergences or upwellings. Leach's Petrel is a migratory species; those birds breeding in the North Atlantic and North Pacific migrate south to winter in the regions of the tropical convergences. Some birds remain in the cooler areas of the North Atlantic during the northern winter. Most adults are presumed to leave their winter habitat by mid-April and arrive in the breeding colonies by late April.

They feed chiefly on planktonic crustaceans, molluscs, small fish and also oily and fatty substances especially from fish offal thrown overboard from ships. Leach's Petrel takes food from the ocean surface while skimming or by hovering and snatching. They rarely settle on the water to feed and apparently never dive.

At the breeding grounds they are gregarious, nesting colonially in burrows. The single egg is incubated by both parents for 41-42 days and the hatched chick is brooded continuously for the first five days. Feeding is by bill-to-bill partial regurgitation and both parents care for the chick. The chicks fledge at 63-70 days.

The adults moult annually with the moult of some body feathers at

the end of the breeding season, though the main moult takes place from November to February in winter quarters and all the feathers are fully grown by April.

3.1.3.5 Hydrobates pelagicus: British Storm Petrel

The British Storm Petrel is a small (14-18cm) sooty black petrel with a white lower rump and upper tail coverts forming a rectangular white patch. The bill, tarsus and toes are black and the iris dark brown. The only other white patches are on the underwing coverts. Their flight is fairly weak-looking, almost bat-like fluttering interspersed with short glides. At intervals they patter on the water with their feet on the surface to pick up food. They feed mainly on surface crustaceans, small fish, medusae, cephalopods and oily and fatty materials. They are usually solitary or occasionally form small groups. Their range is distinctively in the north-east Atlantic and west Mediterranean over pelagic and offshore waters. This petrel is especially found in the intermediate offshore and suboceanic zones between the littoral and deep ocean from the 10⁰C isotherm to the 25⁰C isotherm.

Its current breeding distribution is poorly known in many areas and decreases appear to have occurred in some of the Scottish and Irish colonies. It is both a migratory and dispersive species restricted to the east Atlantic and Mediterranean and to wintering quarters off the south-west coast of South Africa from October to April.

The British Storm Petrel comes to land solely to breed and it starts breeding in it's fourth or fifth year. For breeding, the British Storm Petrel prefers rocky outcrops, narrow crevices between stones or burrows of other species. Egg-laying takes place between mid-June and mid-July and the egg is incubated by both parents. The young hatch blind, are semi-altricial and nidicolous and are fed on

82% of nights until they fledge. The chicks are fed by bill-to-bill partial regurgitation. The period until fledging is 62.8 days.

The adults have a complete annual moult, the wing and tail moult starting after chick-rearing and continuing in winter quarters.

3.1.4 Pelecanoididae: Diving Petrels

These are black and white 'chunky-bodied' petrels, resembling the small alcids of the northern hemisphere. The paired nasal tubes open upward rather than forward as in other petrels, probably as an adaptation to diving. Their flight consists of laboured 'flurries' of rapid wingbeats and short glides just above the ocean surface. They swim underwater with the wings held partly open. The diving petrels feed on crustaceans, cephalopods and possibly small fish. The birds breed on various islands and are strictly nocturnal but nevertheless they are frequent prey of skuas.

3.1.4.1 Pelecanoides urinatrix: Common Diving Petrel

The upperparts of the Common Diving Petrel are black, together with the underwing coverts and inner webs of the primaries. They have a distinct grey-mottled breastband and throat and the feet are blue. They feed on amphipods, copepods and other small crustaceans and may feed so voraciously that they cannot rise from the water.

The Common Diving Petrel is widespread on subantarctic and temperate islands in the Southern Atlantic Ocean (Falkland Islands, Tristan da Cunha group and Gough Island), off southeast Australia and on New Zealand subantarctic islands. They breed colonially on low lying coastal slopes with a heavy vegetation cover. The burrow is dry and shallow and the nest is usually lined with grass and feathers. The petrel arrives on the islands from August to October and the eggs are laid from late November to early January. The single dull-white egg is incubated for 55 days and the newly hatched chick is brooded continually for the first 10 days. The chicks fledge at 54 days and

unlike many Procellariiformes matures at a relatively early age, starting to breed at two years old. The Common Diving Petrel mainly stays in coastal and offshore waters outside the breeding season.

3.2 PENGUINS

3.2.1 Eudyptes chrysocome: Rockhopper Penguin

The Rockhopper Penguin is a small, crested penguin (61cm) with a black forehead. The narrow, pale yellow eyebrows begin just behind the bill but do not meet on the forehead. The fuller crests of the northern subspecies bristle out from the sides of the head together with the elongated black crown feathers making the head appear 'shaggy'. The eye is a dull garnet red, the bill reddish with a fleshy margin, coloured black in Gough Island birds, and the feet are whitish-flesh coloured with black soles. The males are usually larger than the females. On land this species, as the name implies, moves in a series of short hops and it enters the water feet first whereas most other species dive in. They feed mainly on crustaceans including amphipods, copepods and isopods, though squid is also an important part of the diet in birds from the Tristan da Cunha group.

The Rockhopper Penguin breeds in the southern part of its range (E. c. chrysocome) on Prince Edward, Marion, Crozet, Kerguelen, Heard and Macquarie Islands, and in the north (E. c. moseleyi) breeds on the Tristan da Cunha group, Gough, Amsterdam, Saint Paul, Campbell, Auckland, Antipodes and Bounty Islands. After up to five months at sea the birds arrive at the breeding colonies from mid-October to early-November (two months earlier on Tristan da Cunha group, Gough, Amsterdam and Saint Paul Islands). The nest is located near the sea, often among boulders and is a shallow depression in the ground lined with small stones and, occasionally, tussock grass. The 2 greenish-white eggs are incubated for 32-34 days and the chick(s) are brooded

continually by the male for the first 19-25 days. Almost invariably however, only one egg is hatched. Fledging takes place at 67-72 days and the birds first breed between five and seven years of age.

The Rockhopper Penguin is highly pelagic in subantarctic and antarctic waters as indicated by barnacles found adhering to the feet of some individuals.

3.3 STERCORARIIDAE

3.3.1 Stercorariidae: Genus Catharacta species

The skuas of the genus Catharacta are a highly predatory group consisting of a number of well-marked forms, probably best considered as three main species (Catharacta chilensis, C. maccormicki and C. skua, the latter comprising several subspecies). These skuas are mainly subantarctic and antarctic in distribution, with an outlier in the boreal North Atlantic.

The birds are robust, with dark-brown mottled plumage and white flashes on the wings; the female is usually larger than the male. The bill is strong and the upper mandible hooked. The skua family are well known for their aggressive habits, and their rapid powerful flight allows them to overtake and rob birds in flight, the chased seabirds being forced to disgorge their prey which the skua then takes. They also feed on chicks, eggs, small adult petrels, auks and carrion, and fish, crustaceans and cephalopods caught in short shallow dives.

The skuas are strongly territorial, attacking intruders with aggressive swoops and dives using the feet and wings to hit the intruder. The birds nest near seabird colonies and lay 1-3 (usually two) olive brown eggs. The young are precocial and are fed by being given food in the bill or regurgitation on the ground. The juvenile plumages tend to be darker, and they attain breeding status at 4-8 years old. The adults experience two moults per year, the post-

Plate 2 South Atlantic Great Skua Catharacta skua hamiltoni



breeding moult and a smaller pre-breeding moult replacing head and breast feathers.

The Chilean Skua Catharacta chilensis is a large reddish-brown skua found in southern South America. McCormick's Skua Catharacta maccormicki (also known as the Antarctic Skua or South Polar Skua) is closely related to C. skua but shows a distinctly two-toned plumage in the adults with a dark brown cap and upperparts contrasting with a light coffee coloured neck and underparts. This species is found on the Antarctic continent and South Shetland Islands. The Chilean and McCormick's Skuas have, compared to the other skuas, relatively pointed wings and slender bills. They also tend to be more pelagic and migratory, C. maccormicki migrating as far north as Greenland and Japan. The third species, Catharacta skua, has several subspecies; C. s. antarctica, the Falkland Skua, which breeds in the Falklands and Patagonia, C. s. hamiltoni, which breeds on Tristan da Cunha and Gough Island, C. s. lonnbergi, the Brown Skua, which breeds on subantarctic islands and the tip of the Antarctic peninsula, and C. s. skua which breeds in Iceland, Faroes, Shetland, Orkney, north Scotland, Spitzbergen and Norway. C. s. skua is believed to be a descendant of one of the Great Skua species in the southern hemisphere (Furness, 1983).

3.3.1.1 Catharacta skua hamiltoni

The Tristan Skua is a large (64cm) skua with scattered rufous feathers on an overall brown body, excepting the white wing patches. The bill and feet are black. The juvenile is dark brown with some chestnut flecking on the neck and underparts and the bill tends to be weaker looking. The skua feeds on eggs, young and adult birds, prions and petrels forming a large part of their summer diet.

The birds select an extensive nesting territory near the seabird

colonies and the nests are located either on grass tussocks, clumps of Azorella or on moss. The nests usually contain little nesting material unless in rocky areas. Eggs are laid from late October to November and incubated for 29-32 days. The chick is able to leave the nest within 24 hours of hatching. The chicks fledge after 55-60 days but remain dependent on the parents for a further month. In the Tristan da Cunha group the skua is resident all year.

3.3.1.2 Catharacta skua skua: Great Skua

The Great Skua is about the size of a Herring Gull (53-58cm), and is a large billed, broad-winged skua. The plumage is mottled dark brown with prominent white wing flashes on the wings. The sexes are similar in plumage colour but the female is larger than the male.

The Great Skua occupies the middle latitudes to the subarctic fringe in the northeast Atlantic, entirely avoiding summer ice and snow. Outside the breeding season it is highly pelagic and migratory. Its total marine range extends from Greenland and the Norwegian sea south at least as far as Brazil. However, the pattern of migration varies according to the age of the bird. Most recoveries have been from birds ringed in Scotland, especially the island of Foula, and therefore may be used to represent the migratory habits of the skua.

The young birds which fledge in August have a very variable autumn dispersal rate. A few juveniles fly up to 2500km south by the end of August but others remain in British waters until December. Southward movements take place down through the North Sea and eastern Atlantic. After November most recoveries come from off the coasts of France and Iberia. By April many birds have spread over the Atlantic from 50^{0N} to the equator (or even further south). In the summer some birds return to Scottish waters but they range as far west as the coastal waters off New England and Newfoundland. From November onwards the first and second year birds are usually found south of 50^{0N}.

In their third and fourth calendar years the birds tend to occur well north of their natal areas (Greenland, Iceland and Norway). Many return to the eastern Atlantic in November and spend the following winter off the coast of Iberia and north-west Africa.

From the fifth year onwards the birds show signs of attachment to their colonies and there is a much reduced tendency to visit northern colonies or to migrate south in the winter. A more stable migration pattern is set up in the older birds with May-August recoveries being concentrated in the Shetland and Orkney areas and between September and April they are found in the eastern Atlantic as far south as Iberia and in home-waters and the North Sea, areas virtually deserted by younger skuas.

Icelandic birds appear to have a different migration pattern, as most recoveries come from the eastern seaboard of North America. With the use of recovered rings from birds for tracing their movements it must be noted that birds which remain out at sea are under-represented, and over-emphasised in regions where they are taken by man or caught in fish nets.

The Great Skua has been long established in Iceland and Faeroes and spread to Britain in the 18th century and more recently to Bear Island, Spitzbergen and Norway. The Great Skua has been subject to periods of persecution and protection and numbers are now considered stable in Iceland, but in the Faeroes numbers declined to 50-60 pairs in 1972 following severe persecution. In Britain numbers increased quite dramatically once the Great Skua was fully protected during the 1890's. In Shetland in 1774 10 pairs bred, increasing to 60 pairs in 1890 but this was reduced to 37 pairs in 1899 through persecution. The island of Foula in Shetland held the first recorded pair of Great Skuas in Britain. With protection this population had risen to 2670

pairs in 1980 (Furness, 1983), such that Foula now holds 50% of the British and 25% of the world population of Great skuas. From historical records it seems possible that this subspecies of Catharacta skua has only relatively recently colonised the North Atlantic (Furness, 1983).

The food items taken by the Great Skua include sand-eels, whitefish, fish offal, carrion, marine invertebrates, rabbits, berries, eggs and birds (Furness and Hislop, 1981). Fish are obtained either by surface-diving, or by scavenging or by food piracy. However, the main feeding habit of the skuas varies between both individuals and colonies. In the Faeroes the skuas tend to feed by piracy of fish from other birds and take seabird eggs, chicks and adults as prey. In Shetland the main food items are sandeels and discarded whitefish from trawlers, and up to 80% of their food may be obtained this way during the breeding season. Great Skuas on Foula take large numbers of fledgling kittiwakes and some adults but tend not to take eggs or chicks, which is the practice of the Hermaness, Shetland Islands, birds. Individual birds may have dietary preferences or catch prey in different ways, for example an adult puffin may be caught at the entrance to its burrow or in flight over the sea or at the sea surface. In the breeding season the birds feed throughout the hours of daylight with no feeding in the 4 hours of relative darkness around midnight.

Outside the breeding season the birds are usually solitary, though they are occasionally seen in two's or three's. The birds arrive in April at the breeding colony and quickly take up and defend their territories. Birds nearing breeding age collect on club-sites and from here pair, and eventually take up a vacant territory. The eggs are laid in mid to late May in a shallow scrape in the ground lined with grass and other pieces of vegetation. The eggs hatch after 3 weeks and

CHAPTER 4

METHODS OF SAMPLE COLLECTION AND ANALYSIS

4.1 SAMPLE COLLECTION

Most of the numerous studies of the pollutant levels in seabirds have utilised tissues from birds found dead or dying. It is known that both organochlorines and metals are redistributed during stress, and that the weights of organs can change dramatically. For these reasons, all the samples obtained for analysis in this study were from healthy seabirds that were deliberately killed, or from seabirds that had been healthy but had died suddenly as a result of natural predation or accident. Sampling in this way means that abnormally high levels will not be found simply as a consequence of the history of the bird immediately before death. All levels measured can be taken to represent levels in the wild population as a whole. The main limitation of this sampling is that the number is necessarily small, and generally set by the bodies issuing licences allowing collection.

From 1980-1983 samples of several species of pelagic seabirds were collected from the North and South Atlantic, together with items from the food chain, in order to determine if the birds were accumulating potentially toxic substances such as organochlorines, cadmium and mercury. In the North Atlantic the primary species studied was the Great Skua, selected because it is a top predator known to accumulate toxic substances, and because the birds were of known age, having been ringed as chicks. Leach's and British Storm Petrels from the North Atlantic were examined for their metal content in terms of their potential as food items for skuas. Fulmars, a northern Procellariiform, were taken from two populations with different diets in order to observe any differences in metal content of tissues, which may have been related to diet. South Atlantic seabirds (15 species)

were selected for the study both because little work had been done in the past and to allow comparison between the North and South Atlantic.

Sample collection was carried out as outlined below and sample sizes were governed by species abundance and kept to the minimum possible.

a) From the island of Foula, Shetland in June 1980 and May 1983 twenty and seven, respectively, healthy Great Skua adults on breeding territories were shot under licence. Each bird was placed in a polythene bag and deep frozen soon after death, being stored at -20°C until analysis. Tissues were also available from birds collected before 1980.

In May 1983 Fulmars were collected on Foula, killed by cervical dislocation, placed in a polythene bag and stored deep frozen at -20°C . Samples of Great Skua and Fulmar kidney, liver and pectoral muscle were also brought back to the laboratory for analysis, these samples being from freshly killed birds and fresh carcasses found in the field.

In July 1983 Fulmars, Leach's Petrels and British Storm Petrels both breeding and non-breeding individuals of each species were collected from St. Kilda. Fulmars were taken by hand and the petrels by mist-netting at night, and all species were killed by cervical dislocation. The birds were then deep frozen and brought back to the laboratory for analysis.

b) From the South Atlantic island of Gough ($40^{\circ}19'S$ $9^{\circ}57'W$; part of the Tristan da Cunha group) fifteen species of pelagic seabird were sampled by Dr. R.W.Furness during September/October, 1983. The samples consisted of birds found dead due to predation by Great Skuas, or collected at random from nest-sites by day, by handnet and torch at night, or found dead after collisions with overhead wires or outdoor lights. Birds were killed by cervical dislocation and the birds were

measured, sexed and dissected on site. Tissues were stored at -20°C until analyses were performed. Birds available for analysis are summarised in Appendix 1.

c) In order to examine quantities of metals in organisms lower down in the food chain, samples of mixed plankton, copepods, squid and fish were collected as follows. Data for copepods, phyto- and zooplankton were taken from published and unpublished sources. Samples of squid were collected by a commercial supplier from coastal waters off the west coast of Scotland. Sandeels were retrieved from adult and chick regurgitates, and a sample was collected from the fish factory on Bressay, Shetland in June 1983. A mixed sample of fish (Appendix 1) was obtained by a Scalloway trawler off the west coast of Shetland in June 1983. All samples were frozen and stored at -20°C until used in the analyses.

4.2 TISSUE PREPARATION

For whole birds brought back to the laboratory the biometrics (wing length, bill length and depth, weight and tarsus length) were measured, and the birds dissected, the kidney, liver, pectoral muscles, body fat and, where in sufficient quantity, abdominal fat, being removed. Each bird was sexed by examination of the gonads. The dissected tissues were weighed and then homogenised using glass knives to avoid metal contamination. All dissecting instruments (scissors, scalpel and forceps) were washed in water, rinsed with 70% alcohol followed by two rinses in deionised water. All samples were kept frozen at -20°C until used for analysis.

4.3 ORGANOCHLORINE ANALYSIS

4.3.1 Introduction

Several methods have been described using adsorption

chromatography for the preparation of extracts of chlorinated hydrocarbon residues from environmental samples for gas-liquid chromatographic (GLC) analysis with electron-capture detection (ECD).

The method used in this study was based on the column clean-up and separation techniques developed by the United States Food and Drug Administration and refined by Dr. J. Bogan (Bourne and Bogan, 1972; Bogan and Newton, 1977). The method has been used to analyse the organochlorine residues (primarily DDE and PCB's) in animal tissues.

Polychlorinated biphenyls (PCB's) and DDT (*p,p'*-DDT, 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane, metabolised to *p,p'*DDE, 2,2-bis-(*p*-chlorophenyl)-2,2-dichloroethylene) are chemically and microbiologically resistant environmental contaminants, and being lipid-soluble are, therefore, incorporated into various biological systems.

The analysis of PCB's is quite complicated owing to the large number of possible components (more than 209 biphenyls exist) and this difficulty is realised in the methodology used. In the present work the column technique was evaluated for the extraction of PCB's and DDE from skua liver, body fat, pectoral muscle tissue and eggs.

4.3.2 Method of Organochlorine Analysis

Reagents

- a) Solvents: Acetone and Hexane. Chemicals supplied by Rathburn Chemicals Ltd. The chemicals were glass distilled and pesticide-free.
- b) Florisil: 60-100 mesh P.R. Grade. Before use the Florisil is baked overnight at 180⁰C to remove electron-capturing contaminants. The following morning the Florisil is cooled in a dessicator, then deactivated by adding 1ml of distilled water and shaken for 30 minutes. It is then ready for use.

- c) Sodium Sulphate: Anhydrous, hexane-washed and granular.
- d) Sand: hexane-washed.
- e) Deionized and distilled water.
- f) Chlorinated hydrocarbon standard solutions: DDE 0.005ug ml⁻¹.
- g) Column packing was 10%DC200.

Apparatus

- a) Gas chromatograph: Pye-Unicam Pu 4500 chromatograph equipped with a Ni⁶³ electron-detector, automatic injector and microprocessor. The glass column (30cm x12mm) was packed with 10%DC200 and plugged with glass wool. Other operating parameters: carrier gas was nitrogen with a flow rate of 60ml/min, detector temperature=270⁰C, inlet temperature=220⁰C, column temperature, initial=210⁰C, final=210⁰C.
- b) Extraction and clean-up glass columns (350mm x 6mm), with one end tapered and a solvent reservoir at the other.
- c) Extraction of lipids was performed using a Soxhlet quick-fit apparatus with 250ml flasks.
- d) Weighing containers: six 600ml Pyrex beakers and 6 porcelain evaporating dishes.
- e) Water bath for evaporation of solvents (hexane and acetone).

Sample preparation

Muscle, liver, and body fat samples of 5g ± 0.2g were taken from the homogenised tissues of the skuas. All samples were defrosted before use. Homogenised eggs were stored in glass jars and from these, aliquots of 5g ± 0.2g were taken.

Extraction technique

Tissue samples (5g) were placed in small, labelled beakers and homogenised with six spatulas of sand and three of hexane-washed sodium sulphate. The sample was ground with glass rods until a homogeneous powder-like mixture was obtained. More sand and sodium sulphate were added when necessary. The samples were then transferred

to glass thimbles and placed in the Soxhlet apparatus, together with 220ml of hexane and 110ml of acetone, all of which with the exception of approximately 100ml of the hexane-acetone mixture, was placed in the flask. The remaining 100mls was used for rinsing the small beakers to ensure extraction of all the fat and hence no loss of organochlorines.

The fat in the tissue was extracted by the hexane/acetone mixture for a minimum of five hours. The resulting mixture was transferred to weighed 600ml beakers and the excess solvent evaporated off, leaving the extracted fat. The extractable fat content of the sample was determined by reweighing the beakers. This fat was then taken up with 25ml of redistilled hexane, transferred to a labelled measuring cylinder and left to settle for 30 minutes. A 5ml aliquot of this reconstituted residue was used for a clean-up and fractionation procedure using Florisil column chromatography.

Hexane-washed cotton wool balls were used to plug the tapered ends of the glass micro-columns and support the column packing. Three grams of deactivated Florisil were poured into the micro-column and packed by gently tapping the sides of the column. A small amount (200mg) of anhydrous sodium sulphate was placed at the column head to ensure complete dryness of the sample before passing into the adsorbent. Each column was cleaned by the passage of 15ml of a 1:9 ether/hexane mixture followed by 20ml of hexane to ensure that the Florisil was free of contaminants. After these elutions the column was sucked dry. When the level of the sample had reached a point 1-2mm above the surface of the sodium sulphate 20ml of redistilled hexane was carefully poured onto the column. 20ml of the eluate was collected as fraction I. When this fraction had passed through the column, 25ml of the ether/hexane mixture was added and 25ml of the eluate collected as

fraction II. All the fractions were collected in glass measuring cylinders and stoppered until analysed.

The amount of lipid in the sample was checked at this point by taking 10ml of the original fat extract and placing the 10ml into weighed evaporating basins. The sample was then evaporated to dryness and reweighed. The percentage fat content was calculated thus:-

$$\% \text{ lipid/10ml} = \frac{\text{wt. of lipid in 10ml}}{10} \times \frac{25}{\text{wt. taken}} \times 100$$

$$\% \text{ lipid total} = \frac{\text{wt. of total lipid}}{\text{wt. of sample taken}} \times 100$$

The final eluates were injected, at dilutions ranging from x10 to x200, into the gas chromatograph. Identification of the peaks produced were based on the relative retention times in the column using a DDE standard as a reference. Samples in both fractions were quantified by comparing the peak heights with the height of the DDE peak and employing a correction factor (see later for details of the correction factor used). The following protocol was used for each run using the auto-injector: wash, standard, wash, sample, wash, sample, wash, standard. Washes were of redistilled hexane. With the use of the autoinjector up to 51 samples and standards could be injected over 100 hours with a cycle time of 110 minutes, in theory, although in practice the auto-injector proved unreliable and manual injection was necessary on occasions.

4.3.3 Calculation of concentration of organochlorines in samples

Concentrations of organochlorines in fraction I (which contains DDE and PCB's) were calculated as follows:-

concentration

$$\text{in Fraction I} = \frac{\text{Pk. ht. sample}}{\text{Pk. ht. standard}} \times \frac{\text{dilution}}{\text{wt. taken}} \times \text{conc. of std.} \times 5 \times 20$$

where 5 represents the aliquot of the concentrate placed on the column and 20 is the total volume of Fraction I (both in ml). Therefore if a 0.005ug ml^{-1} DDE standard is used then the formula for calculating the concentration of DDE in FI of the sample is as follows:-

$$\text{conc DDE} = \frac{\text{Peak height of sample}}{\text{Pk. ht. of standard}} \times \frac{\text{dilution}}{\text{wt. taken}} \times (5 \text{ml} \times 20 \text{ml} \times 0.005 \text{ DDE} \text{ ug g}^{-1})$$

Since the PCB peaks have been calculated to be 4.2 times less (Bogan, pers. comm.) for the same sample using the same standard, the formula for the calculation of PCB's is

concentration of

$$\text{PCB's} = \frac{\text{Peak height of sample}}{\text{Peak height of standard (DDE)}} \times \frac{\text{dilution}}{\text{wt. of sample}} \times 5 \times 20 \times 0.005 \times 4.5$$

$$= \frac{\text{Peak height of sample}}{\text{Peak height of standard (DDE)}} \times \frac{\text{dilution}}{\text{wt. of sample}} \times 2.1$$

The reference peak height for PCB in the tissues was based on the summation of 8 PCB peaks eluting after p,p'-DDE (Bogan, pers. comm.).

The quantity of dieldrin (HEOD) in fraction II was calculated as follows:-

conc.

$$\text{of HEOD} = \frac{\text{Peak height of sample}}{\text{Peak height of standard}} \times \frac{\text{dilution}}{\text{wt. taken}} \times 5 \times 25 \times 0.005$$

Results are reported in both ug g^{-1} of tissue (including lipid) wet weight and ug g^{-1} lipid.

4.3.4 Modifications

As dieldrin was found only in trace amounts in early analysis, due to time constraints it was considered unnecessary to analyse further, and in later analyses fraction II was not collected from the column.

The quantitative analysis of PCB's is routinely based on a comparison of the gas-liquid chromatographic pattern of the sample with PCB profiles of commercial products, and the concentrations of PCB's are derived from one or several of the 8 major Arochlor peaks based on a comparison with the standard peaks. This method may give realistic results provided that the proportions of the different PCB isomers are similar to those found in commercial PCB's. Unfortunately in practice it is not possible to verify the assumptions of identical, or even similar PCB patterns owing to the complexity of chromatograms from biological samples. For this reason quantitative figures for PCB's reported here on the basis of this method should be regarded as only approximate. The methods developed by Bogan (as described above) have, however, been satisfactory for the determination of PCB levels in a wide variety of bird and animal samples (e.g Bourne and Bogan, 1972; Newton and Bogan, 1978). The use of a conversion factor of 4.2 from a DDE standard is less satisfactory than the use of PCB standards. The most satisfactory method would be to determine the amounts of the individual components of PCB's and sum these to give the total amount of PCB's but, amongst other problems, relative proportions of different isomers vary according to the extent of biodegradation that has occurred; therefore measurement of PCB's is further complicated by this problem.

Subsequent work done at the Department of Agriculture and Fisheries for Scotland Laboratory, Faskally, Pitlochry, has shown that the chromatographic pattern of PCB's in Great Skua tissues matches reasonably closely the pattern of Arochlor 1260. One other

problem that may occur concerns the lipid content of the extracts. It has been found that the elution profile and recovery of organochlorine residues on alumina alters with the increasing lipid content of the sample (Wells and Johnstone, 1977). As the lipid content is increased the elution profile is gradually compressed such that with high fat loadings on the clean-up column the recoveries of residues become variable and unreliable. These variations in column performance with lipid content do not preclude the use of the method for the analysis of animal tissues provided that the weight of lipid transferred to the column is controlled. This lipid limit is easily calculated from the extractable residues. Florisil columns have a higher lipid-holding capacity than alumina, of 700mg and though some of the skua fat samples were near to this limit, none of the samples exceeded it. However, in subsequent fat analyses, to ensure that the problem did not arise only 0.5g samples of fat tissue were taken.

4.4 ANALYSIS OF MERCURY IN TISSUES AND FEATHERS

To determine the quantity of mercury in the tissues and feathers of pelagic seabirds two methods were used. The first involved a Perkin-Elmer MHS-10 Mercury/Hydride System which operated together with an atomic absorption spectrophotometer. The second method used an ultra-violet absorption spectrophotometer set to the wavelength for maximum absorption by the mercury vapour.

The preparation and digestion stages for the two analytical techniques were identical. During the preparation and digestion temperatures were kept as low as possible (always below 60⁰C) to avoid loss of mercury, as it is a very volatile element. Additionally all glassware was thoroughly cleaned, as mercury readily adsorbs onto glass and plastic surfaces. Glassware was cleaned by soaking in Decon 90 (commercial detergent) overnight, then rinsed in tap and deionised

water, placed in a 50% nitric acid bath for at least 2 hours, then rinsed in deionised water and finally placed in a drying cabinet.

4.4.1 Feather laundering

The surfaces of feathers are often contaminated with various debris from the environment, and it was therefore essential that this debris was removed in case any particles adhering to the feather surface were contaminated with mercury. The removal of the particles was achieved through a vigorous washing procedure. The feathers were individually placed in numbered test-tubes ready for the washing procedure.

1. A 50-50 chloroform-acetone mixture was added in sufficient quantity to each tube to cover the feathers.
2. The tubes were placed in an ultrasonic bath for 5 minutes.
3. The mixture was poured off and the procedure repeated with a fresh 50-50 mixture.
4. The liquid was poured off and a rinse using acetone alone was performed.
5. Deionised water was added and the tubes placed in the ultra-sonic bath for 5 minutes (Rinse 1).
6. Repeat 5 (rinse 2)
7. Repeat 5 (rinse 3)
8. The last rinse was poured off and the tubes inverted for 5 minutes to drain.
9. The rack of tubes was then placed mouths uppermost in an oven at 60°C for at least 24 hours.
10. Each feather was then placed into a labelled polythene bag until used in the analyses.

The method described above, however, was inadequate for feathers from museum specimens, because they are often heavily contaminated

with mercury as a mercuric salt was used in the preservation process.

The following method was therefore used to wash these feathers:-

Stages 1 to 5 were as described above.

6. Each feather was placed in 2% 'Micro Solution' and the rack of test tubes put into a water bath at 60°C for one hour.
7. 5 minutes in micro solution in the ultra-sonic bath.
8. 4 deionised water rinses of 5 minutes each in the ultra-sonic bath were performed.
9. The samples were oven-dried for 24 hours and placed in labelled polythene bags ready for analysis.

Samples of homogenised tissue were freeze-dried for mercury analysis using an Edwards freeze-dryer. For the digestions 0.1g to 0.2g of freeze-dried tissue (liver, kidney and pectoral muscle) and up to 0.5g of feather (if available) were weighed into micro-Kjeldahl flasks. 1ml of concentrated nitric acid and 4ml of concentrated sulphuric acid were added to the samples and after 15 minutes the flasks were placed in a shaking water bath set at 58°C. After 2 hours, or up to a maximum of 3 hours if the tissue was difficult to digest, the micro-Kjeldahl flasks were removed from the water bath, cooled and placed in ice. 15mls of 6% potassium permanganate were slowly added to each sample, then each sample was stoppered and left to stand overnight. The precipitate formed was subsequently dissolved by a few drops of 30% w/v hydrogen peroxide, a clear solution being the end result. The samples were filtered and made up to 25ml in volumetric flasks and were analysed the same day.

4.4.2 Standards

A commercial solution ('Spectrosol' Mercuric nitrate standard solution BDH Chemicals, Poole, Dorset) of 1000ug Hg ml was used as the basic stock standard and 100ul of this, 100ul of 6% potassium

permanganate and 1ml of concentrated nitric acid were diluted to 100ml in a volumetric flask to give a working standard of 1ppm. The working standard was prepared daily. The acid was added in order to match more closely the matrix of the sample solutions and potassium permanganate added to stabilise the mercury ions. For calibration, standards of 100ng, 200ng and 300ng, derived from the working standard were used for the tissue samples and 25ng, 50ng and 100ng for feather analysis.

4.4.3 MHS/10 mercury hydride system

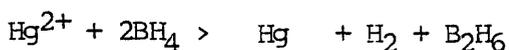
The mercury hydride system which operates together with an atomic absorption spectrophotometer is a manually operated accessory for the high sensitivity determination of mercury and hydride-forming elements.

Apparatus

- a) The light source used was a mercury electrodeless discharge lamp, (wavelength of 253.6nm) which required a 10-30 minute warm up time to achieve operational stability. The slit width was 0.4mm and background correction was used to correct for non-atomic absorption.
- b) The analyser assembly was free-standing and placed adjacent to the sample compartment of the flask, the reservoir for the reducing agent and all the pneumatic components for control of the carrier gas and the transport of mercury vapour to the quartz cell.
- c) The cell assembly consisted of a quartz cell and mount. The quartz cell was 165mm long, 12mm in diameter and open at both ends. The cell was positioned in the light beam of the spectrophotometer and aligned using the burner adjustment controls. The cell was connected to the analyser assembly by a silicone rubber hose.
- d) The inert carrier gas was argon and the flow rate was 1100ml/min.

Reagents

- a) A reductant of sodium borohydride was used to liberate hydrogen on contact with acids as shown by the simplified equation below:-



The reductant of 30% sodium borohydride in 1% sodium hydroxide was placed in the reservoir ready for use. A fresh solution was made every 5 days and filtered before use.

- b) A diluent of 1.5% w/v hydrochloric acid was used for the standard and sample determinations.

Procedure

1ml of sample or micro-litre quantity of standard and 10ml of diluent were placed in the reaction flask and attached to the analyser assembly. A plunger was immediately depressed and the reductant from the reservoir entered the flask and hydrogen and mercury were liberated. Since mercury is very volatile, even at ambient temperatures, metallic mercury was driven out of the sample solution and transported by the hydrogen and carrier gas to the quartz cell where its absorption was measured. The cell was not heated. The depressed plunger was released as soon as the maximum peak height had been recorded.

Standards of 25, 50 and 100ng were used and it was found that for each run several preliminary standards had to be run in order to condition the system. During sequences of analyses standards were added between every 8 samples.

4.4. Mercury vapour detector

Mercury in tissues and feathers was separated from the sample matrix by acid digestion as previously described. Following reduction by stannous chloride, samples and standards were then analysed by cold-vapour atomic absorption spectroscopy using a Mercury Vapour Detector (manufactured by Data Acquisition Ltd., Runcorn, Cheshire.).

Reagents

- a) 2% potassium permanganate:- 10g was dissolved in 500ml of double

distilled water (using a magnetic stirrer, overnight) and stored in a dark bottle.

- b) 50% sulphuric acid:- 250ml of concentrated sulphuric acid (Aristar or Puranal grades) were carefully added to 250ml of double distilled water.
- c) Reducing agent:- 20% stannous chloride, 50% hydrochloric acid. 100g of stannous chloride (Spectrosol) was added to 50% hydrochloric acid and aerated overnight to ensure dissolution and to remove mercury contamination.
- d) Mixed reagent:- Acid Permanganate. Equal volumes of 50% sulphuric acid and 2% potassium permanganate were mixed and allowed to cool before use. The reagent was prepared daily.
- e) Drying tube containing a 1.5cm layer of magnesium perchlorate.

Procedure

Sufficient reagents and standards were prepared daily. The standards were prepared by adding micro-litre quantities of the working standard to 20ml of mixed reagent in a dreschel bottle. The standard was then diluted to 50ml and carried through the procedure described below. A calibration was made at the beginning and end of a run and between every 8 samples using appropriate blanks and standards.

The mercury analyser (DA-1500(DP6)) was switched on two hours before use to allow time for the photocells to reach thermal equilibrium. The analyser's operation is based on the absorption of ultra-violet light by mercury vapour. The system comprises a sample cell, photo detectors, an ultra-violet light source, a solid state amplification and linearisation circuit and a liquid crystal digital readout.

The continuous air flow of 3 litres minute⁻¹ was controlled by an

internal air pump. Zero was set by connecting a tube between sample "IN" and a built-in activated charcoal filter "OUT", and adjusting the zero by means of a potentiometer on the centre of the front panel. The locking screw was applied on the zero potentiometer, the tube removed and the sample tube connected to sample "IN".

For the sample analyses 20ml of mixed reagent was added to the dreschel bottle, 1ml of sample added to the reagent and diluted to 50ml with double distilled water while the dreschel bottle was disconnected from the air supply. 10ml of reducing agent was added to the sample and the dreschel head quickly replaced. The solution was shaken until colourless. The addition of the reducing reagent released the mercury into a volatile elemental form. The mercury vapour was then passed over the drying agent into the sample cell, where the mercury vapour was measured by absorbance of ultra-violet light, and the mercury peak was registered on a digital readout. The dreschel head and bottle were rinsed with water and a blank of double distilled water run to purge the sample cell.

Results were calculated after correction of the standard and sample peak heights for the reagent blank, by plotting ng of mercury in the standards against peak height of the standard to give a calibration line, from which the quantity present in the sample could be determined.

4.5

NEUTRON ACTIVATION ANALYSIS

Neutron Activation Analysis is well established as one of the most sensitive analytical techniques available for determining low concentrations of many elements (Guinn & Hoste, 1980; Nadkarni & Morrison, 1973). The analysis generally involves sample irradiation and subsequent measurement of the gamma spectrum of either the whole sample (instrumental neutron activation analysis, INAA) or a

chemically separated fraction of the sample (radiochemical neutron activation analysis RNAA). The basic theory is that if w grams of an element are irradiated in a flux of a neutrons $\text{cm}^{-2}.\text{sec}^{-1}$ for a time t , the absolute rate of disintegration of the radioactive product I is given by: -

$$I = \frac{(w \times 6 \times 10^{23})}{A} ab(1-e^{-ct})$$

where b is the probability of a neutron transforming an atom of the stable element to a radioactive isotope, c is the disintegration constant of the isotope and A is the atomic weight of the element.

If the above equation was solved for a single sample the result would be inaccurate, since some of the parameters are difficult to determine precisely. This problem can be overcome by comparing the activity of the sample with that from a known weight of the desired element, subjected to the same irradiation and counting techniques. Since many isotopes are produced when real samples are irradiated, the activities of the desired elements have to be separated from the overall activity of the sample. This may be achieved by radiochemical separation or by the non-destructive technique of gamma-ray spectrometric analysis.

The latter technique was usually used and is based on an examination of gamma-rays emitted by an irradiated sample. Recent advances in solid-state counters (and in particular lithium drifted germanium (GeLi) detectors) have provided detectors with much better resolution (0.1%), allowing the resolution of more elements in a single spectrum. A further advantage of GeLi detectors is the ratio of the height of the photopeak to that of the Compton background. The larger the value of this ratio, the smaller the error in detecting a peak above the background. The gamma peaks of interest in activation analysis mostly fall into the range of 0.3-5meV and a typical GeLi

spectrum of an activated sample has up to 400 peaks in this range. The analysis is complex so results are usually transferred to floppy disk using a Digital Computer's mini computer.

In order to obtain a low background level of radiation the detector is surrounded by a lead shield. The lead, however, emits fluorescent X-rays of energies 75 and 85 keV which are absorbed by two layers (each 0.2mm thick) of cadmium and copper.

4.5.1 Determination of selenium and zinc in fish and seabird tissues

For all instrumental neutron activation analysis, tissue samples were freeze-dried (using an Edwards freeze-drier). Once dried 0.1g samples of tissue (liver, kidney or muscle) were placed in acid-washed polythene vials, which were then sealed. In each run, duplicates and samples of the standard reference material (bovine liver NBS 1577) were included.

Standards of 0.1g of selenium and zinc absorbed onto cellulose, a blank vial and a vial of cellulose were also analysed in every run. Each sample was labelled, and weighed flux monitors of iron wire attached. The monitors account for variation in the flux of the reactor. Each sample and standard should receive the same irradiation flux; however, variations may arise resulting from the geometry of the sample's position in the reactor, and it may not receive the same neutron flux as the standard. The monitors have a radioactive half-life of 45 days, and subsequent measurement of this radiation allows the calibration of the radiation flux to the position of the samples and standards in the reactor core.

Samples and standards were wrapped in aluminum foil and irradiated for 18 hours at a thermal neutron flux of $3.6 \times 10^{12} \text{ Nm}^{-2}\text{s}^{-1}$. After irradiation the samples were left for one month to allow short-lived

isotopes to decay, after which the isotopes 120day ^{75}Se and 244day ^{65}Zn were measured on an 80cc GeLi detector. Counting of disintegrations took a minimum of six hours per sample. The Ortec computer system for data storage and handling was then used to calculate the results.

In a few cases sample irradiation had to be repeated, when vials melted in the heat of the reactor core and became unidentifiable.

4.5.2 Determination of Copper by Instrumental Neutron Activation Analysis

The determination of copper in Great Skua tissues (pectoral muscle, liver and kidney) was routinely performed by atomic absorption spectrophotometry. It was thought worthwhile, however, to discover if the method of instrumental neutron activation analysis (INAA) could be applied to measure copper concentrations in the tissues.

Eight samples of 0.1g muscle tissue were placed into polythene vials. In turn each vial and a copper standard were vacuum injected into the core for five minutes, then allowed to decay for 5 minutes and counted for 5 minutes on the 80cc GeLi detector. The ^{66}Cu isotope at 1039 keV gave high percentage errors (20%) due to interferences from other ions active in the same region as copper and the results were highly inaccurate, so only atomic absorption spectrophotometry was used to determine copper levels in tissues.

4.5.3 Determination of mercury by INAA in tissues and feathers

In analysing for mercury by standard techniques other than INAA, serious problems exist as mercury is a common contaminant of many reagents and is extremely volatile. As much as 50% of mercury present may be lost during a prolonged digestion. Neutron activation analysis avoids the problems of sample decomposition and the use of the GeLi detectors should allow mercury to be determined in many matrices.

Apparatus

The East Kilbride Scottish Universities Research and Reactor Centre 300kw water-moderated research reactor was used for all irradiations. A thermal neutron flux of $3.6 \times 10^{12} \text{ Nm}^{-2} \text{ s}^{-1}$ was used. A LEPD thin GeLi detector was used to measure 64 hr ^{197}Hg and for the measurement of the ^{203}Hg peak the 80cc GeLi detector was used.

Procedure

Samples of 0.1g were weighed into quartz tubes (acid-washed) which were sealed to prevent volatilization of mercury. Standards of 1ug Hg and 1ug Se, samples and blanks were placed with flux monitors in the reactor core for 6 hours. Selenium standards were necessary because the selenium isotope at 279keV masks the mercury isotope present at the same energy level and a correction had to be made for this.

After irradiation all vials were checked for completeness and the outside of the tubes cleaned. The samples were first measured after about 60 hours of decay on the thin LEPD GeLi detector for 64 hour ^{197}Hg , which permits relatively short irradiation times to be used and gives high sensitivity. A disadvantage of using ^{197}Hg was the low energy of the emitted gamma radiation, which is difficult to measure in the presence of the more energetic gamma rays of other radioisotopes.

The mercury isotope ^{203}Hg was less suitable because of the loss of sensitivity and longer irradiation times required. The long half-life of this mercury isotope ($T=46.9$ days) had the advantage of allowing a non-destructive determination of mercury after a suitable cooling period to allow the matrix activity to decay.

After three weeks each sample was counted on the 80cc GeLi detector for two hours under constant geometry conditions. Gamma ray spectra were recorded for processing the results. After subtraction of

a computed baseline, peak areas were calculated by Gaussian fitting for the 279keV ^{203}Hg , ^{75}Se and 265keV ^{75}Se peaks. The selenium correction was calculated by measuring the 279keV/265keV ^{75}Se peak area ratio (correction factor) for a pure ^{75}Se standard under geometry conditions identical to those of the samples. The 265keV ^{75}Se peak area for each sample was multiplied by the correction factor and subtracted from the total 279keV peak area to give the 279keV ^{203}Hg peak area. ^{203}Hg activities were corrected for decay to the end of irradiation and the content of mercury in the samples calculated as follows:-

$$\text{Hg ppm} = \frac{^{203}\text{Hg activity of sample}}{^{203}\text{Hg activity of standard}} \times \frac{\text{sample weight}}{\text{standard weight}}$$

This method was used for feathers and liver tissue but time precluded its frequent use and most mercury analyses were performed by cold-vapour atomic absorption spectrophotometry or by a mercury hydride system.

4.6 ATOMIC ABSORPTION SPECTROPHOTOMETRY

Flame atomic absorption spectrophotometry was used to determine the metals copper, zinc and cadmium in tissues of seabirds and fish. Both wet and freeze-dried tissue weights were taken and the wet weight/dry weight ratio determined for each sample.

4.6.1 Analysis of Seabirds and Fish

For the digestions, where possible, 0.5g of freeze-dried tissue or 5g wet weight tissue. Initially, two digestion methods were performed in order to determine a suitable routine analysis.

The first method involved wet-digesting the tissue in a 4:1 v/v mixture of Aristar-grade concentrated nitric and perchloric acids using micro-Kjeldahl flasks. Weighed samples were left to predigest at 40°C overnight and subsequently boiled gently at 120°C for two hours

until approximately 1ml of solution remained. The digests were then cooled and made up to a volume of 25ml with double-distilled water. The samples were then analysed for zinc, copper and cadmium.

In the second method, tissues, freeze-dried or wet, were weighed into 75ml beakers and 20ml of concentrated nitric acid (Aristar grade) was added. The beakers were then covered with watch-glasses and allowed to stand at room temperature for 1-2 hours. The samples were gradually heated to 80°C and then left to stand overnight at room temperature. This slow digestion prevents vigorous frothing. The following morning the samples were heated to approximately 200°C for a fast digest, and the concentrated nitric acid was boiled off until only 5ml were left.

The samples were then filtered into 25ml volumetric flasks and made up to 25ml with double-distilled water. The samples were subsequently transferred to acid-washed Sterilin universal containers for ease of handling and storage.

For both methods, all glassware was soaked in Decon 90 solution water overnight, rinsed with tap and deionized water, and placed in an acid bath (50% nitric acid) for at least one hour. Glassware was then rinsed in deionized water and dried in drying cabinets. Double-distilled and millipore-filtered water were used for methods 1 and 2 respectively.

Since it was found, using standard reference materials (Table 4.1) that the second method, using nitric acid alone, was a suitable digestion technique, and without adequate specialized fume cupboard facilities for perchloric acid digestions, this second method was subsequently used throughout the analyses.

4.6.2 Standard reference materials

For the initial digestions, in order to determine the recovery values for the two techniques, and in every batch of subsequent

Table 4.1

Comparison of the methods of digestion using only nitric acid or perchloric and nitric acids

Results in ug g⁻¹ dry weight

<u>Sample</u>	<u>nitric acid</u>			<u>perchloric acid</u>			<u>publ. results</u>		
	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
oyster tissue	68	826	3.1	64	852	3.5	63	852	3.5
" "	64	850	3.2	60	843	3.2	+3.5	+14	+0.4
" "	69	843	2.7	59	847	3.1			
bovine liver	203	141	-	193	134	-	193	130	.27
" "	192	133	-	187	143	-	+10	+13	+1.1
" "	200	151	-	179	159	-			
Albacore tuna	5	14	-	6	18	-		13.6	
" "	6	13	-	8	15	-		+1.0	

digestions, standard reference materials were included as checks on the methodology. Ideally these should be as close as possible in matrix characteristics to the sample tissue. The following standard reference materials (all from the National Bureau of Standards, Washington DC, USA) were included in the test digestions:

Oyster Tissue St. Ref. Material 1566 NBS

Bovine Liver St. Ref. Material 1577 NBS and 1577a

Albacore Tuna Research Material 50 NBS

Bovine liver was used as the standard in subsequent digestions.

4.6.3 Blanks

Within every batch of digestions two blanks were included, in order to eliminate any contamination from chemicals used, or possible contamination during the digestions. All chemicals used were of Aristar grade (BDH Chemicals). At least 3 duplicates of tissue samples were included in every batch as a further check on methodology.

4.6.4 Working standards

10ppm working standards were made up from a 1000ppm stock solution of the metal nitrate (BDH Chemicals). Nitrate standards were used to match as closely as possible the form of the metal ions in the digests. Appropriate dilutions were made from the 10ppm standard for calibration.

4.6.5 Instrumentation

The digests were analysed for zinc and copper on a Perkin-Elmer 303 double-beam atomic absorption spectrophotometer, and for cadmium using an Instrumentation Laboratory Inc. single-beam instrument. For each metal analysis the specified hollow-cathode lamp, current and wavelength were selected (Cu=324.8nm, Zn=213.8nm and Cd=229nm). Air

and acetylene flows were adjusted, and slit-width and other settings were set as recommended for the instrument employed. The hollow-cathode lamps were allowed adequate time to stabilize before use. For cadmium and zinc analyses background correction, using a deuterium lamp, was measured automatically to allow for non-atomic absorption.

Once the lamps had stabilized the standards were aspirated into the flame first, and a calibration line prepared from the standard range after setting the top standard to a suitable scale deflection. For zinc, standards of in ranges 1-4ppm and 4-10ppm were used, in the latter case using appropriate burner-head adjustments to reduce the sensitivity and realign the calibration curve. For copper, standards of 0.5-2ppm were used for sample solutions and 1-4ppm for standard reference material(NBS 1577 and 1577a). Standards of 0.5-2ppm and 0.1-0.5ppm were required for cadmium analysis, depending on the type of tissue.

The sample solutions were aspirated under the same conditions as the standards, and these were checked every 8 samples as the output of hollow-cathode lamps tends to drift, producing a gradual shift of the zero standard reading. Frequent checking on the instrument controls was the most effective way of counteracting this problem, mainly encountered with zinc. Blank determinations were carried out and subtracted where necessary. All results were calculated from the relevant calibration graph as follows:-

$$\text{Concentration (ug g}^{-1}\text{)} = \frac{\text{Conc. from graph (ppm)} \times \text{soln vol (ml)}}{\text{Sample weight}}$$

CHAPTER 5

ORGANOCHLORINES IN GREAT SKUAS Catharacta skua OF KNOWN AGE

5.1 INTRODUCTION

There is an extensive body of information on contaminant levels in seabirds but much of it is randomly collected and of small sample size, making any statistical assessment of the data difficult. Great Skuas collected from Foula are of known age and form a sufficiently large sample for examining the concentrations of organochlorines (DDE and PCB's) in a top marine predator. Measurements of this type ensure that any increase in concentrations with age or over time can be identified.

The levels of organochlorines found in the liver, muscle and adipose tissue of the Great Skua showed considerable variation and were highly skewed, with few skuas containing very high concentrations. To accomodate this skewness non-parametric tests were used on the data (Mann-Whitney U-test and Spearman's rank correlation) or, alternatively, the data were log transformed to produce a normal distribution.

In all of the skuas the most frequently found organochlorines were DDE (a metabolite of DDT) and polychlorinated biphenyls. Traces of dieldrin were found in the muscle tissue but at levels thought to be well below those concentrations causing harmful effects and further analyses for this compound were not made. PCB's were present in all tissues in greater quantities than DDE.

5.2 RESULTS

5.2.1 Relationships between DDE levels and tissue lipid content

No significant relationships were found between the lipid concentration of DDE and the percentage lipid in the tissue (Table 5.1; Appendix 2, Tables 23-25).

Table 5.1 Values of Spearman's Rank Correlation(r_s) and Product Moment Correlation for DDE lipid concentration and % lipid.

	n	r_s	r	p
Muscle	20	0.206	0.390	n.s.
Liver	17	-0.124	0.037	n.s.
Fat	18	0.064	0.162	n.s.

5.2.2 Relationships between PCB concentrations and percentage lipid in the tissue

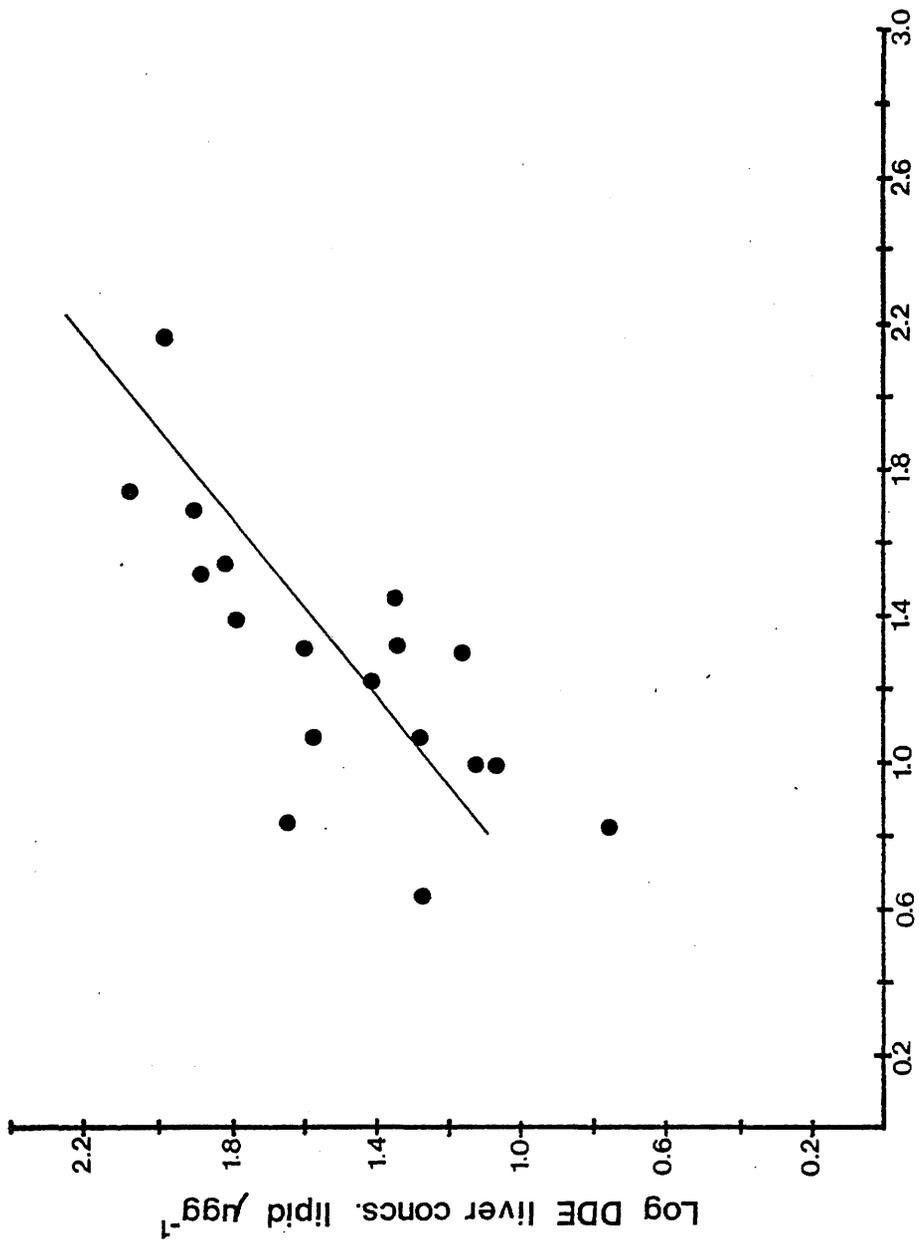
As for DDE, no relationship was found between the percentage lipid content of the muscle, liver and fat tissue and PCB concentrations (Table 5.2; Appendix 2, Tables 23-25).

Table 5.2 Values of Spearman's Rank Correlation r_s and Product Moment Correlation, for PCB lipid concentration and %lipid

	n	r_s	r	p
Muscle	20	0.362	0.440	n.s.
Liver	17	0.005	0.257	n.s.
Fat	18	0.014	-0.104	n.s.

5.2.3 Relationships between DDE concentrations in muscle, liver and fat tissue of individual Great Skuas

DDE concentrations in whole tissues were positively correlated for muscle and liver, but neither were correlated with the fat tissue concentrations (Table 5.3, Figs 5.1-2). For the lipid DDE values a similar relationship was found, with concentrations in the muscle and liver being positively correlated but not correlated with the fat DDE concentrations. The concentrations of both DDE and PCB's were highly variable in all the tissues (Table 5.4, Appendix 2, Tables 23-25).



Log DDE muscle concs. lipid μgg^{-1}

Fig 5.2; Relation between tissue concentrations of DDE ($\mu\text{g g}^{-1}$, log values, wet weight) in muscle and liver tissue of the Great Skua ($n=17$, $r=0.702$, $y=0.75x + 0.27$).

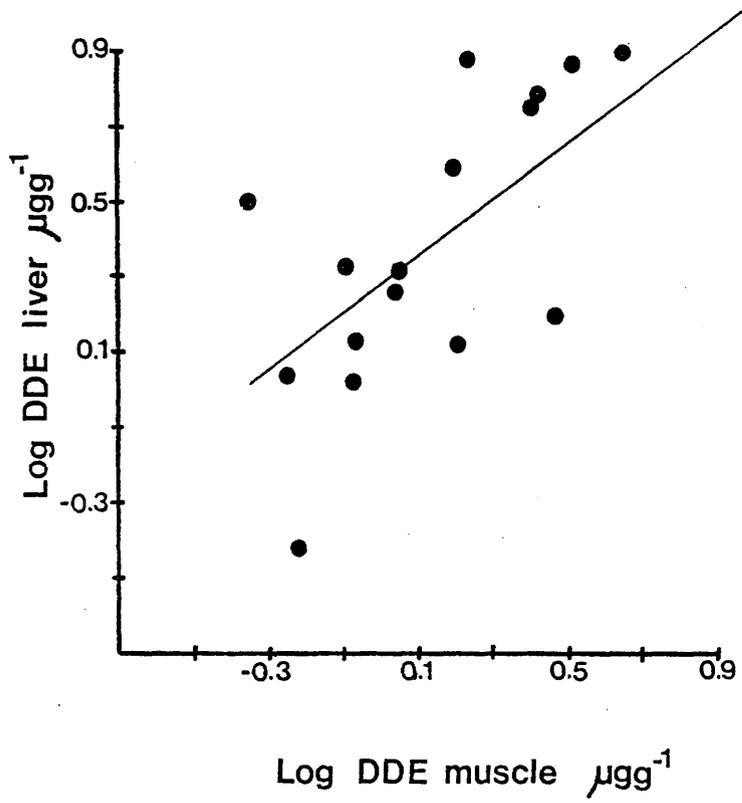


Table 5.3 Correlations (Product-moment (r), Spearman's Rank (r_s) and log-log transformation) between DDE levels in muscle, liver and fat tissues of individual Skuas (tissue and lipid values with 'p' values).

	r	p	r_s	p	log r	p
Mus v Liv	0.650	0.01	0.686	0.01	0.702	0.01
Mus v Fat	0.371	n.s.	0.385	n.s.	0.381	n.s.
Fat v Liv	-0.043	n.s.	0.027	n.s.	0.164	n.s.
<u>Lipid</u>						
Mus v Liv	0.713	0.01	0.807	0.001	0.754	0.001
Mus v Fat	0.337	n.s.	0.420	n.s.	0.377	n.s.
Fat v Liv	-0.104	n.s.	-0.107	n.s.	-0.138	n.s.

Table 5.4 Geometric Means and Ranges of concentrations of PCB's and DDE in liver, muscle and fat tissues of the Great Skua

Tissue	DDE		PCB	
	tissue $\mu\text{g g}^{-1}$	lipid $\mu\text{g g}^{-1}$	tissue $\mu\text{g g}^{-1}$	lipid $\mu\text{g g}^{-1}$
Muscle GM	1.54	21.2	14.2	135.6
Range	0.45-10.3	7-145	1.8-72	6.7-738
Liver GM	2.61	20.7	14.1	126.0
Range	0.38-7.8	3.6-75	1.7-99	16-668
Fat GM	29.1	45.2	205.8	318
Range	6.3-84	10-157	64-581	81-1113

5.2.4 Relationships between PCB concentrations in muscle, liver and fat tissues of the Great Skua

The relationships between PCB concentrations in the tissues for both lipid and whole tissue results were more obvious (and highly significant) than the results for DDE, especially for the correlation

between muscle and fat (Table 5.5, Figs 5.3-8).

Table 5.5 Correlations (Product-moment (r), Spearman's Rank (r_s) and log-log transformation ($\log r$) between PCB concentrations in muscle, liver and fat tissues of individual Great Skuas

Tissue	r	p	r_s	p	$\log r$	p
Mus v Liv	0.709	0.01	0.630	0.05	0.674	0.01
Mus v Fat	0.738	0.001	0.815	0.001	0.798	0.001
Fat v Liv	0.585	0.05	0.788	0.001	0.631	0.01
Lipid						
Mus v Liv	0.827	0.001	0.645	0.01	0.643	0.01
Mus v Fat	0.622	0.01	0.639	0.01	0.654	0.01
Fat v Liv	0.514	0.05	0.500	0.05	0.307	n.s.

5.2.5 Relationships between PCB and DDE within the same tissues, muscle, liver and fat

The relationships between PCB and DDE concentrations in each of the tissues, for both the whole tissue and lipid values, were highly significant (Table 5.6, Figs 5.9-11). The most pronounced correlations were found in the muscle and the weakest in the fatty tissue.

Table 5.6 Relationships between DDE and PCB in muscle, liver and fat tissues of the Great Skua (Spearman's Rank correlations (r_s) and log-log transformations)

Tissue	DDE v PCB tissue $\mu\text{g g}^{-1}$			DDE v PCB lipid $\mu\text{g g}^{-1}$	
Muscle	r_s	0.854	$p < 0.001$	0.907	$p < 0.001$
	$\log r$	0.829	$p < 0.001$	0.794	$p < 0.001$
Liver	r_s	0.537	$p < 0.05$	0.556	$p < 0.05$
	$\log r$	0.744	$p < 0.001$	0.702	$p < 0.01$
Fat	r_s	0.578	$p < 0.05$	0.616	$p < 0.01$
	$\log r$	0.516	$p < 0.05$	0.572	$p < 0.05$

Fig 5.3; Relation between tissue concentrations of PCB ($\mu\text{g g}^{-1}$, log values, wet weight) in fat and muscle tissue of the Great Skua ($n=18$, $r=0.798$, $y=0.56x + 1.68$).

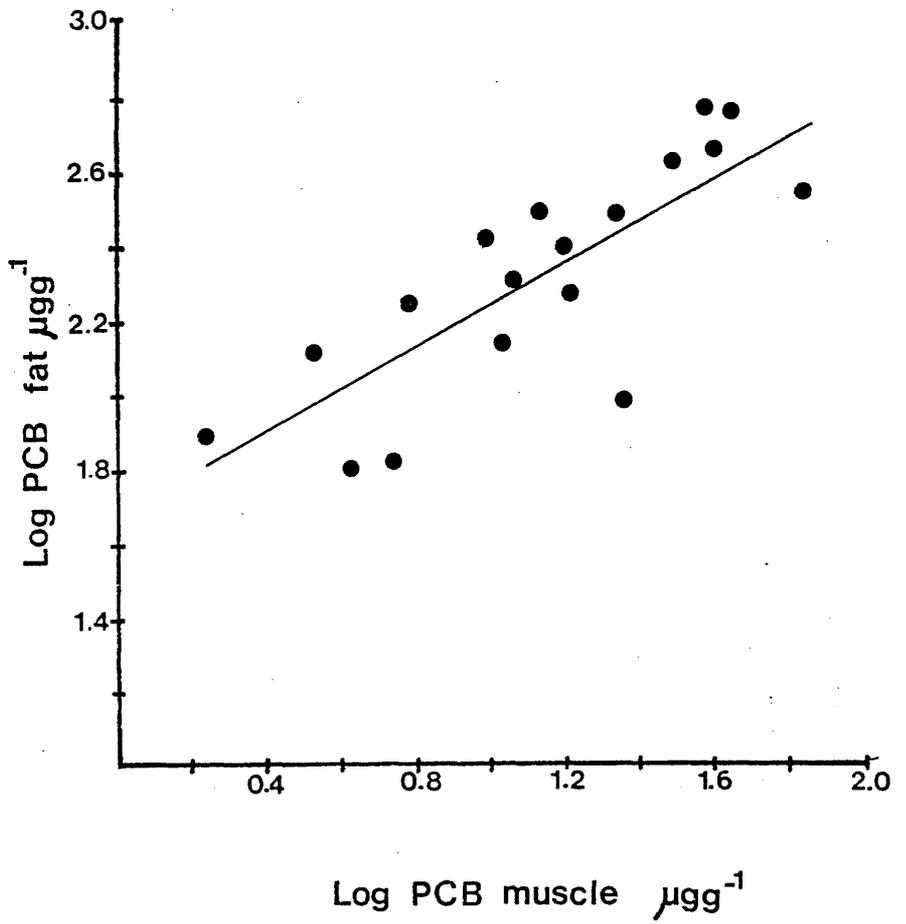
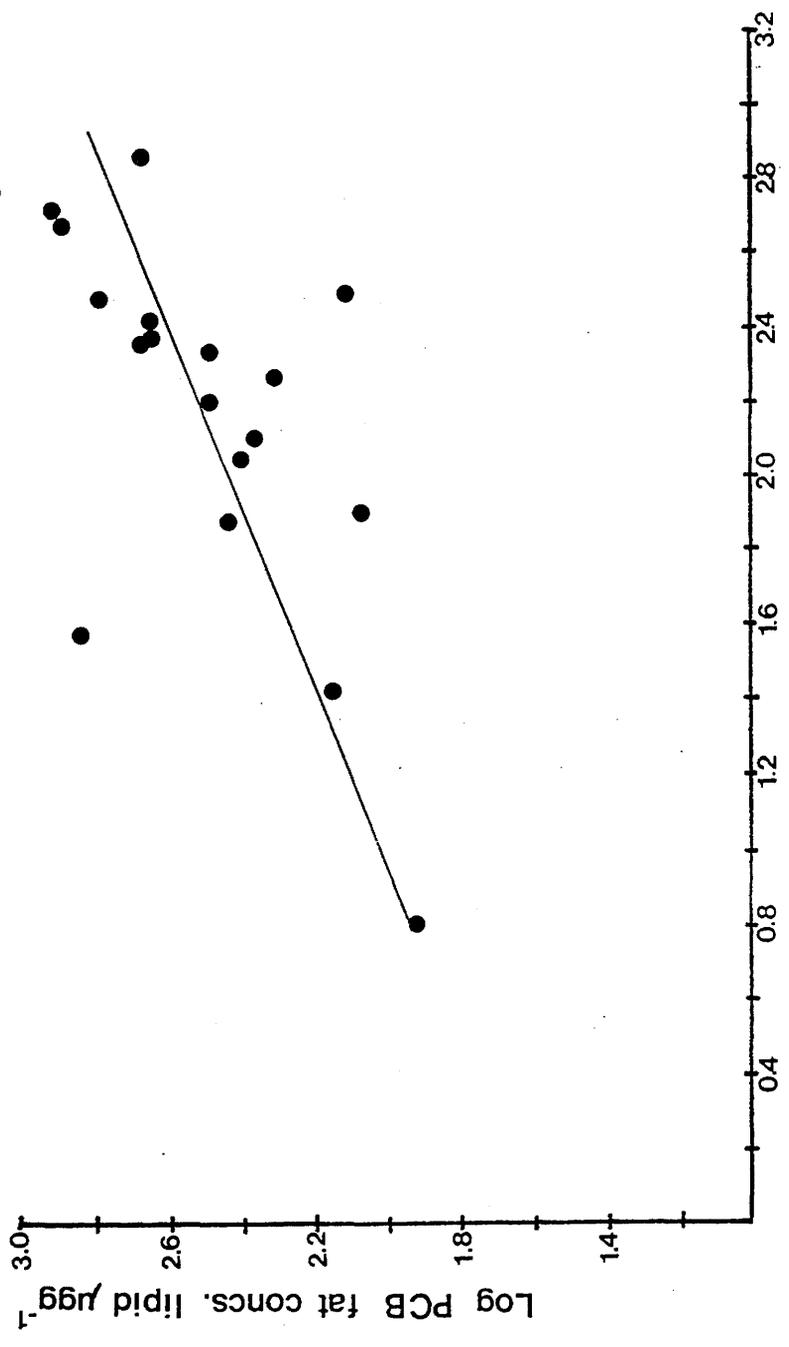


Fig 5.4; Relation between lipid concentrations of PCB ($\mu\text{g g}^{-1}$, log values, wet weight) in fat and muscle tissue of the Great Skua ($n=19$, $r=0.655$, $y=0.40x + 1.61$).



Log PCB muscle concs. lipid μgg^{-1}

Fig 5.5; Relation between tissue concentrations of PCB ($\mu\text{g g}^{-1}$, log values, wet weight) in fat and liver tissue of the Great Skua ($n=15$, $r=0.631$, $y=0.43x + 1.75$).

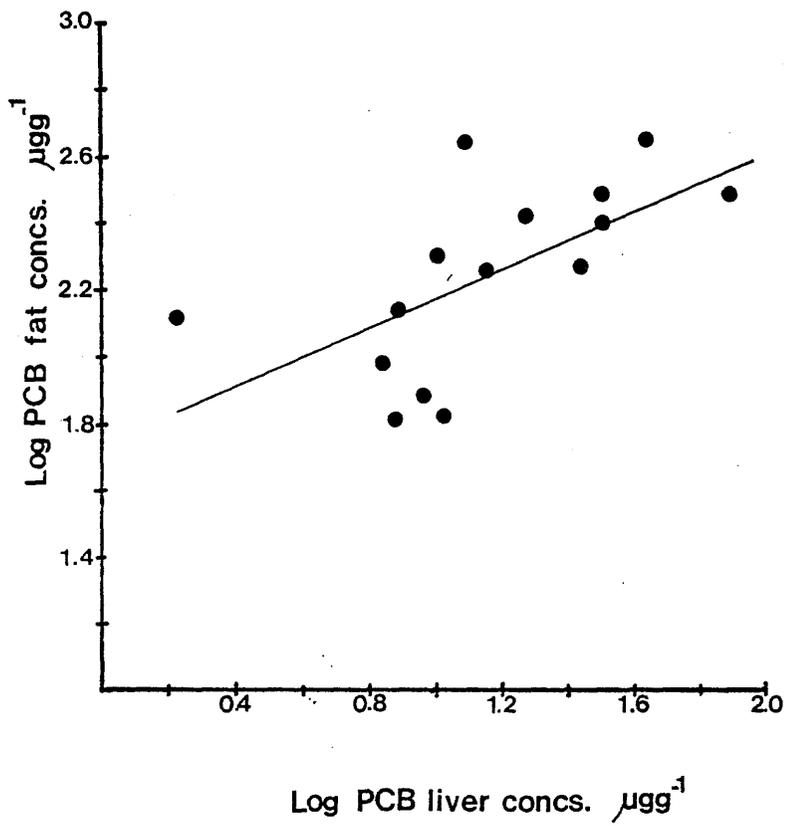


Fig 5.6; Relation between lipid concentrations of PCB ($\mu\text{g g}^{-1}$, log values, wet weight) in fat and liver tissue of the Great Skua ($n=16$, $r=0.307$, $y=0.25x + 1.93$).

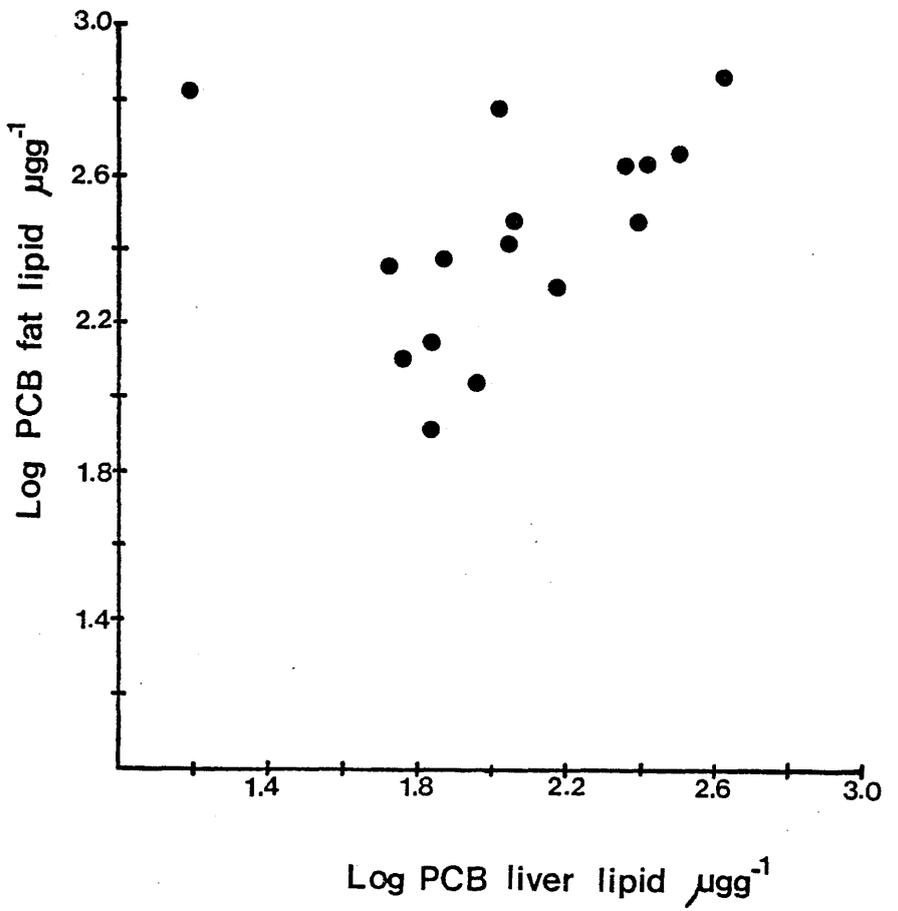


Fig 5.7; Relation between lipid concentrations of PCB ($\mu\text{g g}^{-1}$, log values, wet weight) in liver and muscle tissue of the Great Skua ($n=15$, $r=0.643$, $y=0.52x + 0.10$).

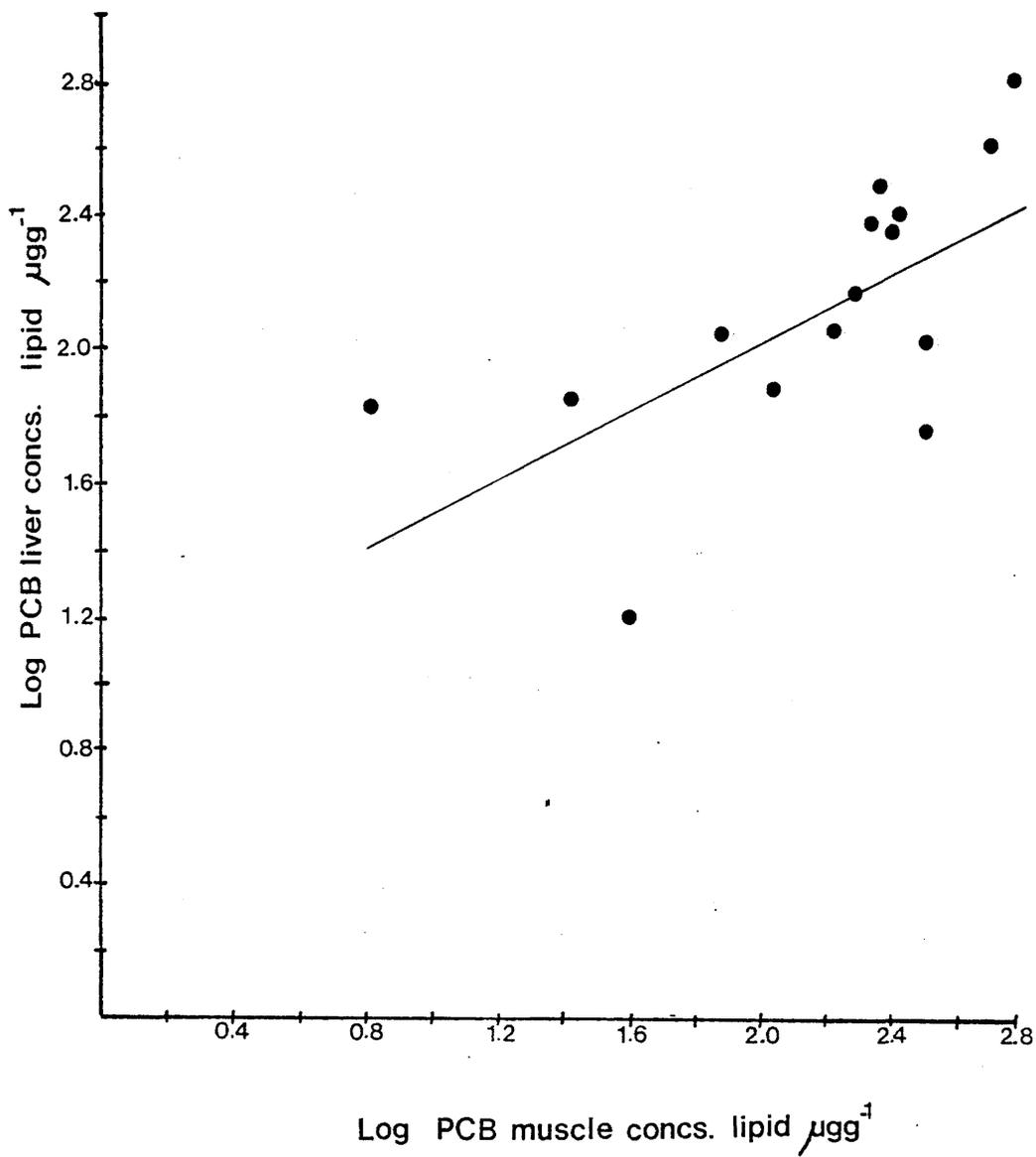


Fig 5.8; Relation between lipid concentrations ($\mu\text{g g}^{-1}$, wet weight) of PCB in muscle and liver tissue of the Great Skua ($n=17$, $r=0.827$, $y=0.89x + 0.50$).

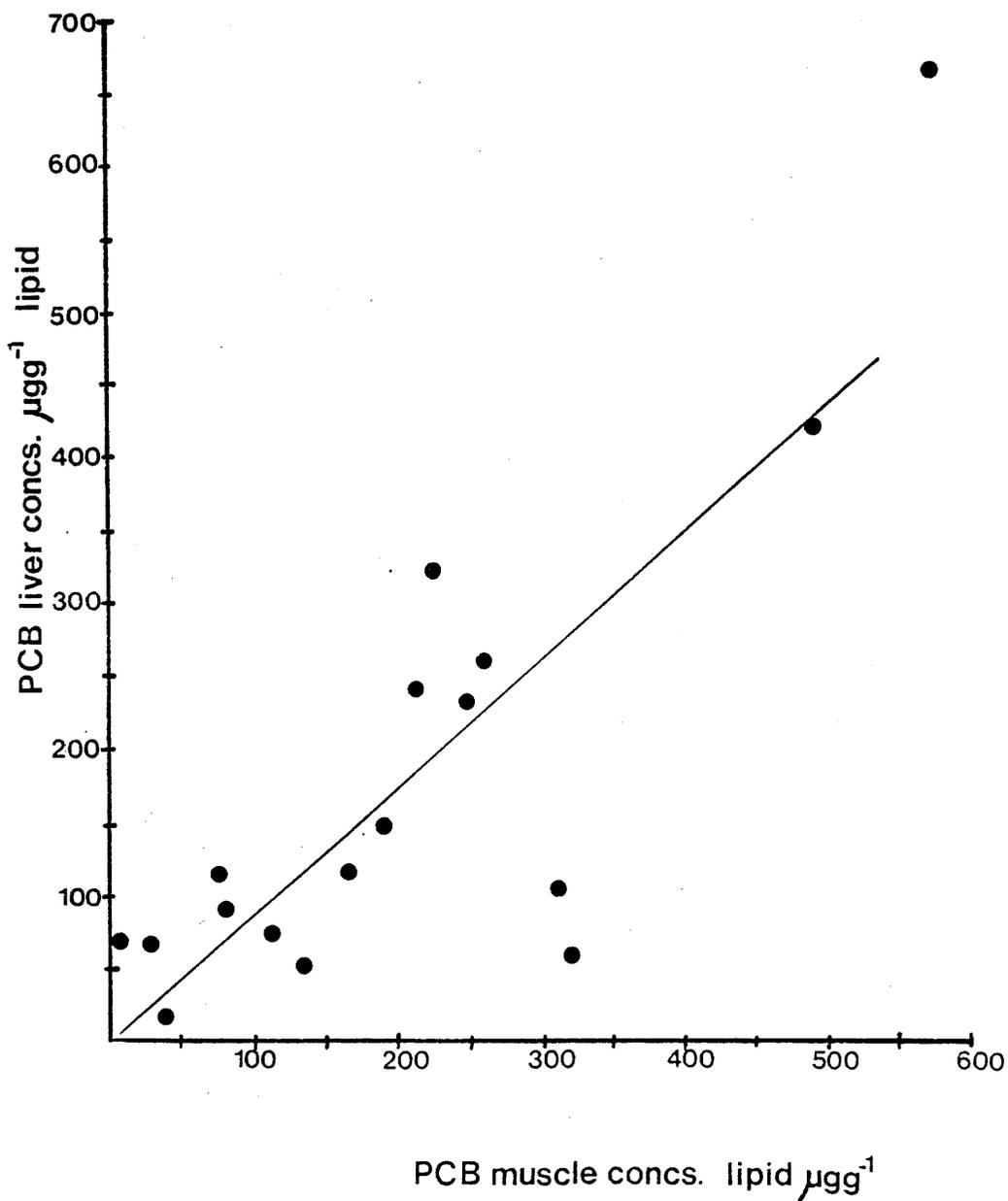


Fig 5.9; Relation between tissue concentrations ($\mu\text{g g}^{-1}$, wet weight) of PCB and DDE in fat tissue of the Great Skua ($n=17$, 0.578 , $y=3.52x + 115.79$).

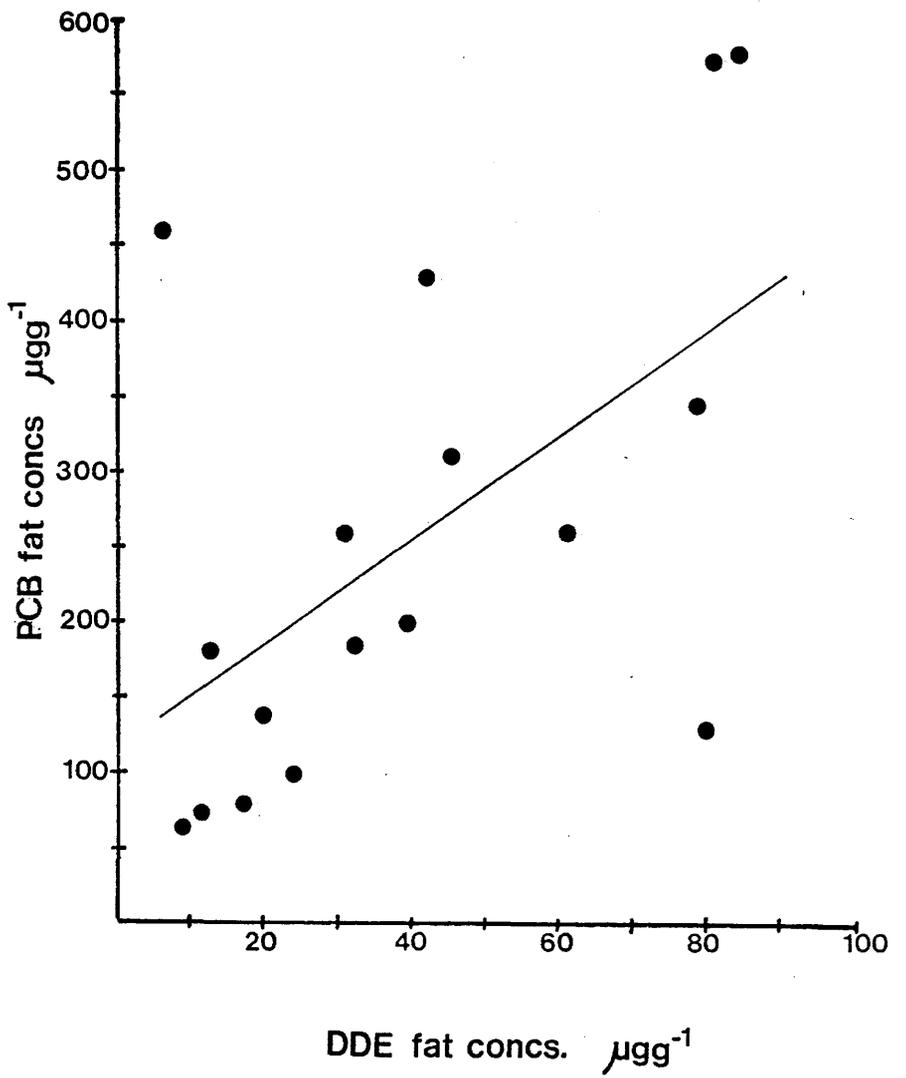


Fig 5.10; Relation between tissue concentrations ($\mu\text{g g}^{-1}$, wet weight) of DDE and PCB in muscle tissue of the Great Skua ($n=20$, $r=0.719$, $y=4.89x + 0.74$).

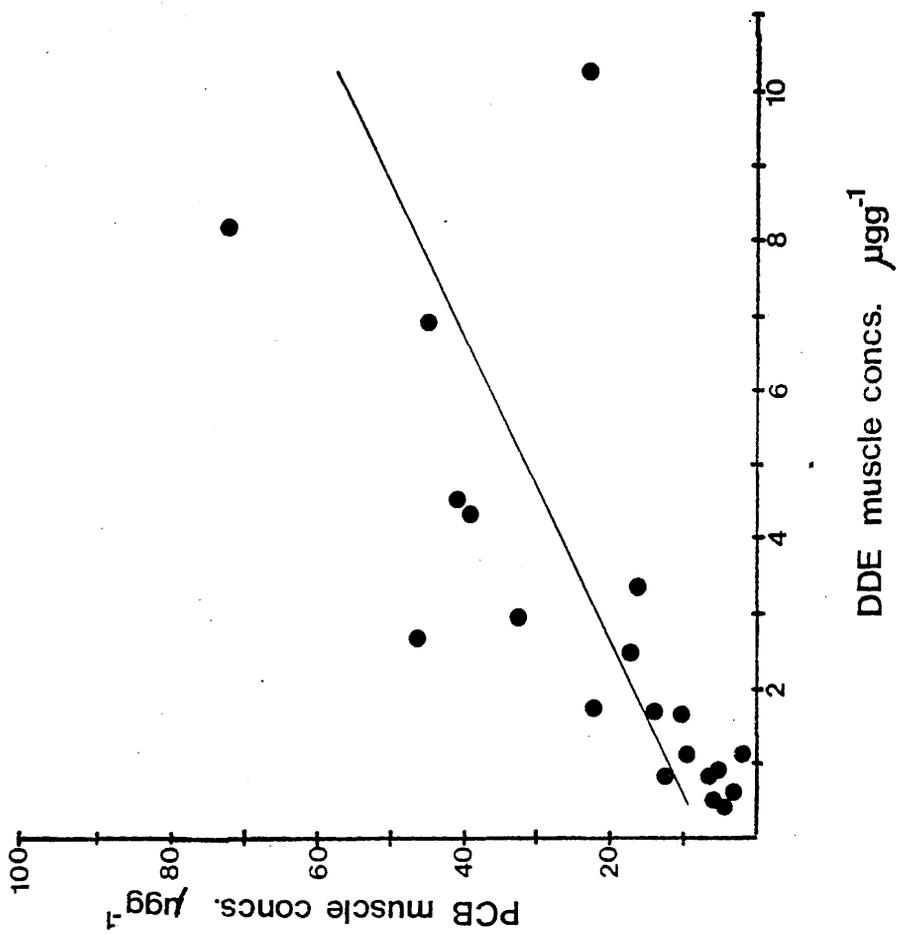
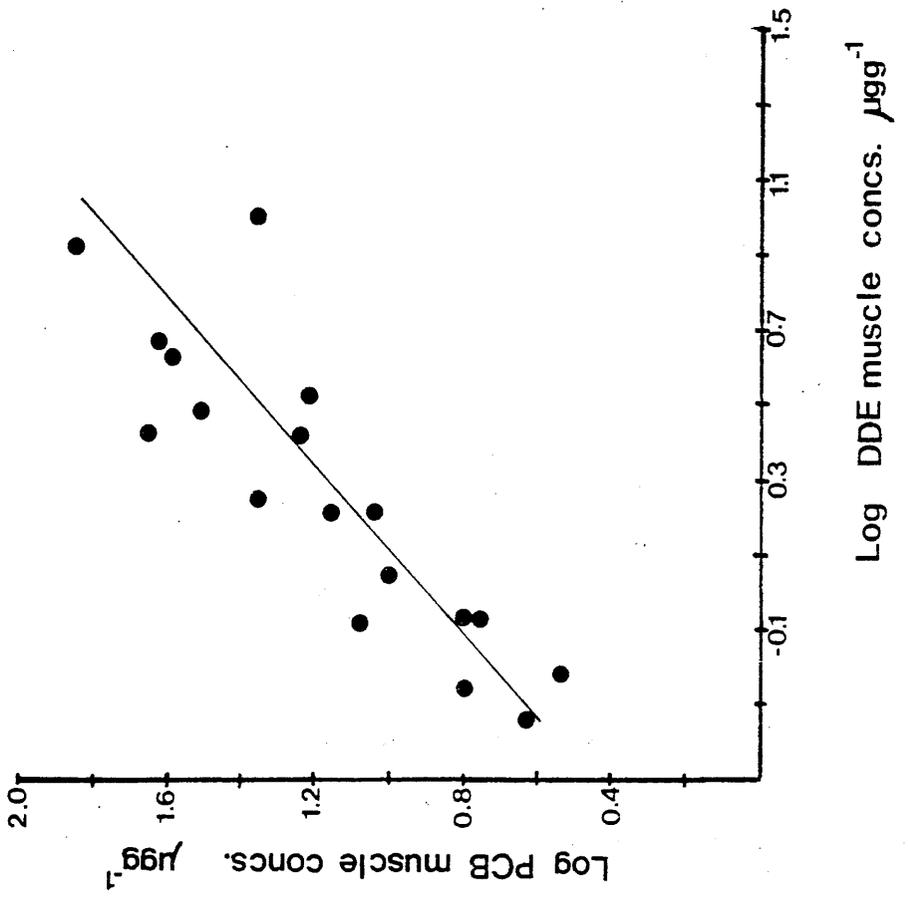


Fig 5.11; Relation between tissue concentrations of DDE and PCB
($\mu\text{g g}^{-1}$ log values, wet weight) in muscle tissue of the
Great Skua ($n=20$, $r=830$, $y=0.89x + 0.90$).



5.2.6 Influence of gender on organochlorine concentrations

In order to observe any differences in the concentrations of DDE and PCB between male and female birds a Mann-Whitney test was performed. No significant differences were found between the concentrations of the organochlorine contaminants in males and females, except for a weakly significant value for PCB in the liver ($n=11$, U-statistic =13, sig. at $U=13$ $p<0.05$). The lipid liver and fat tissue levels of PCB in the female were not significantly different to levels in the male. Overall there appears to be no clear difference between the sexes, though a bias may have been introduced through a large sample size of males relative to females.

5.2.7 Influence of age on the accumulation of organochlorines

No significant correlations were found between the PCB and DDE concentrations in the three tissues and age (Table 5.7). Only in the liver for PCB concentrations and age is there a positive trend.

Table 5.7 Correlations (Spearman's Rank (r_s) and log-log transformations (log r) between DDE and PCB concentrations and age

Tissue		PCB v Age	Tissue	DDE v Age	Lipid
Fat	r_s	0.054	n.s.	0.057	n.s.
	log r	0.034	"	0.025	"
Liver	r_s	0.401	"	0.357	"
	log r	0.453	"	0.343	"
Muscle	r_s	0.011	"	0.035	"
	log r	0.027	"	0.008	"

5.2.8 Organochlorine concentrations in eggs of the Great Skua

The samples of skua eggs analysed were small ($n=6$) though three of these samples were pooled samples of 3, 5 and 7 eggs. However, no significant relationships were found between DDE and PCB

concentrations (whole tissue $r_s=0.371$, lipid $r_s=-0.058$). The sample size was very small and any possible relationships may have been masked. Concentrations in the eggs ranged from 0.40-1.61 $\mu\text{g g}^{-1}$ wet weight tissue DDE (GM=0.35 $\mu\text{g g}^{-1}$), and 2.8-17 $\mu\text{g g}^{-1}$ wet weight tissue PCB (GM=6.13 $\mu\text{g g}^{-1}$).

5.2.9 Organochlorine concentrations in Fulmars

Four Fulmar eggs and two adults were analysed for PCB's and DDE (Table 5.8). Though only four eggs were analysed for, both tissue and lipid results, a relationship was found to exist between DDE and PCB (Table 5.9).

Table 5.8 Concentrations of PCB and DDE in tissues and eggs of the Fulmar ($\mu\text{g g}^{-1}$)

	%lipid	DDE		PCB	
		tissue $\mu\text{g g}^{-1}$	lipid	tissue $\mu\text{g g}^{-1}$	lipid
FS09107					
Muscle	6.63	0.33	4.9	2.37	36
Liver	6.04	0.23	3.6	1.02	17
Fat	32.4	2.43	7.5	15.8	49
FS09240					
Muscle	6.14	0.21	3.2	2.42	40
Eggs					
FS09107	9.92	0.89	9.0	1.81	18
FS09240	11.77	1.66	14.0	3.62	31
FS85430	11.31	0.60	5.3	1.67	15
FS74153	9.56	0.46	4.8	0.85	9

Concentrations in the tissues of the Fulmar appear to be lower than those found in the tissues and eggs of the Great Skua a result which might be expected from their respective positions in the food

chain; these results agree with the findings of Sproul et al. (1975).

Table 5.9 Values for correlations between PCB and DDE in eggs of the

<u>Fulmar</u>			
Tissue	DDE v PCB	GM PCB ug g ⁻¹	GM DDE ug g ⁻¹
	r _s =1.00 p<0.05	1.75	0.80
	r =-0.956 p<0.05		
<u>Lipid</u>			
	r _s =1.00 p<0.05	16.52	7.53
	r =-0.934 p<0.05		

5.2.10 Organochlorine concentrations in eggs of the Golden Eagle

Aquila chrysaetes

Three Golden Eagle eggs from Rhum were analysed for their organochlorine content (Table 5.10). The concentrations of both DDE and PCB are quite high in the Golden Eagle eggs, higher than the levels found in the eggs of the Great Skua and Fulmar. The HEOD concentrations may be similar to levels in the eggs of other species analysed, but only one such sample was analysed specifically for HEOD and this Great Skua egg contained 0.11ug g⁻¹ tissue wet weight HEOD.

Table 5.10 Concentrations of PCB, DDE and HEOD in eggs of the Golden

Sample	%lipid	<u>DDE</u>		<u>PCB</u>		<u>HEOD</u>	
		tissue	lipid	tissue	lipid	tissue	lipid
		ug g ⁻¹					
1	5.60	2.09	37	16.5	294	0.07	1.3
2	3.14	1.43	46	7.5	239	0.32	10.0
3	5.44	1.73	32	13.5	248	0.27	5.0

5.2.11 Ratio of PCB to DDE

The PCB:DDE ratios for all the Great Skuas were high but within the same range for each tissue (Table 5.11).

Table 5.11 PCB:DDE ratios for muscle, liver and fat tissues of the Great Skua

Tissue		PCB:DDE Ratio
Muscle	Mean	8.4
	Range	1.6-15
Liver	Mean	7.3
	Range	0.93-16
Fat	Mean	6.7
	Range	1.6-13

The PCB:DDE ratios are similar to those found by Bourne and Bogan (1972) in the Great Skua. In the analysis DDE cannot be separated satisfactorily from a PCB with a similar retention time, but in the majority of samples where the PCB/DDE ratio is low the interference by PCB's in the determination of DDE is fairly small (Bourne and Bogan, 1972). If the ratio is larger than ten then the interference is substantial (Bourne and Bogan, 1972) and in a few cases the ratios are above this value. The DDE value is calculated from the total height of the peak with a retention time equal to that of DDE (Chapter 4). Therefore where the PCB/DDE ratio is large, it is probably even greater than that recorded.

5.3

DISCUSSION

5.3.1 Tissue Distribution of Organochlorines

The concentrations of PCB in the Great Skua are highest in the

adipose tissue followed in descending order by muscle and liver. The concentrations of PCB in the fat of the Great Skua are comparable to those found in the fat of Black-headed Gulls Larus ridibundus from the Mediterranean Sea, which at its western end provides one of the wintering grounds for the Great Skua. Concentrations in the Black-headed Gull range from 40 to 536ug g⁻¹ wet wt. (GM=240ug g⁻¹) (Vannucchi et al., 1978) as compared to 64-581 ug g⁻¹ (GM=206ug g⁻¹) in the Great Skua.

The presence of PCB's in greater quantities than DDE in the tissues of the Great Skua and Fulmar is a common trait in pelagic seabirds (Bourne and Bogan, 1972; Risebrough et al., 1968; Fisher, 1973; De Kock et al., 1983; Osborn, 1982; Weber, 1983; Norheim and Hanson, 1984). The strong correlations found between DDE and PCB concentrations within tissues and eggs (Fulmar and Great Skua), and the concentrations of each organochlorine between tissues, reflect the patterns of accumulation found in previous studies on the Great Skua, other avian species and seals (Bjerk and Holt, 1971; Gilbertson, 1974; Blus et al., 1977; White and Cromartie, 1977; Newton and Bogan, 1978; Gaskin et al., 1978; Furness and Hutton, 1979; White et al., 1979; Fimreite et al., 1980; Rejinders, 1980; Paasivirta et al., 1981; Enderson et al., 1982; Helander et al., 1982; Norheim and Hanson, 1984). The correlation between DDE and PCB concentrations in the tissues and eggs of the Great Skua and Fulmar might indicate that PCB's and the organochlorine insecticide DDT have the same pattern of distribution in the ocean.

5.3.2 PCB:DDE Ratios

In the North Atlantic the pattern of DDE distribution does not always parallel that of PCB's and the ratio of PCB to DDE is not constant, varying between relatively close localities depending upon the local discharge (Sproul et al., 1975). Over the North Atlantic,

PCB:DDE ratios increase from west to east, declining again only in the Baltic. Despite a few exceptions the ratios of PCB:DDE in the tissues of the Great Skua are similar to those found by Bourne and Bogan (1972), reflecting typical ratios of the north-east Atlantic. This suggests that Great Skuas tend to remain within the eastern sector of the Atlantic, as has been shown by ringing studies (Furness, 1977). These high ratios are similar to those found in other species including gulls and ducks (Bourne and Bogan, 1972; Falandysz and Szefer, 1982), but are more typical of open ocean species than of seabirds found in areas close to industrial localities, for example the Firth of Clyde and the Irish Sea. The cause of these ratio differences between the east and west Atlantic may be due to either greater discharges of PCB's from Europe, or higher levels of DDT discharge from the United States and equal discharges of polychlorinated biphenyls.

5.3.3 Changes in organochlorine concentrations with time

The interpretation of data on organochlorine levels in the Great Skua is complicated by a time factor. The studies on concentrations in the Great Skua range from 1971 to 1983. Before and during this period various restrictions, both voluntary and statutory, have been made on the use of PCB's and DDT. From Table 5.12 it can be seen that the muscle tissue concentration in 1971 of PCB was $15.9 \mu\text{g g}^{-1}$ and in 1973 $16 \mu\text{g g}^{-1}$ in Shetland and Icelandic Skuas respectively. The results for 1980 give a geometric mean value of $14.2 \mu\text{g g}^{-1}$, indicating that a slight decrease in PCB concentrations has taken place over the decade. Concentrations of DDE have apparently decreased from $2.8 \mu\text{g g}^{-1}$ and $4.4 \mu\text{g g}^{-1}$ in Shetland and Icelandic skuas respectively, to $1.54 \mu\text{g g}^{-1}$ in Shetland birds in 1980. Similarly a decline can be seen in both the levels of PCB and DDT in eggs from 1966 to 1980, though due to the

small sample size this must be a tentative conclusion: The adult birds were sampled in a different year and the apparent decrease in PCB in the tissues and eggs may show a continuing trend of declining PCB levels in the marine environment. Concentrations of PCB's and DDE appear to have declined in the Great Skua since 1971, though it should be noted that changes in tissue levels might reflect changes in lipid reserves held by adult Great Skuas in the different years, especially as the PCB muscle concentrations are only slightly different.

Seabirds are long-lived, and due to the persistence of organochlorines, PCB's and DDE may be retained for some time in the tissues. Therefore changes in the amount of PCB discharged into the ocean through restrictions on its use may not be immediately reflected by the levels in the bird tissues (Sproul et al., 1975). PCB concentrations may also still be increasing on the European side of the Atlantic for, despite restrictions to use of PCB's in closed systems only (1972) and in some cases the banning of the manufacture of PCB's altogether (Japan 1979, USA 1979 and Germany 1983), small quantities are still manufactured in many European countries including France and Spain. If PCB's are discharged into the marine environment from these countries, and Mediterranean levels of PCB are high (Geyer et al., 1983), Great Skuas wintering along the Iberian coast may still acquire high concentrations of PCB's.

DDT concentrations in the environment may be declining more rapidly than PCB's because of the earlier ban on its use (early 1970's), and because DDT tends to be more easily degraded than PCB's, which are very persistent and stable compounds (Addison, 1976). The ratio of PCB:DDE in Great Skua eggs (range 2.05-18, mean=8.2) are higher than those found in Icelandic Great Skuas (4.6) but lower than the ratio for the 1976 sample of Great Skuas (Sproul et al., 1975; Furness and Hutton, 1979). The ratio in the Shetland Great Skua eggs

would be expected from the apparent change in the PCB:DDE ratio in moving from west to east (Sproul et al., 1975). A decline in the PCB:DDE ratio of the Shetland birds since 1976 would indicate either a decrease in PCB contamination or an increase in DDE concentrations. The PCB:DDE ratios are much lower for the Fulmar (range 1.85-2.78, mean=2.21, n=4) possibly indicating that these birds feed further out into the Atlantic than the Great Skua.

In the Shag Phalacrocorax aristotelis a significant decline in the concentrations of DDE in eggs was found between 1967 and 1971 reflecting a decline in the levels of DDT insecticide in the environment (Coulson et al., 1972). However, Sproul et al. (1975) found no decline in the concentrations of PCB's between birds collected before and after the implementation of voluntary restrictions in 1972 and 1973.

In a recent study of Norweigan seabird eggs by Barrett et al. (1985), no significant change was found in the levels of DDE and PCB in the eggs of Herring Gulls, Kittiwakes and Guillemots between 1972 and 1983. A decrease in PCB and DDE concentrations was seen in the eggs of the Gannet between 1972 and 1978, but no decline has been observed since that year (Barrett et al. 1985).

The concentrations of DDE in the eggs of the Golden Eagle appear to have declined since the 1960's (Lockie et al., 1969; Corkhill, 1980; this study), but PCB concentrations have increased. The concentrations of PCB are higher than those found in the eggs of the Great Skua and Fulmars. In coastal nesting Peregrine Falcons which feed on seabirds, higher concentrations of PCB's have been found than in inland nesting birds. As the Golden Eagles on Rhum also feed on seabirds they may accumulate high levels of PCB's through the diet. Levels in Great Skuas were lower than in the eagles, possibly because

seabirds do not form a major component of the formers' diet.

Table 5.12 Organochlorine concentrations (ppm wet weight) in Great Skua eggs, muscle and liver tissues collected from Britain and Iceland between 1969 and 1983. Geometric Mean concentrations are given with the range of levels

Tissue	Locality	n	PCB	DDE	Dieldrin
Muscle	Shetland 1971a	5	15.9	2.8	ND
			10.2-32.0	2.2-4.0	
	Iceland 1973b	10	16.0	4.4	0.12
			5.3-47.0	1.8-12.0	0.05-0.35
Foula 1980c	20	14.17	1.54	0.04	
		1.8-72.0	.45-10.3	0.03-0.07	
Liver	Shetland 1971a	6	2.89	-	-
			0.05-18.3	-	-
	Foula 1980c	17	14.13	2.61	-
			1.71-99.0	0.38-78	-
Egg	Handa 1969d	1	25.0	ND	ND
	Iceland 1973b	13	27.0	5.9	0.20
	Britain 1974	-	36.0	3.6	0.05
	Foula 1976e	12	17.6	1.7	0.08
			6.1-36.0	0.43-3.6	0.02-0.15
Foula 1983c	6	6.13	0.53	0.04	
			2.8-17.0	0.40-1.61	-

References: a, Bourne and Bogan, 1972; b, Sproul et al., 1975; c, this study; d, Prestt et al., 1970. ND=not determined.

5.3.4 Organochlorine concentrations in relation to diet

Fish-eating birds occupy the highest trophic levels in the food chain and magnification of toxic chemicals through the birds' prey makes these birds vulnerable to environmental contaminants such as

pesticides. Measurable residues of PCB's and DDE have been found in all British seabirds, the former resulting from industrial uses and the latter as a metabolite of the agricultural insecticide DDT. Both are fat soluble and highly persistent, and therefore open to accumulation through the food chain (Parslow and Jefferies, 1977).

In a study of Arctic seabirds in Spitzbergen, the highest concentrations of p,p-DDE, PCB and HCB were found in the Glaucous Gull and lowest in the Brunnich's Guillemot Uria lomvia, Little Auk and Eider. Fulmars occupied an intermediate position in the series. Although no connection was found between the nutritional condition of the bird and organochlorine concentrations, there was a close relationship between trophic level and chlorinated hydrocarbons (Norheim and Hansen, 1984). A similar correlation was found in Icelandic seabirds (Sproul et al., 1975). The concentrations of PCB and DDE in the Foula Great Skua showed no correlation with the nutritional condition of the bird as assessed by lipid reserves. The organochlorine levels were higher than those in the Fulmar, and as a top marine predator it appears to accumulate high concentrations of chlorinated hydrocarbons. The concentrations in the Great Skuas are above those found in the Glaucous Gull (Norheim and Hanson, 1984), but below those found causing convulsions in a Glaucous Gull on Bear Island in 1972 (Bourne and Bogan, 1972).

Bioaccumulation in the food chain is often greatest in the first stage; marine plankton can accumulate PCB concentrations 10,000 times higher than concentrations in seawater (Geyer et al., 1983). Fish are able to accumulate lipophilic chemicals, but the extent to which this happens is dependent on environmental parameters such as temperature and salinity (Geyer et al., 1984). The bioaccumulation factors for fish may be high; for example 10^5 - 10^6 for Archlor 1254 in fish from

Lake Superior (Veith et al., 1977). In Herring and Cod from the North Atlantic concentrations of 0.03-0.33ug g⁻¹ DDT and 0.003-0.05ug g⁻¹ wet weight DDT were found respectively (Portmann, 1975). In sandeels Ammodytes marinus a major food item of the skua, concentrations of DDE ranged from 0.001-0.009 and 0.03-0.3ug g⁻¹ for PCB (Sproul et al., 1975). The levels of DDE and PCB's may increase in the muscle and especially the liver if the fish occupies a contaminated area, for example the southern North Sea (Portmann 1975). Therefore Great Skuas feeding on discard whitefish may be subject to increased exposure to organochlorines.

The concentrations of organochlorines found in avian species and mammalian predators including the Great Skua are generally higher than the concentrations in their prey. The Great Skua's summer diet mainly comprises whitefish and sandeels which apparently contain relatively low concentrations of organochlorines, although recent data are not available. The winter diet may, however, be different and expose the Great Skuas to greater organochlorine concentrations. Great Skuas feeding on other seabirds, such as storm petrels, Puffins and Fulmars and their eggs would be subjected to much higher concentrations of organochlorines, and this may account for some of the variability found in the tissue concentrations. The type of feeding habit may also be an important factor for the accumulation of organochlorines. Larus species and pelagic seabirds are primarily surface feeders and do not dive regularly for their food. The surface microlayer of the ocean is enriched with PCB's relative to subsurface waters. In the Sargasso sea the enrichment factor has been found to range between 3 and 463, and in the Mediterranean from 23 to 43 (cited in GESAMP Rep. No.26 1985).

Surface plankton may be enriched with organochlorines and these are in turn fed upon by Leach's Petrels, Kittiwakes and Fulmars, all of which form part of the Great Skuas' diet. The Great Skua therefore

exhibits many traits favouring the accumulation of organochlorines, including its habit of feeding at the ocean surface and on seabirds, and remaining in the North Atlantic all year rather than migrating to the southern hemisphere.

In the Antarctic, though levels of chlorinated hydrocarbons are much lower than in the North Atlantic, skuas, by occupying the apex of the food chain in the Antarctic, are found to contain the highest concentrations of organochlorines of seabirds in the region. In Catharacta skua lonnbergi levels of p,p-DDE of 0.13-0.16ug g⁻¹ wet weight in liver, 0.05-0.54ug g⁻¹ in muscle and 0.01-1.42ug g⁻¹ wet weight in fat were found, and in the Southern Fulmar 0.046ug g⁻¹ p,p-DDE was found in the liver and 0.02ug g⁻¹ in the muscle tissue. This bioaccumulation effect through the food chain was also found in piscivorous species off the coast of South Africa (De Kock et al., 1984) and in the Brown Booby found breeding on the St Peter and St Paul Rocks off Brazil (Weber, 1983).

5.3.5 Toxicity of organochlorines

Seabirds of open ocean breeding stations such as Foula appear to be less contaminated with organochlorines than seabirds breeding close to industrial centres, but more highly contaminated than birds from the polar regions. PCB's comprise the major component of organochlorine contamination in seabirds with DDE levels being much lower, except in species such as gulls which have been feeding inland. The highest concentration of PCB ever found in a seabird was recorded in a Great Skua (1079ug g⁻¹ PCB wet weight) found dying in west Wales, and up to 880ug g⁻¹ was recorded in some of the auks which died in the seabird wreck of 1969. In comparison, up to 550ug g⁻¹ PCB was found in the liver of Cormorants during studies in the Netherlands and five experimental animals died with liver concentrations of 210-290ug g⁻¹

and brain concentrations of 55-124ug g⁻¹ (Koeman et al., 1973). The concentrations in the Great Skuas were much lower than in the Cormorants, but although concentrations are perhaps not acutely toxic there may be some detrimental effects on the population through chronic exposure to organochlorines (Furness and Hutton, 1980).

DDE has been implicated in shell-thinning and consequent reduced breeding success in wild bird populations at concentrations as low as 2.5ug g⁻¹ wet weight in the egg of Brown Pelicans (Blus et al., 1974). Concentrations of DDE in Great Skua eggs were lower than these concentrations, but species differ in their sensitivity to the contaminants, as exemplified by apparently normally breeding Razorbills with 60-160ug g⁻¹ wet weight DDE in the eggs. Herring Gulls also appear to be less sensitive to organochlorine pollution, and since Great Skuas are a close relative of the gull family it may be inferred that the Great Skuas are also less sensitive. No shell-thinning has been recorded in either Icelandic or Shetland Great Skuas (Sproul et al., 1975; Furness and Hutton, 1979).

PCB's have been found to affect chick mortality and hatching success (Tumasonis et al., 1973; Newton and Bogan, 1978), and have also been implicated in bird mortality incidents (Parslow et al., 1973). In experimental feeding studies PCB's have caused weight and hormonal changes and reduced immunological responses (Jefferies and Parslow, 1972; Bunyan and Stanley, 1972). All these effects might reduce the survival or breeding success of the species in the wild. Because of the high incidence of chick mortality and chick deformities in the Great Skua population on Foula, Furness and Hutton (1980) suggested that this impairment of reproductive success may be due to PCB's. However, samples taken in 1983 show reduced contamination of the egg and since the population on Foula is not in serious decline this suggests that PCB's are not adversely affecting the population. The results of Heath

et al. (1972) reinforce the conclusion that the PCB concentrations found in Foula Great Skuas are not hazardous; in their experiment, eggs produced by adults Mallards fed on a diet containing Arochlor 1254 at a level of 25ug g^{-1} for almost two years, contained between 33ug g^{-1} and 56ug g^{-1} of PCB, with no detrimental effects to reproduction. The concentration of 6.13ug g^{-1} in the Great Skua egg is well below these concentrations.

Other studies have shown diminished reproduction at much lower levels of PCB's in the diet than in the study by Heath et al. (1972). Ring Doves Streptopelia risoria fed a diet containing 10ug g^{-1} of Arochlor showed a 60% decline in the hatchability of the eggs relative to the controls (Peakall and Peakall, 1973). Comparing wild populations, the concentrations in the Great Skua eggs are below those found in Herring Gulls' eggs and tissues from a population that was breeding normally (Koeman et al., 1973). The polychlorinated biphenyls in the Great Skua resemble the Archlor mixture 1260 (E. Christie, pers. comm.) which has been found to be less toxic than the lower chlorinated biphenyls (Addison, 1976).

There is immense variability in the sensitivity of different bird species to organochlorines, which may be a result of several factors. The position of the species in the food chain and the innate behaviour of the species in relation to such physiological processes as lipid turnover may influence sensitivity. Similarly, the population dynamics of the species and variation in environmental factors such as food availability, weather and habitat conditions may be important (Keith and Gruchy, 1972).

Walker (1975) indicated that detoxification mechanisms may have evolved independently in response to the selective pressure of foreign compounds. Species may therefore differ in their biochemical response

to toxic compounds. Species with simple food chains such as the Shag and Brown Pelican are expected to have a narrow range of detoxification mechanisms, whereas species with wide and opportunistic diets like the Great Skua and Herring Gull may be expected to have a wider potential for detoxification.

In healthy birds, organochlorine concentrations in the organs such as liver are low and are highest in the subcutaneous fat deposits, as is evident in the Great Skua. At times of stress, however, the organochlorines may be mobilised and may move to other organs (Subramanmain et al., 1986), which may then be detrimentally affected (Jefferies and Parslow, 1972). Therefore, a bird dying after a period of debilitation may have higher organ concentrations of organochlorines than a bird dying suddenly. PCB'S have been implicated in contributing to the deaths of Gannets and auks in wrecks along the Irish Sea coast (Jefferies and Parslow, 1972). Some of the Great Skuas exhibiting high residues of PCB's in their fat deposits, may if subjected to stressful conditions, be adversely affected by the chlorinated hydrocarbons. In Herring Gulls, it was found that changes in lipid metabolism were closely related in chronology to changes in residue dynamics over a yearly period (Anderson and Hickey, 1976). PCB's have been shown to affect the hepatic microsomal enzyme function of the liver (Bunyan and Stanley, 1982), which is assumed to be a major site of lipid metabolism in birds, and a connection between lipid-metabolizing enzymes and halogenated hydrocarbons has been suggested (Anderson and Hickey, 1976).

A general relationship between steroid metabolism and organochlorines has been established (Bunyan and Stanley, 1982). Any changes in enzyme induction and liver function could change the retention status of the organochlorine residues (Anderson and Hickey, 1976). Seasonal changes in the diet may affect the status of the lipid

metabolism in Great Skuas from Foula. The Great Skuas were sampled in June, a relatively short time after their arrival from wintering grounds and the organochlorine concentrations may reflect their winter diet. Later in the season as the birds lose weight through the breeding period, a redistribution of organochlorines in the body may be exhibited.

Seasonal changes have been shown in Long-billed Dowitchers Limnodromus scolopaceus, Western Sandpipers Calidris mauri and American Avocets Recurvirostra americana which showed a doubling in DDT residues, a five-fold increase and a three-fold increase respectively in DDT concentrations on their arrival on the winter feeding grounds in Texas from October to December (White et al., 1983). These birds were feeding in a highly contaminated area and the more ubiquitous distribution of organochlorines in the open Atlantic may only cause minor seasonal changes in dietary concentrations.

In the Great Skua no correlation was found between organochlorine levels and age. Similar results were found for the Herring Gull (Hickey, 1975; Lemmetyinen, 1982) and Kittiwakes (Robinson et al., 1967). The only significant relationship between organochlorines and the sex of the bird was for PCB concentrations in the liver, but Sarkka et al. (1978) found DDE concentrations to be higher in male Common Gulls Larus canus and Lemmetyinen et al. (1982) found levels of DDT and PCB'S were higher in male Arctic Terns. Conversely no differences were found between the sexes for the Herring Gull (Lemmetyinen et al. 1982). The Great Skuas, as with the Herring Gulls, show almost no differences in organochlorine concentrations between male and female birds. It appears that the female Arctic Tern is able to release the pollutants into the egg and though the exact biochemical nature of this action is unknown, it may be related to

differences in the lipoprotein structures of the Arctic Tern and Herring Gull eggs (Lemmetyinen et al., 1982).

Though several studies have been carried out to investigate the effects of organochlorines on avian species, extrapolation to the wild state is difficult due to the varying sensitivities of the species and other, environmental, factors. Organochlorines are ubiquitously distributed in the north-east Atlantic and the Great Skua and Fulmar are subject to chronic pollution. However, with further restrictions on the use of these chemicals levels should decline, as has been the case with DDE. Both DDT and PCB's are bioaccumulated in the fat of marine mammals found long distances away from any apparent points of injection of DDT and PCB's, contamination of the oceans probably having been through aerial transport. Organochlorines have therefore demonstrated how widespread such substances can become. Species such as the Great Skua, a top predator, show a definite accumulation of organochlorines relative to their prey. However, in monitoring the ocean distribution of organochlorines, the many environmental factors involved probably preclude the use of one species such as the Great Skua as an indicator species of any detrimental effects caused by DDE or PCB's to marine life.

CHAPTER 6

METALS IN ATLANTIC GREAT SKUAS AND PROCELLARIIFORMES IN RELATION TO DIETARY LEVELS OF METALS

6.1 INTRODUCTION

Several studies of mammals and birds have pointed to the diet as the principal source of metals, which concentrate primarily in the liver and kidney (Sergeant and Armstrong, 1973; Nagakura et al., 1974; Roberts et al., 1976; Bryan, 1984). Though there is evidence of the initial accumulation of metals from seawater by phytoplankton, there is little evidence for the amplification of metals from invertebrates to small fish and then to larger organisms (Bryan, 1984). In the case of mercury, however, there does appear to be an increase in mercury concentrations with trophic level, from plankton-feeding clupeids to large predatory species (Bryan, 1984). Thus, whilst the process of biomagnification through the food chain is generally accepted for mercury, only in isolated cases has biomagnification of other metals been described.

In this study metal levels in nineteen species of seabirds from both the North and South Atlantic were examined in relation to each of the species' diets. Values are expressed as micrograms per gram wet weight, unless stated otherwise.

6.2 METALS IN SOUTH ATLANTIC PROCELLARIIFORMES AND GREAT SKUAS

6.2.1 Copper

The liver, kidney and muscle tissue concentrations of copper, excluding those for the Wandering Albatross, in the species from the North and South Atlantic were similar to each other. For eleven of the eighteen study species copper concentrations were higher in the liver than in the kidney, although this pattern was variable between

individuals because of the small range in tissue concentrations. For example, the copper concentrations in the male Wandering Albatross were higher in the liver than the kidney, but this is reversed in the female (Table 6.1). The copper concentrations for all the species ranged between 1.2 ug g^{-1} and 24 ug g^{-1} but this includes outliers and the mean value was 6 ug g^{-1} (Table 6.1). Exceptions were for the Great Shearwater, Kerguelen Petrel, British Storm Petrel and Little Shearwater, which showed quite high degrees of variation in liver and kidney copper concentrations. Any high values obtained were checked by analysing replicates of the sample.

The mean concentrations in the kidneys of the Yellow-nosed Albatross, Fulmar and Rockhopper Penguin were lower than the levels found in the other species. The Great Shearwater, Atlantic Petrel, Soft-plumaged Petrel, Leach's Petrel, British Storm Petrel and the South Atlantic Great Skua had higher concentrations of copper in the kidney than the liver or muscle. The lowest recorded level of copper in the kidney was 1.2 ug g^{-1} in the kidney of the Fulmar and the highest (24 ug g^{-1}) was found in a Little Shearwater. Many of the Procellariiformes and Great Skuas showed mean kidney concentrations within the range of 4 to 8 ug g^{-1} (Appendix 2) with low standard deviations, the exception being the British Storm Petrel.

Muscle tissue was available for analysis from only seven of the nineteen species sampled (Table 6.2). Copper concentrations in the muscle were slightly lower than those in the kidney or liver with the exception of the Grey-backed Storm Petrel, where the mean muscle concentration was higher than the means for kidney and liver.

Table 6.1 Means, Standard Deviations, Medians and Ranges of copper concentrations in kidney and liver tissue of North and South Atlantic

Procellariiformes and Great Skuas

Results as $\mu\text{g g}^{-1}$

SPECIES	n	KIDNEY				LIVER			
		MEAN	SD	MEDIAN	RANGE	MEAN	SD	MEDIAN	RANGE
Wandering a		4.7				8.4			
Albatross b		5.6				4.9			
Sooty 8		4.6	0.35	4.7	4.2-5.3	6.3	1.27	6.5	4.1-8.5
Albatross									
Yellow-nosed Albatross	9	3.3	0.71	3.3	2.8-4.9	5.0	1.20	4.6	3.5-7.0
Common Diving Petrel	17	5.5	1.54	5.3	2.8-8.0	6.9	1.42	6.3	5.3-10
Broad-billed Prion	31	4.4	0.71	4.3	3.2-6.0	6.4	1.06	6.2	3.6-8.4
Great Shearwater	12	6.1	1.96	5.5	4.7-11	5.9	0.99	5.6	5.1-8.4
Little Shearwater	13	5.8	5.48	5.5	2.8-24	7.9	2.53	7.3	5.5-13
Atlantic Petrel	13	6.1	1.40	6.3	4.5-9.3	4.9	2.39	4.5	3.6-13
Kerguelen Petrel	14	4.9	1.16	4.7	3.8-8.4	6.4	3.23	5.7	3.4-17
Soft-plumaged Petrel	18	5.9	1.09	5.9	4.1-8.0	5.2	1.82	4.7	3.5-12
White-bellied Storm Petrel	8	6.4	0.78	6.4	5.2-7.5	6.3	1.50	6.1	3.4-8.1
Grey-backed Storm Petrel	8	6.5	1.47	6.7	4.5-8.3	7.6	2.76	7.2	4.9-15
White-faced Storm Petrel	7	7.0	0.80	6.6	6.2-8.4	8.5	1.22	8.9	5.7-11
Leach's Petrel	13	6.9	1.61	6.6	4.2-9.7	6.4	1.18	6.3	4.8-8.2
British Storm Petrel	7	10	2.75	9.8	7.2-15	5.5	1.23	6.1	3.5-6.5
Fulmar	25	3.4	0.75	3.4	1.2-4.4	5.1	0.97	5.1	3.3-11
Rockhopper Penguin	12	3.8	0.98	3.8	2.7-6.1	4.1	1.02	4.0	2.8-5.8
South Atlantic Great Skua	13	4.6	0.94	4.4	3.3-6.6	4.2	0.66	4.3	3.1-5.4
North Atlantic Great Skua		5.3	1.19	5.2	3.2-8.4	5.9	1.01	5.9	3.9-7.7

a= male
b= female

Table 6.2 of Means, Standard Deviations, Medians and Ranges of copper concentrations in muscle tissue

SPECIES	n	MEAN ug g ⁻¹	SD	MEDIAN ug g ⁻¹	RANGE ug g ⁻¹
North Atlantic Great Skua	43	5.6	0.56	5.8	4.1-7.3
Fulmar	25	4.0	0.56	3.9	2.8-4.9
British Storm Petrel	8	6.8	0.69	6.9	5.6-7.7
Leach's Petrel	13	6.0	0.54	6.0	5.2-6.8
White-faced Storm Petrel	7	6.5	0.22	6.6	6.3-6.8
Grey-backed Storm Petrel	8	8.5	3.35	7.1	6.4-16
White-bellied Storm Petrel	8	6.3	0.80	6.1	5.6-7.2

6.2.2 Zinc

Twelve of the North and South Atlantic species contained higher concentrations of zinc in the kidney, compared with concentrations of zinc in the liver (Table 6.3). The concentrations of zinc in the kidneys of the Wandering and Sooty Albatrosses were significantly higher than those in the closely related Yellow-nosed Albatross (Mann-Whitney, $p < 0.05$). The levels of zinc in the kidneys of the various species show a high degree of variation, both between species and between individuals of the same species (Table 6.3). This may be due to some mobilisation of metals after death, but this appears unlikely as samples were frozen immediately after the bird's death and stored at -20°C until analysed.

The kidney tissue of Leach's Petrel shows relatively low concentrations of zinc (mean=19) compared to the other species. The Rockhopper Penguin and Atlantic Petrel had the highest kidney zinc concentrations (Table 6.3).

Table 6.3 Means, Standard Deviations, Medians and Ranges of zinc concentrations in kidney and liver tissue of North and South Procellariiformes and Great Skuas

Results as $\mu\text{g g}^{-1}$

Species	n	KIDNEY				LIVER			
		MEAN	SD	MEDIAN	RANGE	MEAN	SD	MEDIAN	RANGE
Wandering σ	2	45				57			
Albatross ρ		52				49			
Sooty Albatross	8	56	7.74	57	42-65	67	12	64	47-86
Yellow-nosed Albatross	9	35	3.5	35	31-42	48	10	49	29-59
Common	17	46	10	46	33-78	38	7.4	38	28-51
Diving Petrel									
Broad-billed Prion	31	36	5.9	37	29-47	44	9.9	43	30-75
Great Shearwater	12	46	8.0	48	27-88	38	3.7	38	33-45
Little Shearwater	13	50	8.7	49	34-66	40	7.0	42	28-54
Atlantic Petrel	13	62	6.3	64	50-71	45	8.8	43	33-64
Kerguelen Petrel	14	45	6.3	46	35-54	44	13	42	29-81
Soft-plumaged Petrel	18	50	11	47	36-78	43	7.9	40	30-56
White-bellied Storm Petrel	8	38	4.3	38	35-48	38	5.4	40	28-46
Grey-backed Storm Petrel	8	28	12	28	15-49	42	15	40	29-77
Storm Petrel									
White-faced Storm Petrel	7	39	5.2	38	30-46	34	8.0	34	20-44
Leach's Storm Petrel	13	19	3.3	19	14-24	20	3.4	19	16-29
British Storm Petrel	8	37	7.3	41	26-43	25	5.3	26	16-32
Fulmar	25	37	12	35	22-86	37	16	33	24-79
Rockhopper Penguin	12	63	16	64	41-86	40	11	38	27-61
South Atlantic Great Skua	13	37	7.1	35	28-53	22	4.0	20	18-32
North Atlantic Great Skua	47	41	12	40	26-75	30	9.1	28	21-73

Table 6.4 Means, Standard Deviations, Medians and Ranges of zinc concentrations in muscle tissue

SPECIES	n	MEAN ug g ⁻¹	SD	MEDIAN ug g ⁻¹	RANGE ug g ⁻¹
North Atlantic Great Skua	43	21	4.9	20	15-39
Fulmar	25	21	4.7	22	11-28
British Storm Petrel	8	11	1.2	11	10-13
Leach's Petrel	13	7.6	0.7	7.5	6.6-9.2
White-faced Storm Petrel	7	16	1.2	16	14-17
Grey-backed Storm Petrel	8	15	7.3	14	10-33
White-bellied Storm Petrel	8	15	2.0	15	14-20

The liver tissue of the Sooty and Yellow-nosed Albatrosses, Broad-billed Prions and Grey-backed Storm Petrels had higher concentrations of zinc than the kidney (Table 6.3). All the species apart from Kerguelen Petrel, White-bellied Storm Petrel, White-faced Storm Petrel, Leach's Petrel and the Fulmar showed significant differences between zinc concentrations in the kidney and liver (see Appendix 6). The North Atlantic species appeared to contain lower concentrations in their tissues than the South Atlantic species, which may be related to cadmium concentrations (see Chapter 7).

For the species where muscle tissue was available, zinc concentrations were markedly lower than in the kidney or liver (Table 6.4). The small South Atlantic petrels had quite similar muscle concentrations, while levels in the Fulmar and Great Skua were slightly higher (Table 6.4). In the muscle tissue of the Grey-backed Storm Petrel and Great Skua values of 33ug g⁻¹ and 39ug g⁻¹, respectively, were found in two individuals, but the values are assumed to be correct as replicates of the tissue gave results in

agreement with each other.

6.2.3 Cadmium

Cadmium concentrations in the kidney showed a high degree of intra- and inter-specific variation (Table 6.5). The concentrations of cadmium found in the kidney tissue of the Wandering and Sooty Albatrosses were very high and levels in the other larger South Atlantic Procellariiformes and Rockhopper Penguin were greatly elevated above expected tissue concentrations. The concentrations in the storm petrels, Common Diving Petrel, Broad-billed Prion and North Atlantic Procellariiformes were much lower in comparison. As for copper and zinc, cadmium concentrations in the kidney of the Yellow-nosed Albatross were significantly lower than in the other two species of albatross (Mann-Whitney U-test, $n=10$, $U=0$, $p<0.05$).

Concentrations in kidney tissue of the North Atlantic and South Atlantic Great Skuas were significantly different (Mann-Whitney U-test, standard normal deviate=3.11, $n=47$, $p<0.01$, Fig 6.1), and the concentrations were not as high as those in kidney tissue of some of their prey items, for example Leach's Petrel, British Storm Petrel, Broad-billed Prion and Atlantic Petrel.

The closely related Great and Little Shearwaters had significantly different kidney concentrations of cadmium (Mann-Whitney U-test, $n=13$, $U=21.5$, $p<0.05$), although liver levels were more comparable. The kidney tissue of the Great Shearwaters contained very high concentrations of cadmium (Table 6.5; Appendix 2).

One bird (not in Table 6.5) had a kidney cadmium concentration of $16\mu\text{g g}^{-1}$; this bird was found dead. At death some mobilisation of metals takes place in the major organs and this mobilisation could result in higher concentrations in the tissues than when the bird was alive (NERC, 1983). Since this could have been the case, the metal concentrations for this bird were not included in any means or

statistical tests.

The sample of 25 Fulmars was taken from the islands of St. Kilda, Outer Hebrides and Foula, Shetland. Despite the differences in the feeding habits of the two populations (Furness and Todd, 1984) no significant differences were found between the cadmium concentrations in the kidney of the two populations (Mann-Whitney U-test, $U's=69.5$ & 66.5 , $p>0.05$). The geometric mean cadmium concentration for the Fulmars was the lowest for all the species sampled.

The cadmium concentrations in the liver (Table 6.5) of all the Procellariiformes, Rockhopper Penguin and skuas were significantly lower than kidney concentrations (see Appendix 6, Mann-Whitney U-test $p<0.05$). The hepatic tissue of the Wandering and Sooty Albatrosses contained the highest concentrations but these values were only 16-34% of the renal concentrations. This marked difference was also evident for the Rockhopper Penguin (liver levels 19% of renal values) and in the larger petrels (liver concentrations were about 30% of kidney concentrations). Only in the liver tissue of the Grey-backed and White-bellied Storm Petrels do mean liver concentrations reach 50% of kidney levels. For the North and South Atlantic Great Skuas liver cadmium concentrations were 11 and 10% respectively of renal values, and a significant difference was found between the two for liver cadmium concentrations. As with the kidney, the concentrations showed a high degree of variation. The results suggest that the kidney is the main storage organ for cadmium.

The muscle concentrations of cadmium were very low compared to the liver and kidney. The highest value found was in the muscle tissue of a Grey-backed Storm Petrel, while for the North Atlantic Great Skua levels were often below the detection limit (0.01 ug g^{-1}) (Table 6.6).

Table 6.5 Means, Standard Deviations, Medians and Ranges of Cadmium concentrations in North and South Atlantic Procellariiformes and Great Skuas

Results as $\mu\text{g g}^{-1}$

SPECIES	n	KIDNEY				LIVER			
		MEAN	SD	MEDIAN	RANGE	MEAN	SD	MEDIAN	RANGE
Wandering ♂ Albatross ♀	2	127				41			
Sooty Albatross	8	76	12	79	58-92	26	5.3	26	22-33
Yellow-nosed Albatross	9	25	9.3	23	15-46	8.7	4.1	8.7	3-17
Common Diving Petrel	17	32	12	32	17-74	6.8	2.9	6.6	3-14
Broad-billed Prion	31	33	10	30	19-72	16	5.2	16	9-26
Great Shearwater	12	74	20	79	38-99	15	5.8	15	6-27
Little Shearwater	13	43	15	46	23-71	14	6.4	16	9-21
Atlantic Petrel	13	61	20	59	42-102	19	10	18	9-40
Kerguelen Petrel	14	45	14	44	22-68	15	4.1	15	10-21
Soft- plumaged Petrel	18	48	15	47	32-90	15	8.4	15	8-41
White-bellied Petrel	8	21	2.6	21	18-26	11	1.7	11	9-15
Grey-backed Storm Petrel	8	23	5.9	21	18-36	12	2.9	13	8-18
White-faced Storm Petrel	7	33	10	30	25-55	7.6	2.1	7.6	6-12
Leach's Petrel	13	25	5.0	25	19-37	8.8	3.0	8.0	5-14
British Storm Petrel	8	19	8.5	16	7-30	5.7	2.5	4.9	3-10
Fulmar	25	8	5.2	7	2-25	1.9	1.6	1.9	0.5-17
Rockhopper Penguin	12	72	28	66	32-112	14	7.1	16	4-26
South Atlantic Great Skua	13	26	9.4	23	13-45	2.6	1.3	2.2	0.97-5
North Atlantic Great Skua	46	12	10	15	1.7-43	1.2	1.3	1.9	.17-4.4

Table 6.6 Means, Standard Deviations, Medians and Ranges of cadmium concentrations in muscle tissue

SPECIES	n	MEAN ug g ⁻¹	SD	MEDIAN ug g ⁻¹	RANGE ug g ⁻¹
North Atlantic Great Skua	43	0.07	0.06	0.75	ND-0.23
Fulmar	25	0.35	0.21	0.29	0.10-0.92
British Storm Petrel	8	0.63	0.17	0.71	0.40-0.80
Leach's Petrel	13	1.2	0.55	1.07	0.60-2.1
White-faced Storm Petrel	7	0.80	0.54	0.62	0.40-1.70
Grey-backed Storm Petrel	8	1.50	1.06	1.30	0.50-3.60
White-bellied Storm Petrel	8	1.40	0.73	1.40	0.80-2.70

6.2.4 Mercury

The concentrations of mercury in the liver tissue of the Wandering and Sooty Albatrosses are the highest yet recorded in pelagic seabirds (80-271ug g⁻¹) (Table 6.7). Of the other species only the Atlantic and Soft-plumaged Petrel contain very high concentrations in the liver tissue (14-55ug g⁻¹, 3.6-103ug g⁻¹ respectively). The other species contain much lower concentrations, ranging from 0.14 ug g⁻¹ to 20ug g⁻¹ (Table 6.7). The liver tissue was selected for analysis as mercury has been found to accumulate primarily in this tissue (Parslow *et al.*, 1982). The renal and hepatic tissue of the Great Skua, however, contained comparable concentrations of mercury (Mann-Whitney U-test, n=20, standard normal deviate=1.83, p>0.05), but muscle concentrations were significantly lower than in either the kidney or the liver (Table 6.8, Mann-Whitney U-test, n=20, standard normal deviate=5.30, p<0.05). The concentrations of mercury in the hepatic tissues of the North and South Atlantic Great Skuas were not significantly different (Mann-Whitney U-test, standard normal deviate=1.66, n=20, p>0.05). As found for cadmium, mercury

concentrations in the tissues were highly variable between individuals. Results for mercury concentrations in the tissues of the Great Skua are given in Table 6.8.

Four samples of body and abdominal fat from the North Atlantic Great Skua were analysed and the concentrations of mercury in fat were found to be lower than concentrations in liver, kidney or muscle tissue. The concentrations in the body fat were 0.29 ug g⁻¹ and 0.56 ug g⁻¹ dry weight and in abdominal fat were 0.26 ug g⁻¹ and 0.59 g⁻¹. Since only organic mercury is fat soluble the mercury in fat was assumed to be methyl-mercury.

Table 6.7 Means, Standard Deviations, Medians and Ranges of mercury concentrations in liver tissue of North and South Atlantic

Procellariiformes

SPECIES	n	MEAN ug g ⁻¹	SD	MEDIAN ug g ⁻¹	RANGE ug g ⁻¹
Wandering male		271			
Albatross female		266			
Sooty Albatross	8	141	48	135	80-227
Yellow-nosed Albatross	9	7.7	5.1	5.7	4.8-20
Common Diving Petrel	17	0.54	0.34	0.47	0.17-1.54
Broad-billed Prion	31	0.38	0.21	0.33	0.14-1.1
Great Shearwater	12	2.0	1.66	1.4	0.80-6.5
Little Shearwater	13	1.2	0.31	1.3	0.60-1.6
Atlantic Petrel	13	28	11	27	14-53
Kerguelen Petrel	14	4.6	1.48	4.5	1.9-6.8
Soft-plumaged Petrel	18	21	23	14	3.6-103
Rockhopper Penguin	12	2.3	0.94	2.2	0.97-3.7
South Atlantic Great Skua	13	7.4	5.4	6.4	0.91-17

Table 6.8 Means, Standard Deviations, Medians and Ranges of mercury

concentrations in North Atlantic Great Skua tissues (dry weight)

TISSUE	n	MEAN ug g ⁻¹	SD	MEDIAN ug g ⁻¹	RANGE ug g ⁻¹
Muscle	19	1.7	1.42	1.54	0.75-6.86
Liver	20	10	7.9	12	4.3-40
Kidney	20	8.4	4.3	7.9	3.1-18.5

6.2.5 Selenium

The geometric means, medians and ranges of concentrations of selenium in liver, muscle and kidney tissues of the Great skua show that comparable levels are found in the liver and kidney tissue (Mann-Whitney U-test, $p > 0.05$), with significantly lower concentrations in the muscle tissue than the liver or kidney (Mann-Whitney U-test, $p < 0.05$; Table 6.9).

Table 6.9 Means, Standard Deviations, Medians and Ranges of Selenium

Concentrations in Great Skua tissues (dry weight)

TISSUE	n	MEAN ug g ⁻¹	SD	MEDIAN ug g ⁻¹	RANGE ug g ⁻¹
Muscle	19	7.3	0.93	6.82	4.46-17
Liver	19	70.3	5.47	68.50	48.67-103
Kidney	19	72.14	5.71	95.50	51.43-121

Only seven liver samples from the Broad-billed Prion were analysed for selenium as it was only possible to use the method of neutron activation for 18 South Atlantic seabird tissue samples. The levels found were an order of magnitude higher than the mercury concentrations in the same tissue ranged from 1.09 to 19.3ug g⁻¹ wet weight).

Seven liver samples of the Little Shearwater were analysed for

selenium and the results showed a wide range of values (mean=33 $\mu\text{g g}^{-1}$, range 1.34-59 $\mu\text{g g}^{-1}$ wet weight). The four values obtained for selenium in the liver of the Soft-plumaged and Atlantic Petrels also showed a high degree of variability (Appendix 2).

6.3 CONCENTRATIONS OF COPPER, ZINC, CADMIUM AND MERCURY IN FISH AND SQUID

A selection of fish species from waters west of Shetland were analysed for metal concentrations in the flesh, gut and liver. Concentrations of all the metals in the fish were low compared to levels in seabird tissues. Concentrations of zinc in Cod, Haddock, Dab, Sole, Whiting and Sand-eel flesh ranged between 4 and 38 $\mu\text{g g}^{-1}$ (Appendix 4). Copper concentrations in the fish flesh ranged between 0.08 and 1.4 $\mu\text{g g}^{-1}$. Cadmium and mercury concentrations in the fish flesh were very low, the highest concentrations of 0.16 and 0.57 $\mu\text{g g}^{-1}$ respectively being found in the flesh of Whiting.

Liver and gut concentrations of metals were slightly higher, especially for zinc and copper (Appendix 4). Gut concentrations of copper and zinc in the Whiting reached levels of 4.7 and 163 $\mu\text{g g}^{-1}$ respectively. Cadmium concentrations for the Whiting ranged between 0.20 and 4.29 $\mu\text{g g}^{-1}$. Gut concentrations of cadmium in the other fish species sampled were much lower (Appendix 4).

Liver concentrations of zinc ranged from 6 to 47 $\mu\text{g g}^{-1}$, copper from 0.51 to 4.92 $\mu\text{g g}^{-1}$ and cadmium from 0.10 to 1.39 $\mu\text{g g}^{-1}$ (Appendix 4). As for the seabirds, fish muscle concentrations of metals were lower than liver concentrations and there was also considerable variation between individual fish and between species.

A number of squid Loliago sp from British coastal waters were analysed. Zinc and cadmium mantle concentrations were low (14-26 $\mu\text{g g}^{-1}$ and 0.02 to 0.70 $\mu\text{g g}^{-1}$ respectively), whilst copper concentrations

were found to be quite high, ranging from 6 to 47ug g⁻¹. Mercury concentrations were very low, ranging from undetectable to 0.62ug g⁻¹ in the head region of the squid.

6.4 SEXUAL DIFFERENCES IN THE ACCUMULATION OF THE METALS CADMIUM AND MERCURY

Possible sexual differences in the accumulation of cadmium and mercury were examined in twelve of the South Atlantic species (White-bellied Storm Petrel, Sooty Albatross and Wandering Albatross were excluded due to extreme sexual bias in the sample, or, in the last case, too small a sample size). Female birds are able to excrete toxic metals not only through the feather but also via the egg, and this may be particularly important for mercury. Most of the species showed no significant differences between males and females for mercury levels, exceptions being the Kerguelen Petrel and the Rockhopper Penguin (Kerguelen Petrel U-statistic=3, n=14, p<0.05; Rockhopper Penguin U-statistic=1, n=12, p<0.05). Perhaps surprisingly, more sexual differences were observed for cadmium concentrations, this being the case for the Rockhopper Penguin (U-statistic=3, n=12, p<0.05), Broad-billed Prion (U-statistic=59, n=31, p<0.05) and the South Atlantic Great Skua (U-statistic=4, n=13, p<0.05). For these relationships both cadmium and mercury the concentrations were lower in the female birds than the males.

The North Atlantic species showed no differences between the sexes in the concentrations of the metals (Mann-Whitney U-test, p>0.05).

6.5 CHANGES IN METAL CONCENTRATIONS WITH AGE IN THE NORTH ATLANTIC GREAT SKUA

Pearson correlations and Spearman's Rank correlations were calculated, for both male and female North Atlantic Great Skuas

together, between age and metal concentration in the various tissues since a normal distribution of the data could not always be demonstrated (Table 6.10, see Chapter 7).

Table 6.10 Correlation coefficients (r) and Spearman's rank coefficients (r_s) for Great Skuas of known age and metal concentration in tissues.

Tissue	Cd ^a		Zn ^a		Cu ^a		Hg ^b		Se ^b	
	r	r_s								
Liver	-0.05	-0.05	0.15	0.12	-.18	-.30	0.35	0.29	0.18	0.25
Kidney	0.33	0.32	-0.22	-.09	0.00	0.04	0.21	0.32	-.09	-.01
Muscle	0.40	0.40	-0.16	-.22	0.06	-.14	-.22	0.21	-.02	-.23

a= n=27, b= n=20

Correlations with age were not statistically significant for any of the metals in the kidney, liver or muscle, except for cadmium in the muscle. This one significant correlation may be due to chance; there were difficulties with cadmium analysis in muscle since levels were often close to the limit of detection.

6.6

DISCUSSION

6.6.1 Changes in metal concentration with age in Great Skuas

In the Great Skua, no significant correlation between age and metal levels in tissues was found, except for cadmium in the muscle tissue ($r=0.402$, $r_s=0.401$, $p<0.05$). In the liver and kidney tissues, mercury, cadmium and selenium were all significantly positively correlated with age in Great Skuas collected from Foula in 1976 (Furness and Hutton, 1979). However, on examination of the data the increasing concentrations of the metals with age were largely due to an outlying point caused by a twelve year old bird which had much higher concentrations of all the metals than the other birds, including birds up to ten years of age. The metal concentrations in

the liver and kidney of the twelve year old bird were sufficiently high above the others to be considered anomalous, as none of the other eleven 10 to 15 year old birds analysed in this study contained such high concentrations. If this data point is removed no significant correlations between metal concentrations and age are found.

In this sample of twenty-seven skuas, therefore, no clear correlation was found with age. However, Sooty Terns have been found to accumulate mercury in the liver over time (cited in Stoneburner et al., 1980). Cadmium and lead levels have been shown to increase in the kidney with the age of the bird in Laughing Gull, Louisiana Heron Hydranessa tricolor and Cattle Egret Bululcus ibis (Hulse et al., 1980; Cheney et al., 1981). In these latter two studies only three age classes of birds were examined; downy young, pre-fledging birds and adults, which suggests that only differences between adults and young are noted rather than accumulation over time with age. Cadmium is not transferred from the female to the egg as mercury is, so cadmium is either below the limit of detection or found at very low concentrations in the young chick. The birds, through their diet, were found to accumulate up to the pre-fledging stage, but the rate of accumulation subsequent to this and through adult life in relation to age was unknown.

The accumulation of metals may occur at a critical stage in the life cycle of the animal as found in rats, where age specific differences were found in the pharmacokinetics of metals in sucklings. Kostial et al. (1979) concluded that the early neo-natal period was a 'critical' and 'vulnerable' period for metal accumulation and therefore for metal toxicity. A single skua chick available for analysis contained less than $1 \mu\text{g g}^{-1}$ wet weight of cadmium and mercury in its liver, kidney and muscle tissues, which suggests that there is

some accumulation at a young age. This could continue up to four years of age, as no birds were available for analysis below this age. The pharmacokinetics of the metals in later life is unclear, but age-accumulation appears to be non-existent in adult Great Skuas.

The accumulation of cadmium with age has been shown in the insectivorous Common Shrew Sorex araneus (Hunter, 1984) and humans (Schroeder and Balassa, 1967). Mercury concentrations have been positively correlated with age in seals from British coastal waters (except Shetland seals) and cadmium levels in the kidney also increased with age (Heppleston and French, 1973). The tissue concentrations of total mercury increased with age in Common Seals from the Wadden Sea (Reijnders, 1980). This effect was most pronounced in the liver but was also found in the kidney and the brain. Most of the mercury in the seal tissues was recovered as the inorganic form of the metal and since mercury is present in fish (their food) predominantly as methyl-mercury, it appears that the methyl-mercury taken up by the seals is converted to inorganic mercury, though to a different extent within the various age-classes (Reijnders, 1980).

Various studies on fish have found a linear relationship between the age of the fish (often determined by length) and mercury concentration (Johnels and Westermarck, 1969; Mackay et al., 1975). The Great Skua did not show the type of correlation found in fish between mercury in the muscle tissue and age of the fish. Hares Lepus capensis showed no accumulation of metals with age, but did show some sexual differences in zinc and copper concentrations (Wojcik, 1980). No sexual differences in metal accumulation were found in the Great Skua and this corresponds with the work on the Cattle Egret (Hulse et al., 1980) and Long-tailed Ducks Clangula hyemalis (Szefer and Falandysz, 1983) In Oystercatchers, both zinc and cadmium concentrations were age and sex related (Hutton, 1981).

Evidence of the accumulation of mercury and cadmium has been shown in certain pelagic seabirds and here and in similar studies the values suggest that there is considerable individual variation, not necessarily related to age or sex (Fimreite, 1979; Furness and Hutton, 1979; Osborn et al., 1979). Investigations into the accumulation of metals in natural populations are fairly limited since few species can be aged accurately. The Great Skua though accumulating elevated levels of potentially toxic metals, does not appear to do so with age, and is the only species of pelagic seabird in which sampled birds are of known age. Marine mammals and fish which accumulate metals with age cannot necessarily be directly compared to birds as significant physiological differences may exist between the groups. Possibly the ability of birds and mammals to excrete some metals into feathers and fur during feather and fur growth may allow them to eliminate metal burdens more easily than can be achieved by fish.

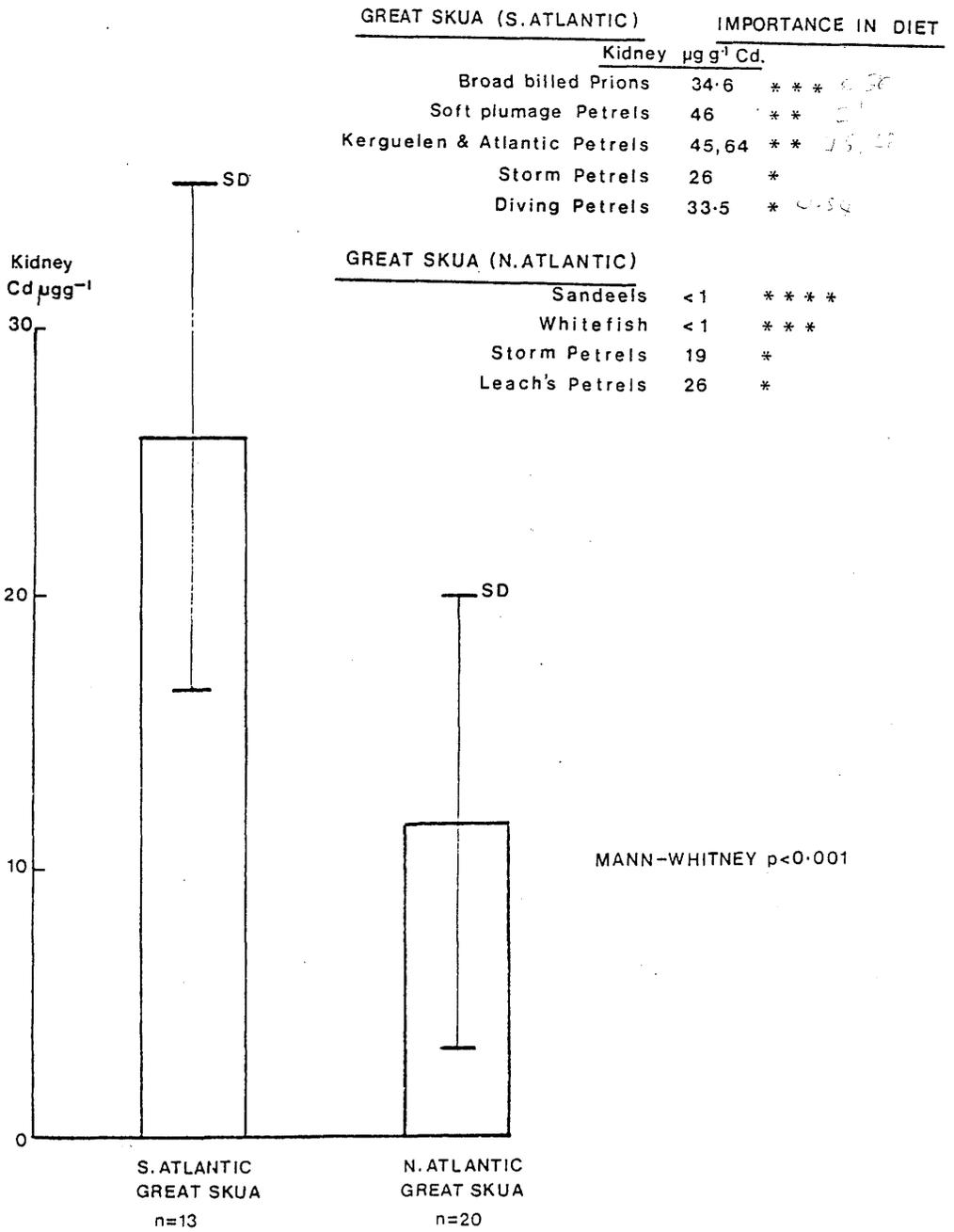
6.6.2 Differences in concentrations of Metals in North and South Atlantic Great Skuas, Catharacta skua skua and C.s. hamiltoni

The only significant difference in tissue metal concentrations between the two populations of skua was found for cadmium (Fig 6.1). This difference is probably related to the dietary concentrations consumed by the skuas. The diet of the South Atlantic Great Skua consists mainly of seabirds (R.W. Furness, pers. comm.) and these contain higher concentrations of cadmium than items from the diet of the North Atlantic Great Skua. The levels of cadmium in the tissues of the Great Skuas from Gough Island therefore reflect the dietary intake of cadmium, although tissue levels are lower than those of the prey, suggesting that a relatively small amount of the total cadmium intake is absorbed through the gut wall. This also suggests that the cadmium

FIG 6.1

KIDNEY CADMIUM LEVELS IN N. AND S. ATLANTIC GREAT SKUAS

AND THEIR PREY



is not biomagnified through the food chain from seabirds to skuas. The effect of diet on the accumulation of metals has been shown in several species, for example the Laughing Gull (Hulse et al., 1980) and ducks (Parslow et al., 1982; Lindsay and Dimmick, 1983).

A dietary study of the Foula Great Skuas (Furness, 1979) illustrated that a large variety of food items are consumed by the North Atlantic Great Skua, with fish being of prime importance, especially sandeels and whitefish discards. Cadmium concentrations in the fish are generally low, up to $0.65 \mu\text{g g}^{-1}$ wet weight, although a few fish gut samples contained concentrations between 1 and $4.29 \mu\text{g g}^{-1}$. These latter levels would considerably increase the dietary intake of the Great Skua. Other fish-eating species such as the Gannet also contain relatively low concentrations of cadmium (Parslow and Jefferies, 1977). The Great Skuas from Foula contained elevated concentrations of cadmium but there was a great deal of variation between individuals. This may partly be due to differences in feeding habits, those birds feeding mainly on petrels possibly containing higher concentrations of cadmium, due to the higher cadmium accumulations in the petrels as compared to fish.

Mercury concentrations are not significantly different between the two skua subspecies and this could be related to diet. Though the seabirds fed on by the South Atlantic Great Skua contain mercury, levels in most of these species are comparatively low ($1.1 \mu\text{g g}^{-1}$ in storm petrels, $0.38 \mu\text{g g}^{-1}$ in Broad-billed Prions, $4.6 \mu\text{g g}^{-1}$ in Kergulen Petrels and $0.54 \mu\text{g g}^{-1}$ wet weight in Common Diving Petrels, all values as geometric means). The fish diet of the North Atlantic Great Skua is also relatively low in mercury (maximum in fish muscle of $0.57 \mu\text{g g}^{-1}$) and birds feeding on the Storm and Leach's Petrels in the North Atlantic will also obtain comparatively small quantities of mercury from their diet.

Few sources of data are available on the levels of heavy metals in southern ocean seabirds, including Great Skuas. Levels of copper and zinc in Maccormick's Skua are comparable to those in the South Atlantic Great Skua from Gough Island. Concentrations of cadmium in both the kidney and the liver of Maccormick's Skua from Gould and Atka Bays in Antarctica are higher than those in Gough Great Skuas (Schneider et al., 1985). Though the concentrations of mercury are higher in the Gough Great Skua than Maccormick's Skua, the levels are directly comparable to the concentrations in the Brown Skua Catharacta skua lonnbergi (Norheim et al., 1982). The higher concentrations in the Brown Skua were assigned to the body-burden achieved during migration combined with a high position in the food chain (Norheim et al., 1982), but the Gough Great Skua is resident on the island and therefore must accumulate mercury 'on site', from its possibly migratory prey.

6.6.3 Tissue distribution of copper, zinc, cadmium and mercury

Copper concentrations in the liver of the North Atlantic Great Skua were similar to those found in Common Terns (Connors et al., 1975) but lower than the concentrations found in the Puffin (Parslow et al., 1972). Copper concentrations were higher in the liver than the kidney of the Great Skua and most of the Atlantic Procellariiformes and this was also found for Crested Terns Sterna bergii (Howarth et al., 1982).

The highest zinc concentrations were found in the kidney tissue of the Great Skuas, and for most of the Atlantic Procellariiformes, rather than liver tissue, and this tissue distribution has been reported in the Puffin and Manx Shearwater (Osborn et al., 1979), Herring Gull and Great Skua (Hutton, 1981) and Herring Gull (Nicholson, 1981). Higher zinc concentrations in the liver as opposed

to the kidney were found for the Broad-billed Prion and Grey-backed Storm Petrel and this has been reported for the Oystercatcher (Hutton, 1981), Knot (Evans and Moon, 1981) and the Fulmar (Osborn et al. 1979). Similar concentrations in both the kidney and liver were found for the Fulmar, Kerguelen Petrel, White-bellied Storm Petrel and White-faced Storm Petrel and this has also been found for the Common Tern (Connors et al., 1975).

Zinc and copper as essential metals are metabolically regulated in the tissues. However, zinc and copper levels decreased in ducks as the proportion of animal food in the diet increased (Parslow et al., 1982) and dietary intake of copper and zinc by the Procellariiformes may have some influence on tissue concentrations. The levels in the South Atlantic Great Skua are similar to those in their prey, while the concentrations in the North Atlantic Great Skua are higher than the levels found in fish. Tissue concentrations in the two subspecies of Great Skua are similar for copper and zinc, suggesting that these two metals are metabolically regulated. As copper and zinc are essential micronutrients rather than accumulated toxic metals, appreciable levels would be expected to occur in a wide range of species (Parslow et al., 1982) and this has been found for the study species. The individual variation in levels, especially for zinc, is more difficult to explain, but it may be related to the seasonal changes in the physiological requirements for metals in individuals depending upon their breeding and, more importantly, their moulting cycle (Ward, 1978).

Tissue concentrations and distribution of the metals for the Foula Great Skua are similar to those found by Furness and Hutton (1979) in Foula Great Skuas of known age collected in 1976. Cadmium levels have been found to be higher in the kidney than the liver for a number of species where data are available including Royal and Sandwich Terns

(Maedgen et al., 1975), Puffin, Fulmar and Manx Shearwater (Bull et al., 1977), Herring Gull (Nicholson, 1981), Sooty Terns (Stoneburner et al., 1980), Crested Terns (Howarth et al., 1982), Laughing Gull (Hulse et al., 1980), Great Skua and Oystercatcher (Hutton, 1981). Significantly higher concentrations of cadmium were found in the kidney than the liver for all the Procellariiformes.

Pelagic seabirds have been found to contain high residues of cadmium (Anderlini et al., 1972; Bull et al., 1977) in their kidneys and livers. Elevated levels are indeed found in the North Atlantic seabirds, but pelagic seabirds from the South Atlantic including Catharacta skua hamiltoni have much higher concentrations of cadmium, and mercury, in the renal and hepatic tissue (Anderlini et al., 1972; Chapter 7). The pattern of cadmium accumulation in the Great Skua and Procellariiformes also follows that of mammals which have high concentrations of cadmium in the kidney, for example the Common Shrew, and seals (Heppleston and French, 1973; Hunter, 1984). Pelagic seabirds such as the Fulmar, Puffin and Manx Shearwater from St Kilda contain apparently elevated concentrations of metals in their tissues. The Great Skua contained higher concentrations of cadmium than mercury in its kidney tissues but levels were greater than those found in the Puffin, comparable to the Manx Shearwater and less than in the Fulmar (Osborn, 1979; Osborn et al., 1979). The higher concentrations of mercury in the liver than the kidney have been found in several studies (Osborn et al., 1979; Parslow et al., 1982).

6.6.4 Dietary influence on the accumulation of metals by

Procellariiformes

Many difficulties exist in examining the influence of diet on the accumulation of metals in Procellariiformes. Although there has been much work on the analysis of coastal and estuarine species of birds,

data remain relatively sparse for oceanic birds. Using the data available the sources of the high concentrations of non-essential metals in South and North Atlantic seabirds have been examined.

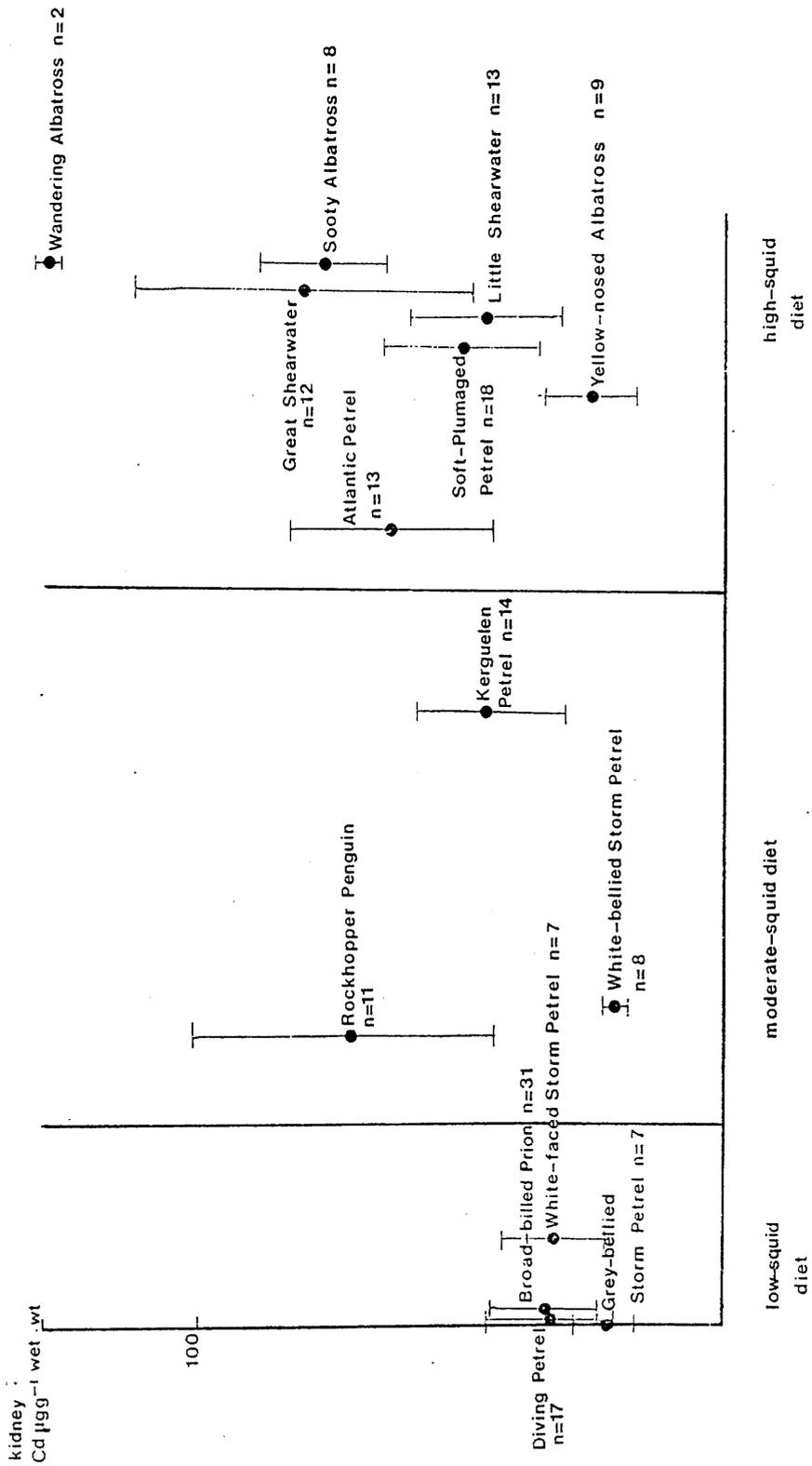
The exact diets and general feeding habits of many of the South Atlantic Procellariiformes have been little studied. Squid (especially Teuthoidea spp) appear to be the main source of food in the larger species, and copepods and euphausiids in the smaller species. The Rockhopper Penguin feeds on squid, crustacea and fish (Strange, 1982; Williams and Imber, 1982; R.W. Furness, pers. comm.). The mass of the cephalopod prey is positively related to Procellariiform body mass, and cephalopod beaks dominate food remains in stomach contents and regurgitations of these seabirds. However the persistence of the squid beaks in the stomach may mask the true abundancies of other food sources (Imber and Berruti, 1981).

Squid therefore constitute a high percentage of the diet of albatrosses (especially Wandering and Sooty Albatrosses), shearwaters and the larger petrels. The smaller petrels (Diving Petrels and Storm Petrels) and Prions feed mainly on copepods, euphausiids, amphipods, barnacles and small fish (Imber and Berruti, 1981; R.W. Furness, pers. comm.). The seabirds with the high squid diets also tend to have the highest concentrations of cadmium in the kidney (Fig 6.2). The Yellow-nosed Albatross and Rockhopper Penguin form the only exceptions to this. The former may feed to a greater extent on fish than is indicated by the data available from observations at its breeding sites (Williams and Imber, 1982; R.W. Furness, pers. comm.), as it is known to follow fishing boats and take discards while wintering in the Benguela Current area (Abrams, 1985). The Rockhopper Penguin may also take crustaceans which are able to accumulate heavy metals and this accumulation may vary depending on the geology of the area (Davies et

Fig 6.2 Diagram to illustrate the relationship between cadmium concentrations in the kidney ($\mu\text{g g}^{-1}$, wet weight) and the amount of squid in the diet (Appendix 5) of the South Atlantic Procellariiformes.

RELATIONSHIP BETWEEN SQUID IN THE DIET AND CADMIUM ACCUMULATION

IN THE KIDNEYS OF SOUTH ATLANTIC SEABIRDS



al., 1981). Recent evidence also suggests that squid form a greater part of the diet than originally considered (J. Croxall, pers. comm.).

Few data on metal concentrations in squid are available and this problem is compounded by the large number of species present in the oceans. In the stomach of Sooty Albatrosses, from the southern Indian Ocean, 60% of squid beaks found consisted of the family Cranchidae with the main weight due to Onychoteuthidae squid, while in the Wandering Albatrosses, as from the same area, 60% of the squid were Histioteuthidae (Williams and Imber, 1982).

The only data available on squid gives values for metal concentrations in the digestive gland of three species; Symplectoteuthis oualeansis, Omastrephes bastrami and Loligo opalescens of 782, 287 and 121ug g⁻¹ dry weight of cadmium respectively (Martin and Flegal, 1975). The squid digestive glands also contained very high concentrations of copper (up to 8370ug g⁻¹) and zinc (up to 513ug g⁻¹ dry weight), but if the albatrosses, shearwaters and petrels were being exposed to such levels the latter two essential metals must be successfully metabolically regulated (Bryan, 1984). The analysis of squid tissue in this study revealed, except in the digestive gland, very low levels of cadmium, zinc and mercury. In Martin and Flegal's (1975) study the two species with the highest cadmium concentrations were large (up to 45cm) open ocean squid and so may be atypical of squid taken by the birds. Furthermore, no results were given for mercury.

Heavy metals usually occur in the sea at rather low trace concentrations, though levels vary depending on the location. Surface waters in upwelling areas, for example, may contain 50ng kg⁻¹ Cd (cited in Nurnberg, 1983). Concentrations of cadmium in surface waters ranged from 6.3ng kg⁻¹ at 31°31'N 44°41'W to 2.7ng kg⁻¹ at 24°40'N 57°00'W (Nurnberg et al., 1983). Cadmium increases in concentration

with depth from surface waters to 1000m in both the Atlantic and Pacific Oceans. The enrichment factor with depth is however different in each ocean. Copper similarly increases with depth, for like cadmium it is actively removed from surface waters primarily by phytoplankton.

Phytoplankton, which are able to accumulate heavy metals (Hardy et al., 1984), form the basis of the marine food chain and may contain up to 180-200ppb mercury (Lowman et al., 1971; Knauer and Martin, 1972). Zooplankton from the Pacific Ocean were found to accumulate up to $0.12\mu\text{g g}^{-1}$ Hg dry weight (Hirota et al., 1979), but their overall role in controlling the flux and biological activity of trace metals has hardly been investigated.

Phytoplankton have been found to concentrate trace metals from ambient water in the laboratory but problems exist in relating laboratory work to the oceans for example abnormally high concentrations of algae have been used in some experiments. The marine copepod Pseudodiaptus coronatus took up significant amounts of cadmium from the ambient water and algae (Sick and Baptist 1979). However, transposing such experiments to nature may be difficult due to mixed algal populations, the chemical nature of the water and the possibility of chelation of metal ions.

Euphausiids, which are important food items for both the smaller Procellariiformes and squid, are also able to accumulate and concentrate cadmium in internal tissues by the intake of food or water. In it's natural environment the Euphausiid Meganyctiphanes norvegica, an important item in the diet of Fulmars (Furness and Todd, 1984), can reach cadmium concentration factors of approximately 1500 (Benayoun et al., 1974). Further studies on M. norvegica from the Mediterranean illustrated that ingested material played a significant

role in the accumulation process, with the mixed plankton food source containing $2.1\mu\text{g g}^{-1}$ Cd dry weight giving a five-fold magnification of cadmium concentration from phytoplankton to the euphausiid (Benayoun et al., 1974).

Nearshore decapods have been found to contain up to $1\mu\text{g g}^{-1}$ dry weight cadmium, but the oceanic decapod Systemaspis debilis from the eastern Atlantic Ocean contained 11.1 to $31.8\mu\text{g g}^{-1}$ cadmium. The cadmium data gave no indication of a relationship with size (taken to be equivalent to age), and it was suggested that diet may provide the major source of cadmium (Ridout et al., 1985). Such organisms may therefore pass on these metals to the next trophic level in the food chain, which may include pelagic seabirds.

The possibility that a metal such as cadmium may be an environmental pollutant has caused concern, and it has been concluded that the certain seabirds become contaminated through feeding near areas of local pollution (Bourne, 1976). However, Bull et al. (1977) concluded that the cadmium was of natural rather than anthropogenic origin, illustrating this point with the high residues found in St Kildean seabirds and the high concentrations of cadmium in marine insects Halobates spp (sea-skaters), which inhabit the sea surface feeding on zooplankton trapped at the air-sea interface. Both the birds and the insects inhabit areas some considerable distance from possible anthropogenic sources of cadmium. This was also demonstrated for Cory's Shearwater Calonectris dimedeia and Puffins (Harris, 1985; Renzoni et al., 1986).

Fish, which form a major part of the seabird's diet, appear to be able to accumulate metals both through the gills and food intake (Pentreath, 1976), though the former plays a relatively minor role. Fish analysed from Scottish waters for various metals had concentrations of cadmium less than $0.03\mu\text{g g}^{-1}$ Cd wet weight in the

muscle tissue (Topping, 1973). Fish such as tuna and swordfish, however, are able to concentrate mercury in muscle tissue (Boush and Thieleke, 1983).

Most marine fish contain less than 0.05ug g^{-1} Hg wet weight, the exceptions including species such as the Black Marlin (Hg in liver= 41.6ug g^{-1} dry weight and muscle= 29.2ug g^{-1} dry weight) (Mackay et al., 1975). Cadmium and selenium concentrations are also comparatively high in these species but levels in fish are usually below 0.2ug g^{-1} , 0.50ug g^{-1} and 1ug g^{-1} for cadmium, mercury and selenium respectively (Bryan, 1976). Fish, therefore do not apparently account for the high levels of cadmium, and in four species mercury, in the South Atlantic Procellariiformes. It must be noted that most of the data available are for fish species in the northern hemisphere, but it appears unlikely that unusual accumulations would occur in southern hemisphere fish.

The concentrations of metals found in several of the South Atlantic species exceed levels found in other pelagic seabirds. Concentrations in the Wandering and Sooty Albatrosses, for both cadmium and mercury, are possibly the highest found in any pelagic seabird. Levels of cadmium in the Little and Great Shearwaters, Rockhopper Penguin, Kerguelen, Atlantic and Soft-plumaged Petrels all exceed or are comparable to concentrations found in the Puffin, Manx Shearwater, Sooty tern, Herring Gull, Lesser Black-backed Gull, Wilson's Petrel, Ashy Petrel, Snow Petrel Pagodroma nivea, Fulmar, Common Tern and Crested Terns (Anderlini et al., 1972, Connors et al., 1975; Lande, 1977; Osborn et al., 1979; Howarth et al., 1981; Nicholson, 1981; Stoneburner and Harrison, 1981).

Mercury concentrations in the livers of the Diving Petrel, Rockhopper Penguin, Broad-billed Prion, Great Shearwater, Little

Shearwater and Kerguelen Petrel are comparable to those in the Crested Tern, Fulmar, Puffin and Sooty Tern (Osborn et al., 1979; Howarth et al., 1981; Stoneburner and Harrison, 1981). The Yellow-nosed Albatross, Sooty Albatross, Wandering Albatross, Atlantic Petrel and Soft-plumaged Petrel, however, carry much higher loads of mercury. The levels in these birds are well above that at which signs of mercury poisoning might be expected to appear (25ug g^{-1} wet weight) (Fimreite, 1973). Toxicity, however, is dependent on the proportion of total mercury present as methyl-mercury. Fimreite (1973) and Osborn et al. (1979) have shown that the mercury present is largely as methyl-mercury in Canadian ducks, Fulmars, Puffins and Manx Shearwaters. Mercury residues found in birds experimentally poisoned with methyl-mercury were $17\text{--}20\text{ug g}^{-1}$ wet weight in Red-tailed Hawks Buteo borealis borealis and $103\text{--}144\text{ug g}^{-1}$ wet weight in Goshawks (Borg et al., 1970; Fimreite and Karstad, 1971).

If a high proportion of methyl-mercury was present in the albatrosses, signs of poisoning should be evident, but apparently this was not the case although the Wandering Albatross is declining in numbers. A recent decline would point to anthropogenic sources of toxic metals but this appears unlikely in the southern oceans. Up to 128ug g^{-1} wet weight has been found in the livers of scavenging and fish-eating birds from a contaminated Canadian river system, with symptoms of poisoning only appearing at the highest levels. Great Northern Divers Gavia immer and Red-breasted Mergansers had concentrations of 90.5 and 87ug g^{-1} of mercury respectively in the liver and though the birds appeared healthy they were failing to reproduce (Fimreite, 1973). The albatrosses have concentrations higher than those found in a contaminated system but apparently suffer no ill-effects.

The heavy metal residues in the South Atlantic Procellariiformes

are probably accumulated from the diet. If cadmium is accumulated from food, especially squid, the pattern found (Fig 7.2) explains the elevated levels quite successfully, and the data available on cadmium concentrations in squid and the concentrating abilities of decapods, euphausiids and copepods support this possibility.

Mercury accumulation in the liver of the Procellariiformes is more difficult to explain as concentrations are high in the squid feeders, the Sooty and Wandering Albatrosses and Atlantic and Soft-plumaged Petrels, but not in the Little or Great Shearwaters. The Great Shearwater is a trans-equatorial migrant; each winter the bird migrates to the eastern seaboard of North America where it might be expected to acquire its cadmium load, but this appears not to be the case as it does not explain the high concentrations in the other species. Mercury concentrations in the Great Shearwater are comparatively low and it may be that a change in diet over the wintering period allows excretion of mercury. Again this seems unlikely as squid is still a major component of the diet and it does not account for the reduction in mercury concentration compared to cadmium in other species, for example the Little Shearwater.

The accumulation of these toxic metals therefore appears to be through dietary intake. Cadmium in some cases illustrates a normal distribution although mercury does not (see Chapter 7), indicating possible regulation of cadmium, and this suggestion has also been put forward by Schneider et al. (1985). Schneider et al. (1985) suggest that the similarity in the tissue cadmium concentration of the species analysed indicates that cadmium is metabolically regulated. The cadmium accumulations were very high in the kidney as compared to the liver, suggesting, as in other studies (Furness and Hutton, 1979; Osborn et al., 1979; Howarth et al., 1981; Stoneburner and Harrison,

1981), that the kidney is the main excretion and storage organ for cadmium. The cadmium concentrations in the kidneys of the South Atlantic seabirds are high enough to potentially cause kidney damage in pelagic seabirds (Nicholson et al., 1983; Chapter 8).

Mercury concentrations are usually highest in the liver, and the storage and detoxification of mercury is probably different to that for cadmium. Selenium may also be involved in the detoxification of mercury in seabirds (Furness and Hutton, 1979; Hutton, 1981; Chapter 8).

The highest concentrations of tissue mercury in the Great Skua were found in the liver and the lowest in body fat, which is similar to the results found for Wood Ducks (Lindsay and Dimmick, 1983) and Cory's Shearwater (Renzoni et al., 1986). Vermeer and Armstrong (1972) found the liver to be the main concentrating organ for mercury in waterfowl. The actual values obtained coincide more closely to the data found by Dale et al. (1973) for pelagic seabirds. Kittiwakes, Fulmars and auks had liver concentrations of mercury under 10ug g^{-1} wet weight. Very high liver concentrations of mercury have been found in European and Atlantic Common Seals; one individual from the Netherlands coast contained 200ug g^{-1} Hg in the liver (Heppleston and French, 1973; Koeman et al., 1973).

No attempt was made in this study to determine the chemical form of the mercury in the tissues. In the pelagic seabirds examined by Osborn et al. (1979) most of the mercury in the liver and kidney was in the methylated form, and the tissue distribution of mercury in the Great Skua was similar to that found in organisms dosed with methylmercury (Heinz, 1974).

In the accumulation of metals through the diet it is the initial accumulation of metals from seawater by phytoplankton which provides much of the momentum along the food chain (Preston et al., 1972. Hardy

et al., 1984). Eighteen metals were examined for their ability to bioaccumulate in animal tissues through the food chain by Bryan (1976), but only mercury concentrations in fish were found to exceed those in phytoplankton or seaweed. Mercury was also found to be the least well regulated of the trace metals (Bryan, 1984).

The diet is the principal source of metals in marine mammals and birds and for mercury there is an increase in concentration with trophic level. For example, in the muscle of baleen whales, which feed on krill, mercury concentrations ranged from 0.01 to 0.03ug g⁻¹ mercury, while in the muscle of the Sperm Whale, which feeds on squid and fish, the concentrations ranged from 0.54 to 1.57ug g⁻¹ (Bryan, 1984). Age may also have an effect on the accumulation of metals as this appears to be, in some cases, an important factor (Stoneburner and Harrison, 1981; Bryan, 1984), although this was found not to be the case for the Great Skua.

If the diets of the Procellariiformes comprise, for example, squid carrying high body loads of cadmium, as in the squid from the Pacific (Martin and Flegal, 1975), the birds will inevitably take up considerable quantities of cadmium. Mice have been shown to take into the body 2% of the cadmium given in the diet (Hardy et al., 1984), and even if this was the case for the seabirds they would be accumulating high body loads of cadmium.

In North Atlantic Procellariiformes the concentrations of the toxic metals mercury and cadmium were not as high as in the South Atlantic Procellariiformes. The levels were comparable to those found by Bull et al. (1977) and Dale et al. (1973) in Storm Petrels and Fulmars, but cadmium concentrations were higher in the St Kilda Fulmar (Osborn et al., 1979) than the results given here. For the three species there was a great deal of intraspecific variability in the

concentrations of cadmium, and this was also the case in the study by Bull et al., (1977).

The British Storm Petrel, Leach's Petrel and the Fulmar are all surface feeders taking a variety of copepods, euphausiids (especially Thysanoessa and Meganctiiphanes), amphipods and isopods. The Fulmar also takes offal and sandeels. The concentrations of cadmium in fish and sandeels are usually below 0.65ug g^{-1} Cd wet weight. The liver metal concentrations, although low in the fish sampled, are usually higher than the concentrations in fish muscle. Therefore a diet of offal taken by the Fulmars would increase the metal intake of the birds.

Phytoplankton and zooplankton are able to accumulate quite high concentrations of metals such as iron or zinc, though little data are available for cadmium or mercury accumulations. The Euphausiid Meganctiphanes norvegica had a concentration of cadmium equal to 0.84ug g^{-1} dry weight and this sample came from the Firth of Clyde. Copper or zinc levels in these species cannot be taken as a guide to cadmium levels as these essential metals are concentrated in larger quantities (M. norvegica copper concentrations = 43.3ug g^{-1} , zinc concentrations 43ug g^{-1} dry weight) (P.S. Rainbow, pers. comm.). A mixture of copepods sampled from the North West Atlantic contained $9\text{--}16\text{ng mg}^{-1}$ copper and $0.9\text{--}3.1\text{ng mg}^{-1}$ cadmium dry weight (Windom, 1972). Pelagic Goose Barnacles Lepas anatifera, which are taken by Great Skuas, contain in their soft tissue 69ug g^{-1} Zn dry weight, but no data are available for cadmium or copper (Rainbow, 1975), although benthic barnacles can accumulate up to 50ug g^{-1} Cd dry weight (Rainbow and White, unpubl.).

It therefore appears that the cadmium is accumulated naturally rather than from anthropogenic sources, and it has been postulated that the birds have evolved, through natural selection, mechanisms

which enable them to tolerate potentially toxic metals, a factor discussed in the following chapter. However, a lack of detailed knowledge of the diets of these seabirds has made it difficult to reach any firm conclusions as to the source of the metals.

CHAPTER 7

CORRELATIONS BETWEEN CONCENTRATIONS OF DIFFERENT ELEMENTS AND BETWEEN CONCENTRATIONS IN DIFFERENT TISSUES

7.1 INTRODUCTION

Information concerning tissue concentrations of heavy metals in seabirds is relatively scarce (Anderlini et al., 1972; Bull et al., 1977; Parslow and Jefferies, 1977; Osborn et al., 1979; Osborn, 1979; Schneider et al., 1985). Cadmium and mercury are of interest because they have no proven requirement in any physiological process and may be toxic to organisms. As the elements cadmium and mercury are chemically similar to copper and zinc, the aim of this part of the study was to identify any correlations between the metals of biological significance.

Copper and zinc are essential metals for the functioning of many enzymes and proteins in animal tissues, and are therefore required as part of the diet. Zinc and cadmium may act antagonistically towards copper (Bremner, 1978), and the physiological accumulation of zinc has been found to be accompanied by cadmium accumulation in the tissues of seabirds (Osborn et al., 1979). Correlations between the metals were thus looked for to observe any trends in the accumulation of zinc and cadmium between species. This relationship was of especial interest as cadmium is known to interfere with zinc metabolism (Bremner, 1978).

In this study a large number of seabirds was available in which to examine any trends in metal accumulation with diet or any relationships between the metals, especially correlations between zinc and cadmium. Although this was the case for most species, only a small sample was available for some of the others.

The data for cadmium and mercury were not always normally distributed, although the test for skewness showed that both the essential and non-essential elements were skewed and normally

Table 7.1 Relationships between the metals copper and cadmium in the kidney and liver of North and South Atlantic Great Skuas and Procellariiformes

SPECIES	n	KIDNEY		LIVER	
		r	r _s	r	r _s
South Atlantic Great Skua	13	0.319	0.481	0.471	0.570*
North Atlantic Great Skua	47	0.593***	0.526***	0.362*	0.332*
Sooty Albatross	8	-0.638	-0.419	0.598	0.575
Yellow-nosed Albatross	9	0.409	0.661*	0.600	0.377
Great Shearwater	12	0.447	0.417	0.001	-0.067
Little Shearwater	13	0.259	0.319	0.715**	0.526
Atlantic Petrel	13	0.522	0.498	-0.027	0.456
Soft-plumaged Petrel	18	0.175	0.130	0.096	0.330
Kerguelen Petrel	14	0.069	0.377	-0.528	-0.141
Broad-billed Prion	31	0.282	0.364*	0.390*	0.328
Common Diving Petrel	17	0.478	0.470	0.502*	0.547*
Grey-backed Storm Petrel	8	0.190	0.393	0.631	-0.084
White-bellied Storm Petrel	8	-0.599	-0.524	0.461	0.398
Rockhopper Penguin	12	0.379	0.568	0.277	0.371
Fulmar	25	0.264	0.255	0.028	-0.027
Leach's Petrel	13	0.529	0.489	0.664*	0.669*

distributed (Snedecor, 1946). The non-parametric Spearman's Rank correlation (r_s) was therefore used together with the Product-moment correlation (r). In most cases the value for Spearman's Rank test is taken as the value of significance, but the Product-moment correlation is included as some of the data is normally distributed. For examination of sexual differences in metal accumulation the non-parametric Mann-Whitney U-test was used. Significance values (p) are represented in the text as follows:- $*=p<0.05$, $**=p<0.01$ and $***=p<0.001$.

7.2 RELATIONSHIPS BETWEEN COPPER AND CADMIUM IN THE GREAT SKUAS AND PROCELLARIIFORMES

In order to identify any general trends for all the species, the relationships between copper and cadmium are summarised in Table 7.1. Overall, very few significant correlations exist between cadmium and copper, existing only in the kidney of the North Atlantic Great Skua (Fig 7.1), Yellow-nosed Albatross (Fig 7.2) and Broad-billed Prion, and in the liver of the North and South Atlantic Great Skuas, Little Shearwater (Fig 7.3), Common Diving Petrel, Broad-billed Prion and Leach's Petrel. Some of the results are not significant, though giving a high correlation coefficient, because of the small sample size. For example the coefficient is greater for the relationship between cadmium and copper in the kidney of the Sooty Albatross than the statistically significant value for the North Atlantic Great Skua. This trend for the Sooty Albatross was reversed in the liver (Figs 7.4 & 7.5).

The North Atlantic Great Skua had highly significant relationships in the kidney between the metals copper, zinc and cadmium. These relationships were only weakly significant in the liver and there were no correlations between the metals in the muscle tissue. The

Fig 7.1 Relation between cadmium and copper concentrations ($\mu\text{g g}^{-1}$, wet weight) in the kidney tissue of the North Atlantic Great Skua Catharacta skua skua ($r=0.593$, $y=0.07x + 4.16$, $n=47$).

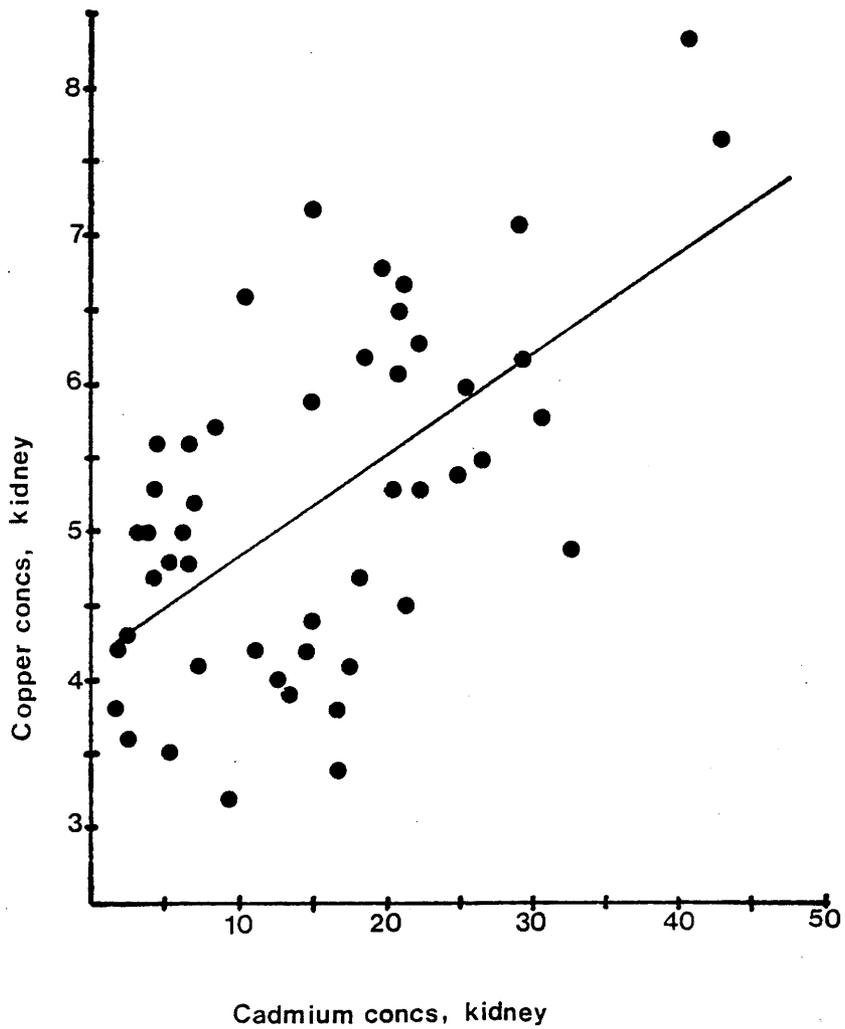


Fig 7.2 Relation between cadmium and copper concentrations (log values, $\mu\text{g g}^{-1}$, wet weight) in the kidney tissue of the Yellow-nosed Albatross Diomedea chlorhynchus ($r=0.534$, $y=0.87x + 0.93$, $n=9$).

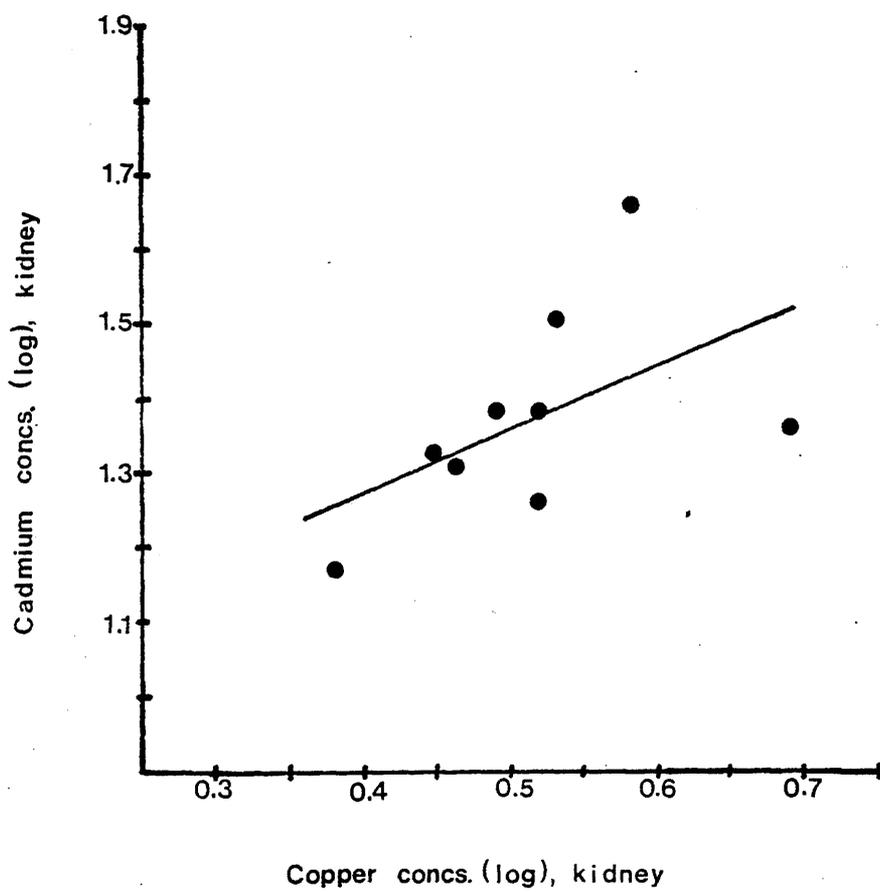


Fig 7.3 Relation between copper and cadmium concentrations ($\mu\text{g g}^{-1}$, log values, wet weight) in the liver of the Little Shearwater Puffinus assimilis ($r=0.679$, $y=1.22x + 0.05$, $n=12$).

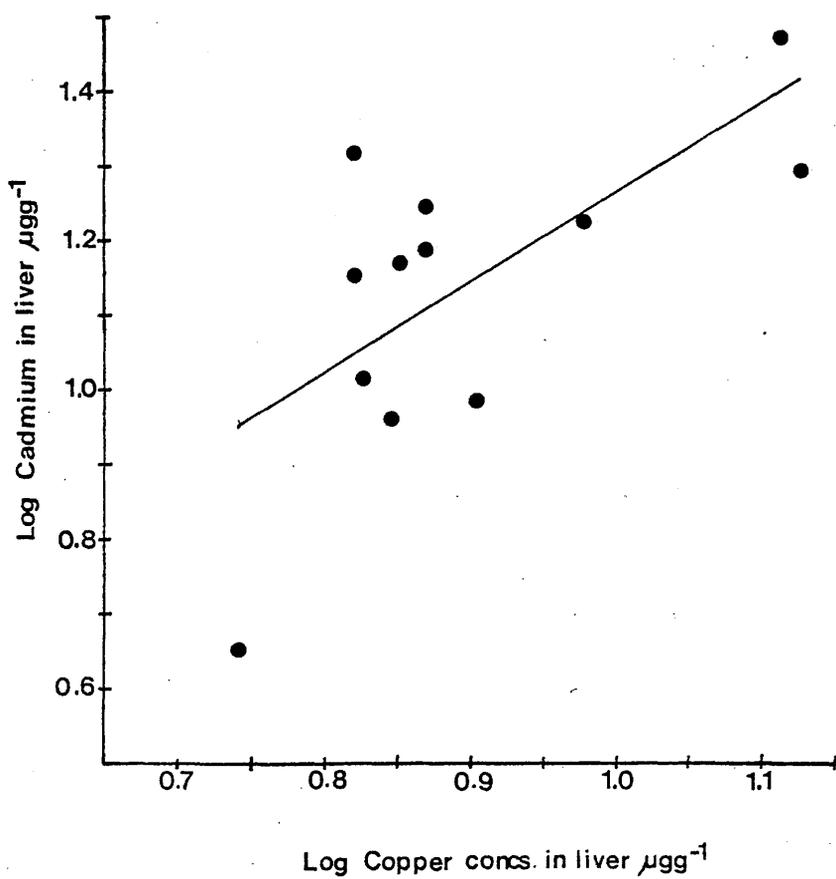


Fig 7.4 Relation between copper and cadmium concentrations ($\mu\text{g g}^{-1}$, wet weight) in the kidney of the Sooty Albatross Phoebastria fusca ($r=-0.638$, $y=-22.12x + 178.68$, $n=8$).

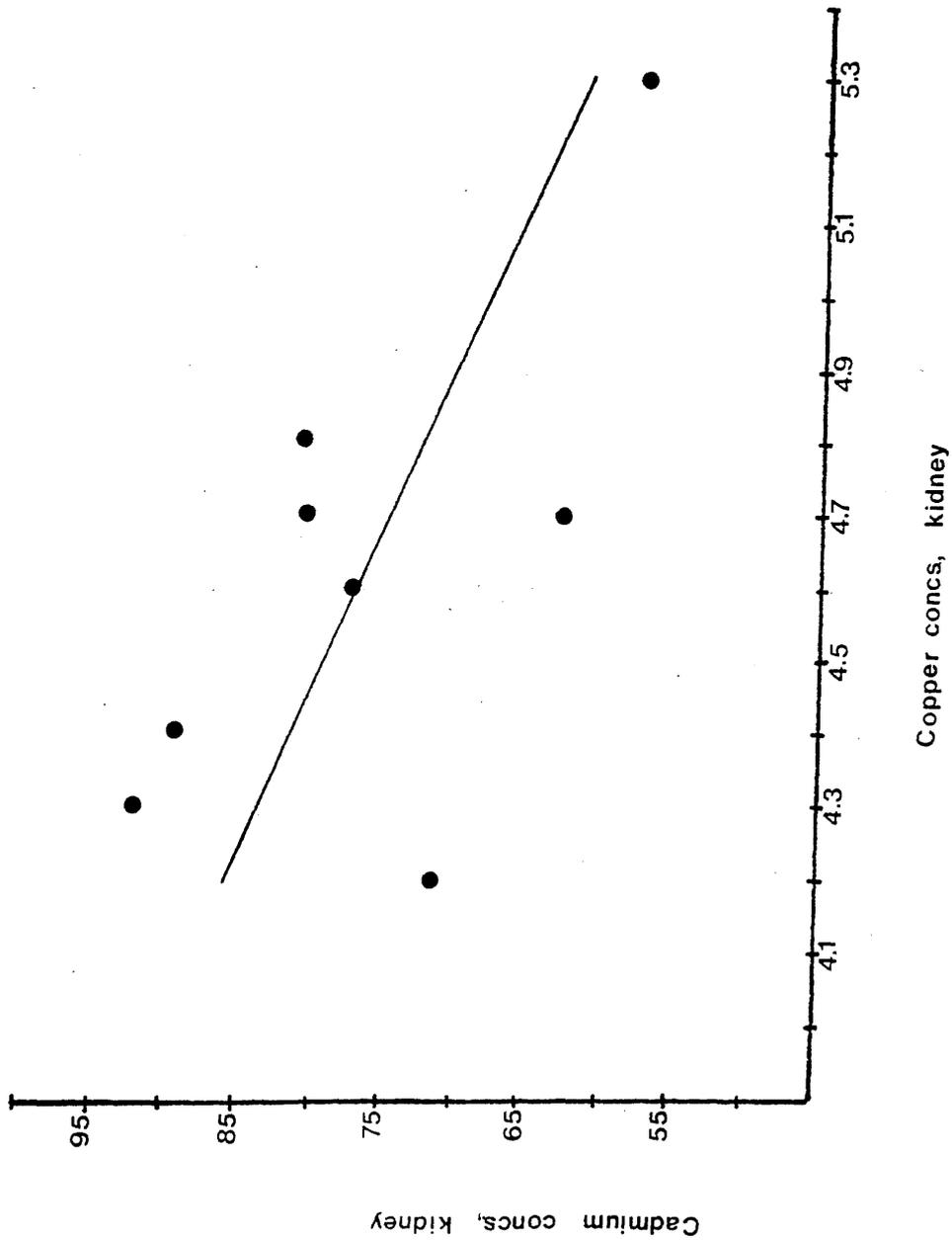
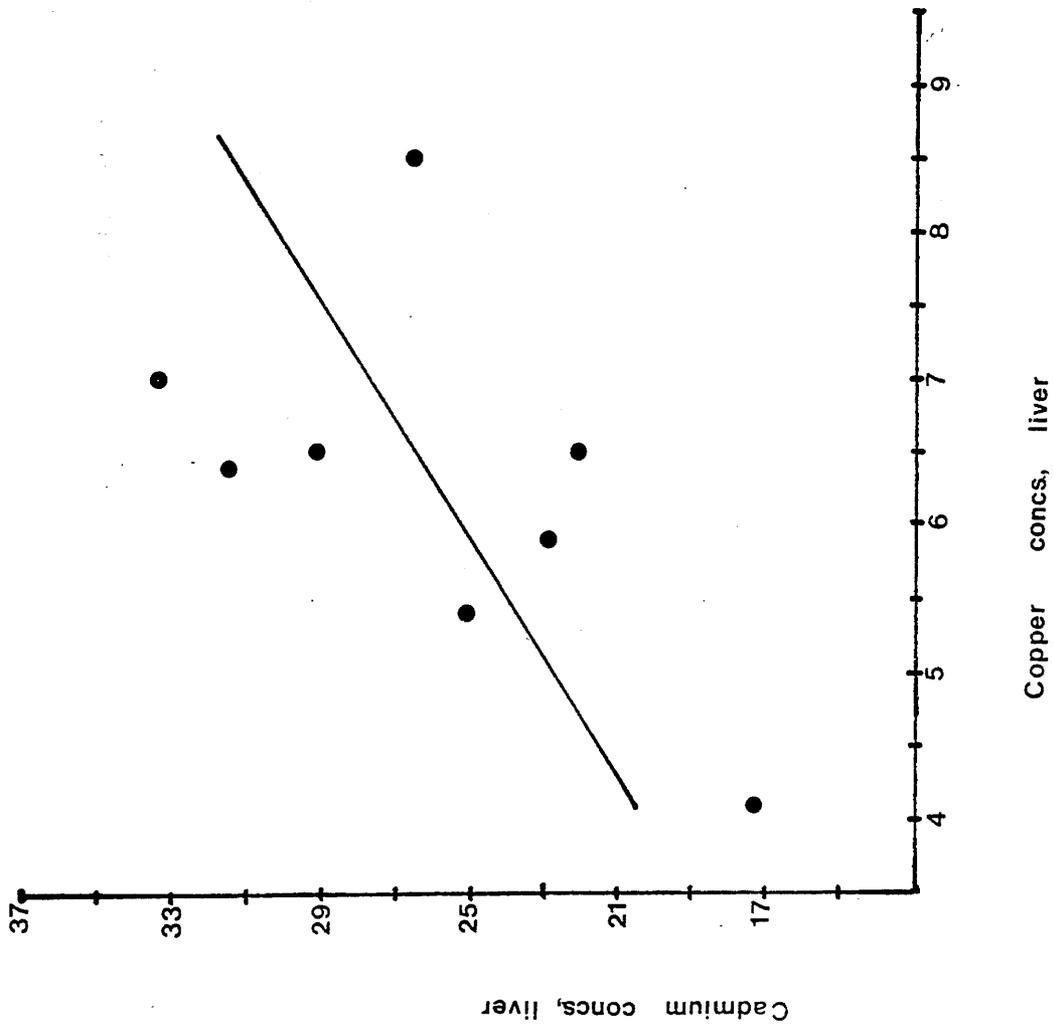


Fig 7.5 Relation between cadmium and copper concentrations ($\mu\text{g g}^{-1}$, wet weight) in the liver of the Sooty Albatross Phoebastria fusca ($r=0.598$, $y=2.50x + 10.28$, $n=8$).



correlation coefficients (Tables 7.1 and 7.4) were stronger than for the South Atlantic Great Skua, but this may have been assisted by the larger sample size for the North Atlantic Great Skua.

Copper and cadmium concentrations in the liver of the Kerguelen Petrel appear to show a strong trend towards a significant negative correlation but examination of the data and non-parametric tests show an outlying point which heavily biases the data. Without this point there is no correlation within the data. A negative relationship between copper and cadmium was found in the kidney of the White-bellied Storm Petrel.

7.3 RELATIONSHIPS BETWEEN ZINC AND CADMIUM IN THE LIVER AND KIDNEY OF THE GREAT SKUAS AND PROCELLARIIFORMES

The number of positive significant relationships between cadmium and zinc for all species were greater than for cadmium and copper. There was, however, considerable variability between the species. The Yellow-nosed Albatross (Fig 7.6), Great Shearwater (Fig 7.7) and Broad-billed Prion, Common Diving Petrel and Soft-plumaged Petrel show highly significant correlations between zinc and cadmium levels in the liver. The Rockhopper Penguin had highly significant relationships between the two metals in both the kidney and the liver (Figs 7.8 & 7.9).

Most species show weak or strong correlations in either the liver or the kidney. The exceptions to this are the Atlantic Petrel and the Grey-backed Storm Petrel, although the latter may be too small a sample to be of statistical significance. The relationship between zinc and cadmium in the kidney was highly significant in the South and North Atlantic Great Skuas (Figs 7.10 & 7.11), the Soft-plumaged Petrel (Fig 7.12), Common Diving Petrel, Leach's Petrel (Fig 7.13),

Fig 7.6 Relation between zinc and cadmium concentrations ($\mu\text{g g}^{-1}$, log values wet weight) in the liver of the Yellow-nosed Albatross Diomedea chlorhynchos ($r=0.951$, $y=2.07x - 2.57$, $n=9$).

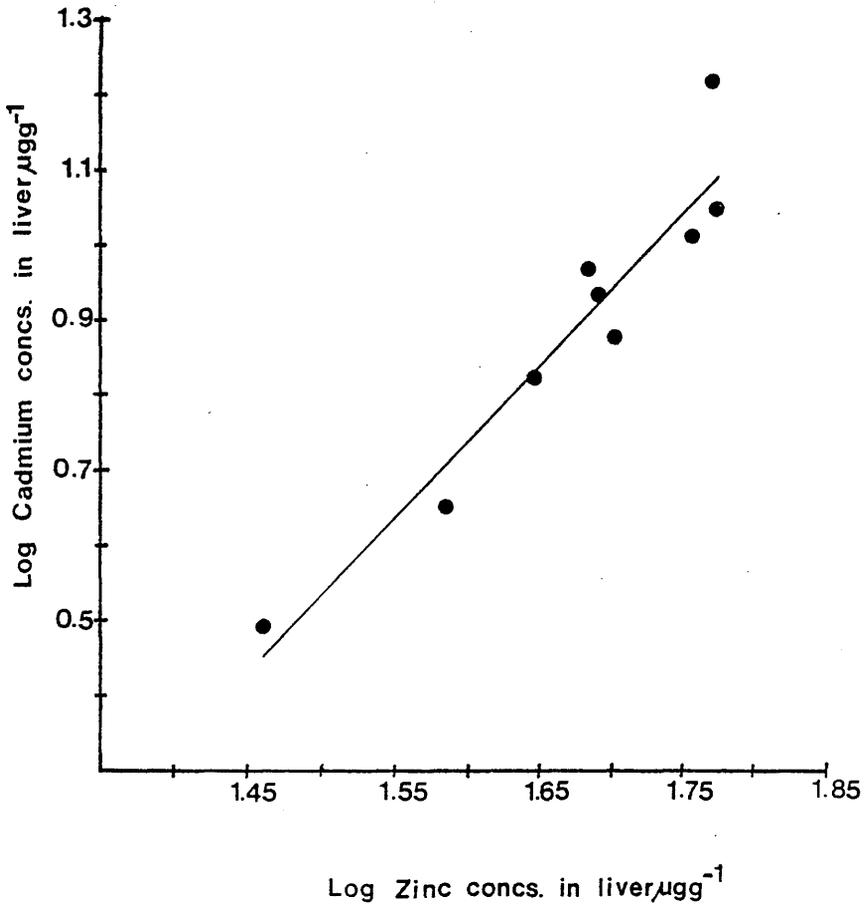


Fig 7.7 Relation between zinc and cadmium concentrations ($\mu\text{g g}^{-1}$, log values, wet weight) in the liver of the Great Shearwater Puffinus gravis ($r=0.747$, $y=3.36x - 4.16$, $n=12$).

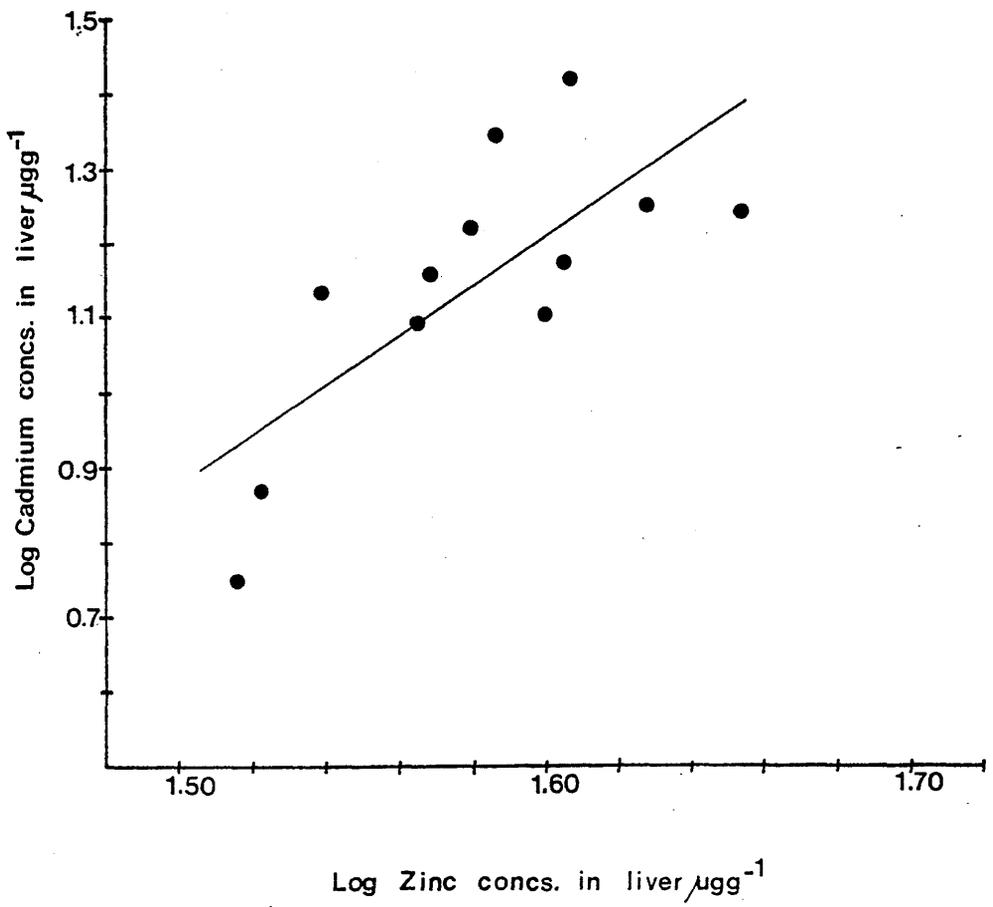


Fig 7.8 Relation between cadmium and zinc concentrations ($\mu\text{g g}^{-1}$, wet weight) in the kidney of the Rockhopper Penguin Eudyptes chrysocone ($r=0.806$, $y=1.43x - 18.67$, $n=12$).

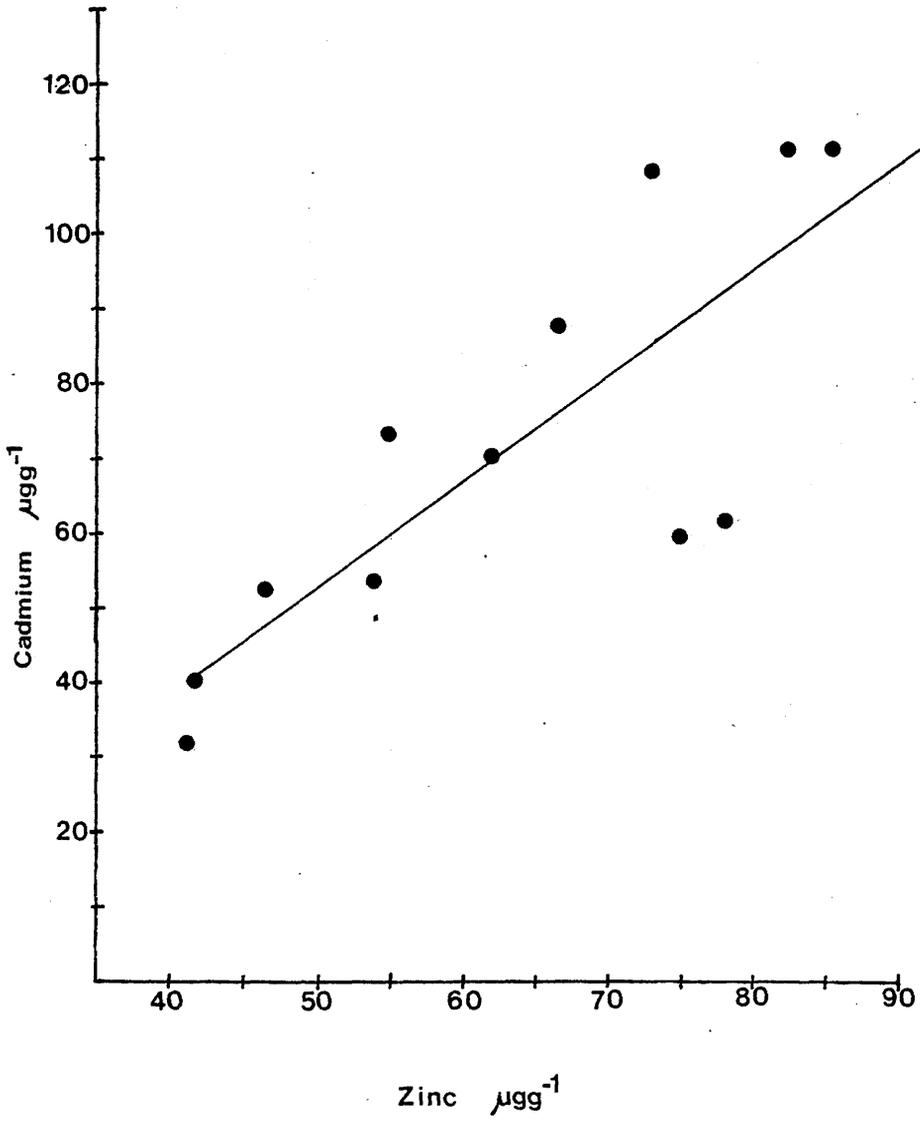


Fig 7.9 Relation between cadmium and zinc concentrations ($\mu\text{g g}^{-1}$, wet weight) in the liver of the Rockhopper Penguin Eudyptes chrysocome ($r=0.850$, $y=0.53x - 6.61$, $n=12$)

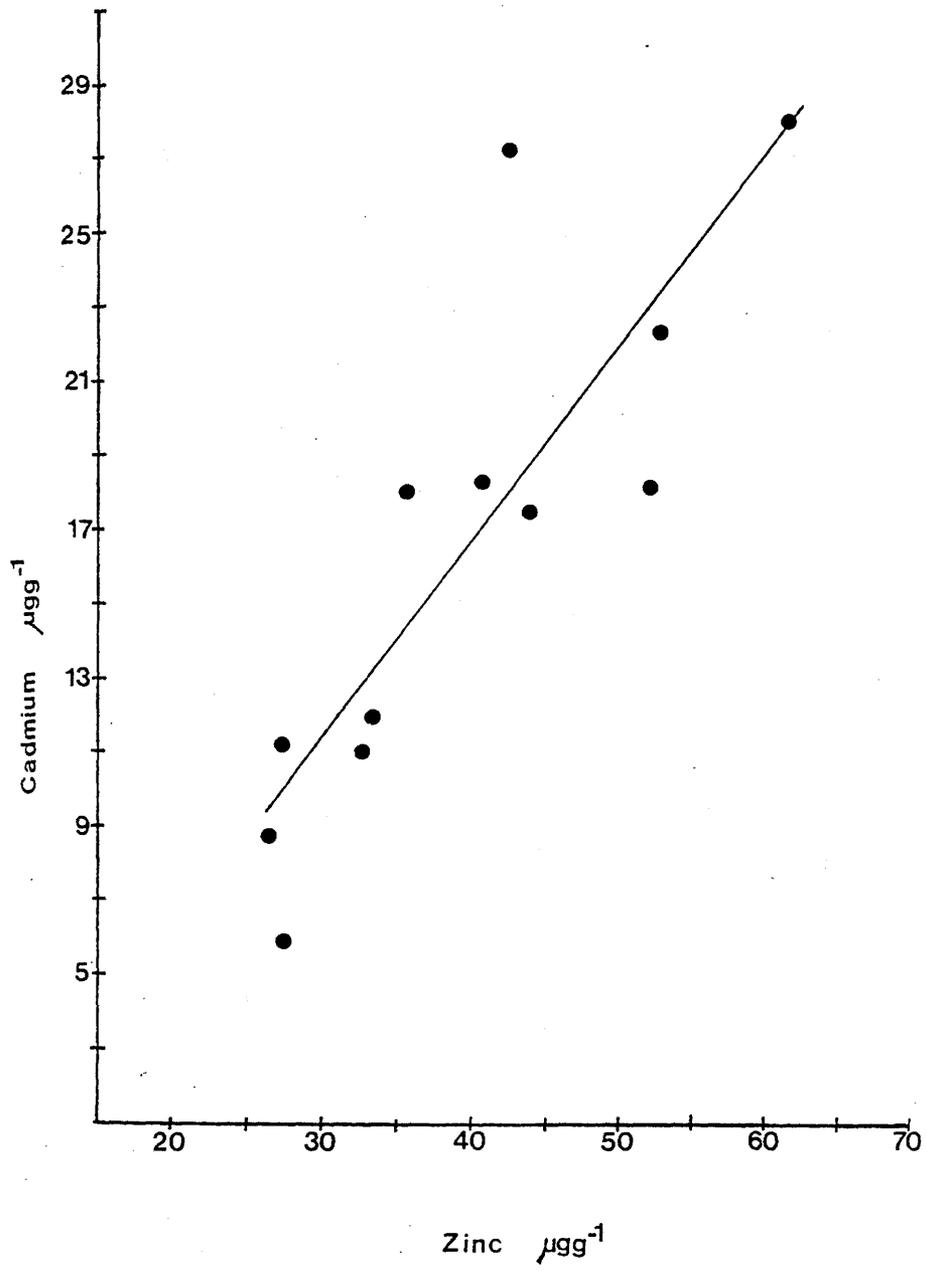


Fig 7.10 Relation between cadmium and zinc concentrations ($\mu\text{g g}^{-1}$, wet weight) in the kidney of the South Atlantic Great Skua Catharacta skua hamiltoni ($r=0.834$, $y=1.11x - 15.32$, $n=13$).

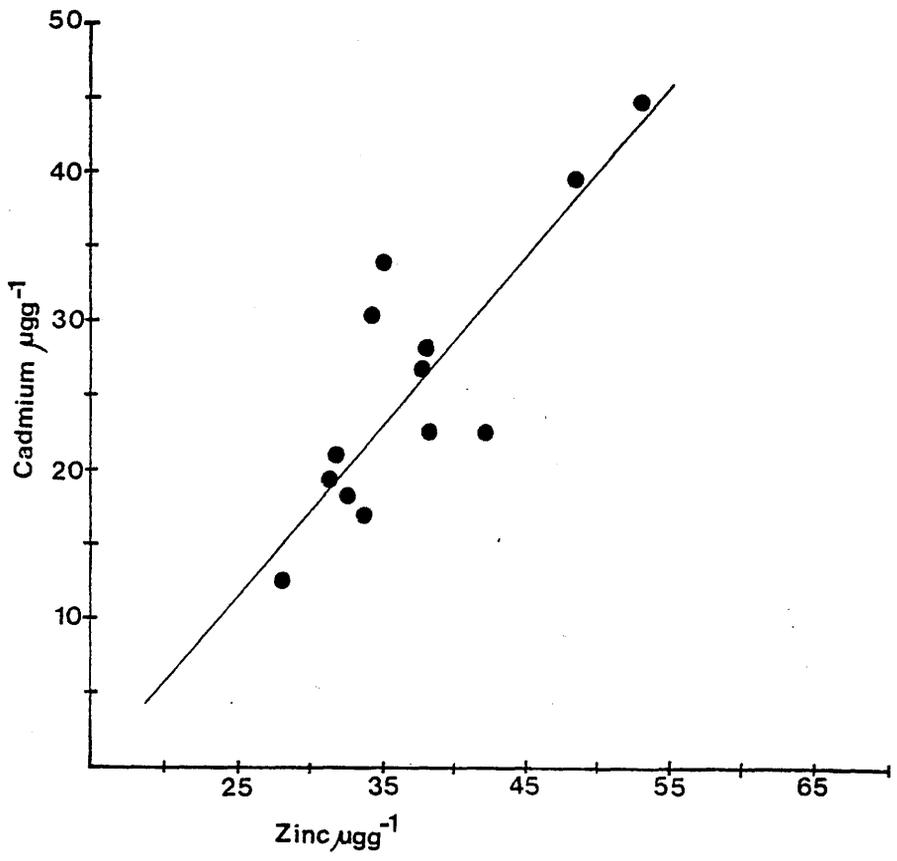


Fig 7.11 Relation between cadmium and zinc concentrations ($\mu\text{g g}^{-1}$, wet weight) in the kidney of the North Atlantic Great Skua Catharacta skua skua ($r=0.834$, $y=0.80x + 29.13$, $n=47$).

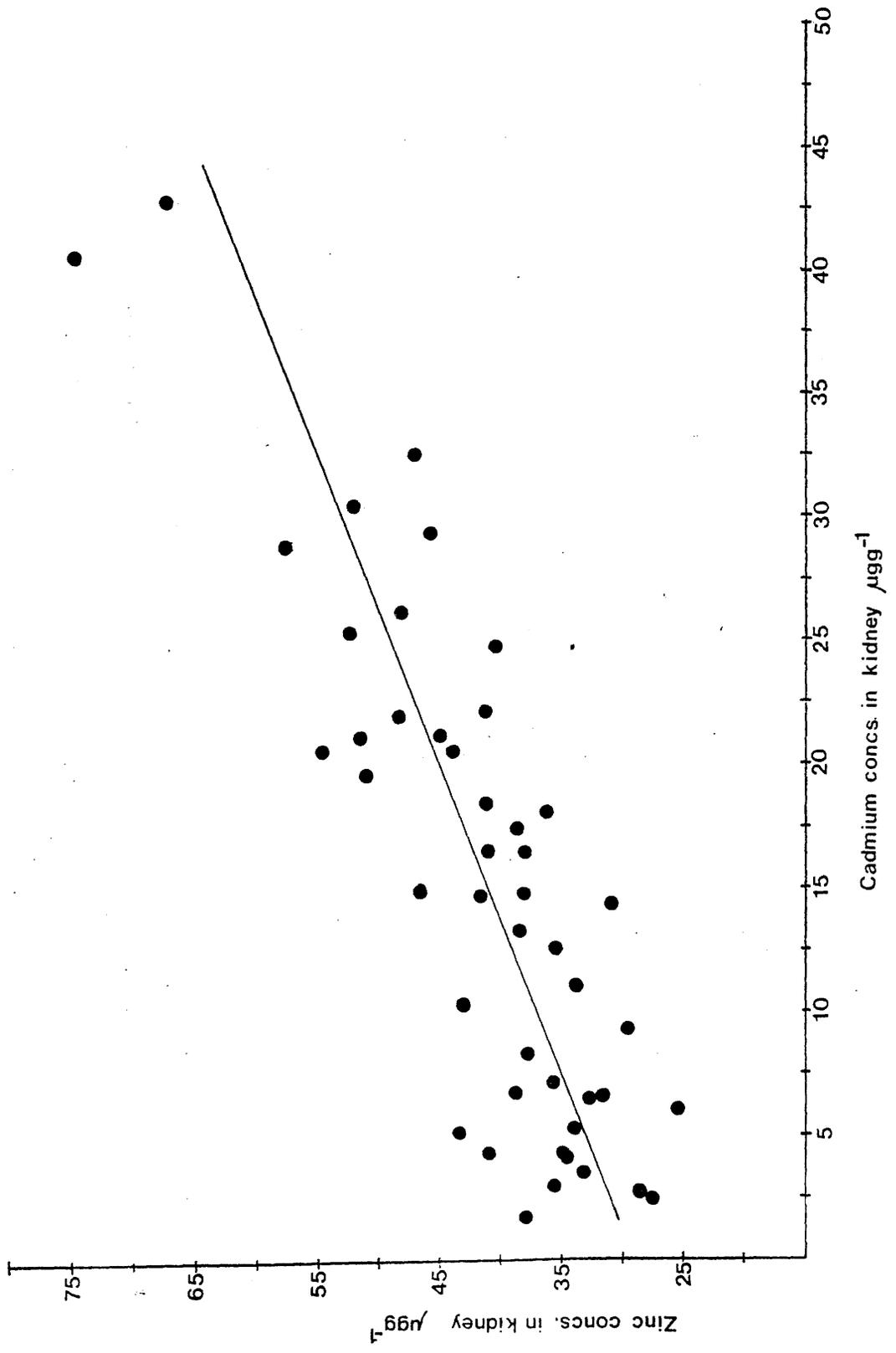


Fig 7.12 Relation between zinc and cadmium concentrations ($\mu\text{g g}^{-1}$, log values, wet weight) in the kidney of the Soft-plumaged Petrel Pterodroma mollis ($r=0.774$, $y=1.03x - 0.05$, $n=18$).

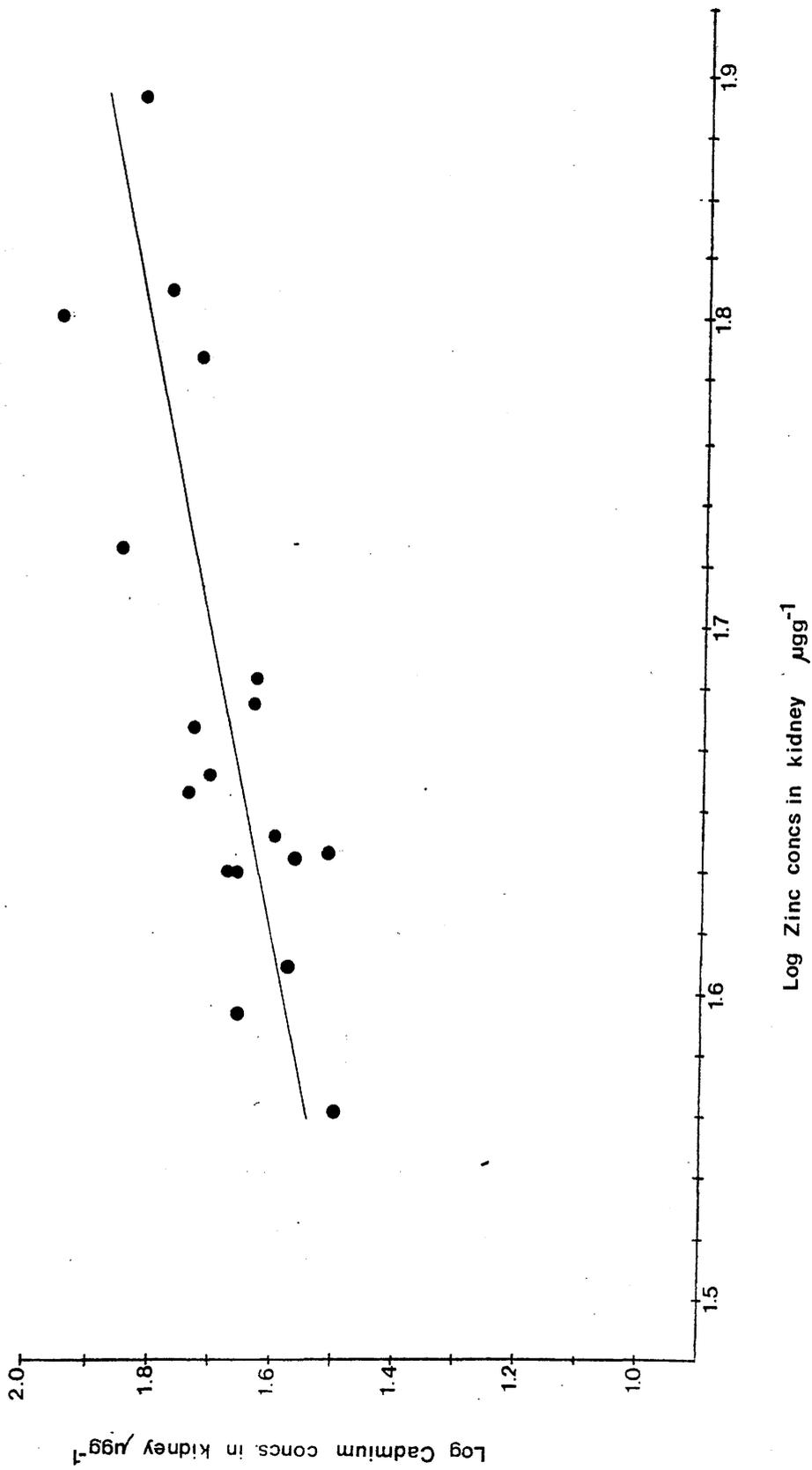


Fig 7.13 Relation between zinc and cadmium concentrations ($\mu\text{g g}^{-1}$, wet weight) in the kidney of Leach's Petrel Oceanodroma leucorhoa ($r=0.694$, $y=0.96x + 7.6$, $n=13$).

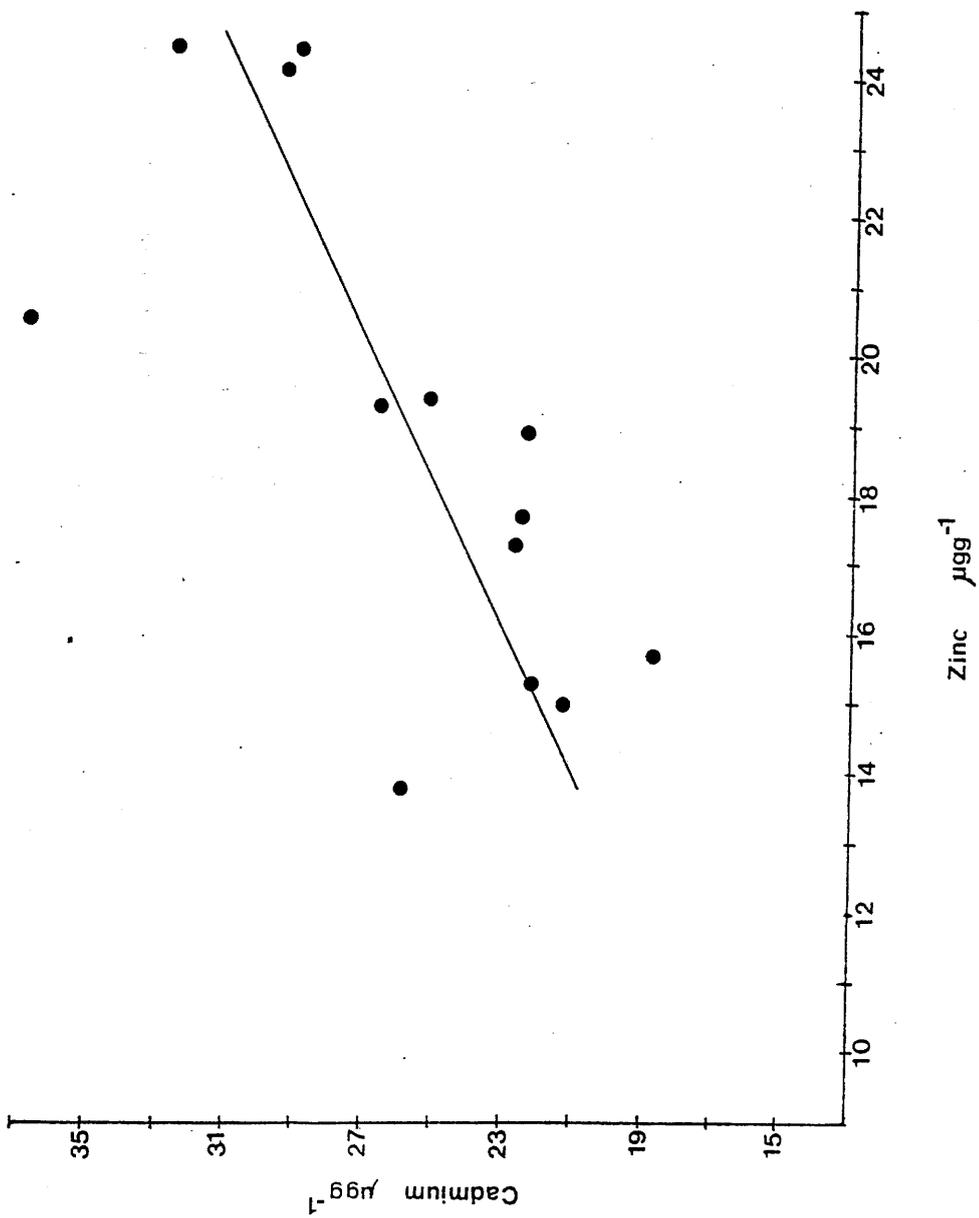


Table 7.2 Relationships between cadmium and zinc in the liver and kidney of South and North Atlantic Great Skuas and Procellariiformes

SPECIES	n	KIDNEY		LIVER	
		r	r _s	r	r _s
South Atlantic Great Skua	13	0.834**	0.769**	0.450	0.637*
North Atlantic Great Skua	47	0.834***	0.798***	0.306*	0.352*
Sooty Albatross	8	0.707*	0.691	0.386	0.286
Yellow-nosed Albatross	9	0.101	0.233	0.878***	0.917***
Great Shearwater	12	0.392	0.315	0.663*	0.790**
Little Shearwater	13	0.559*	0.611*	0.621*	0.604*
Atlantic Petrel	13	0.351	0.357	0.367	0.363
Soft-plumaged Petrel	18	0.746***	0.727***	0.528*	0.591**
Kerguelen Petrel	14	0.760**	0.748**	0.469	0.590*
Broad-billed Prion	31	0.179	0.272	0.580**	0.484*
Common Diving Petrel	17	0.914***	0.728***	0.543*	0.644**
Grey-backed Storm Petrel	8	-0.117	-0.143	0.320	0.524
White-bellied Storm Petrel	8	0.870**	0.762*	0.645	0.419
Rockhopper Penguin	12	0.805***	0.823***	0.850***	0.867***
Fulmar	25	0.207	0.491*	0.263	-0.135
Leach's Petrel	13	0.694**	0.754**	0.427	0.418

Kerguelen Petrel and the Rockhopper Penguin (Table 7.2). There was also a weak relationship between zinc and cadmium in the kidney of the Sooty Albatross (Fig 7.14).

The South Atlantic Great Skua showed few strong correlations between metals. The highest correlation was for zinc and cadmium in the kidney with a much weaker relationship in the liver. The Little Shearwater shows a weak relationship between cadmium and zinc in the kidney and liver. The Soft-plumaged Petrel showed significant relationships between zinc and cadmium in both the kidney and liver and the only significant correlations between metals in the tissues of the Kerguelen Petrel were for zinc and cadmium concentrations in the kidney. Both Leach's Petrel and the Fulmar had significant correlations between zinc and cadmium in the kidney.

7.4 RELATIONSHIPS BETWEEN CADMIUM CONCENTRATIONS IN THE LIVER AND KIDNEY OF THE SKUAS AND PROCELLARIIFORMES

A significantly positive correlation exists between cadmium concentrations in the liver and kidney for some of the study species (Table 7.3). Species such as the Fulmar show a highly significant correlation between cadmium concentrations in the liver and kidney but the relationship between zinc and cadmium is weak for the kidney. The Rockhopper Penguin shows the reverse of this with a weak correlation for cadmium concentrations in the liver and kidney, but highly significant relationships between cadmium and zinc in both the liver and kidney.

There was a highly significant relationship between cadmium concentrations in the kidney and liver of the South Atlantic Great Skua ($r=0.978$, $p<0.001$; $r_s=0.962$, $p<0.001$; Fig 7.15). Since there is a relationship between zinc and cadmium in the kidney and in the liver,

Fig 7.14 Relation between zinc and cadmium concentrations ($\mu\text{g g}^{-1}$, log values, wet weight) in the kidney of the Sooty Albatross Phoebetria fusca ($r=0.693$, $y=0.78x + 0.54$).

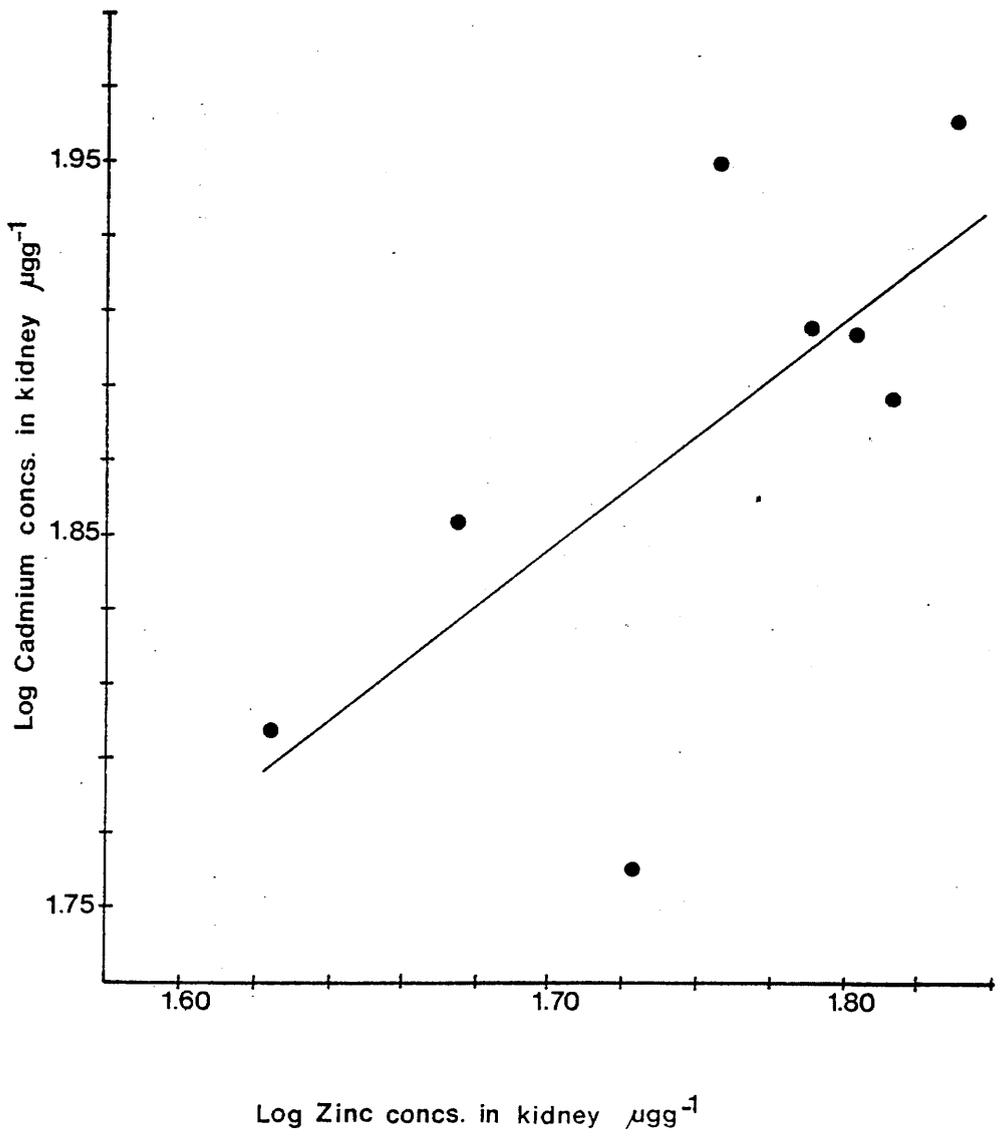


Fig 7.15 Relation between cadmium concentrations ($\mu\text{g g}^{-1}$, wet weight) in the liver and kidney of the South Atlantic Great Skua Catharacta skua hamiltoni ($r=0.978$, $y=0.14x - 0.96$, $n=13$).

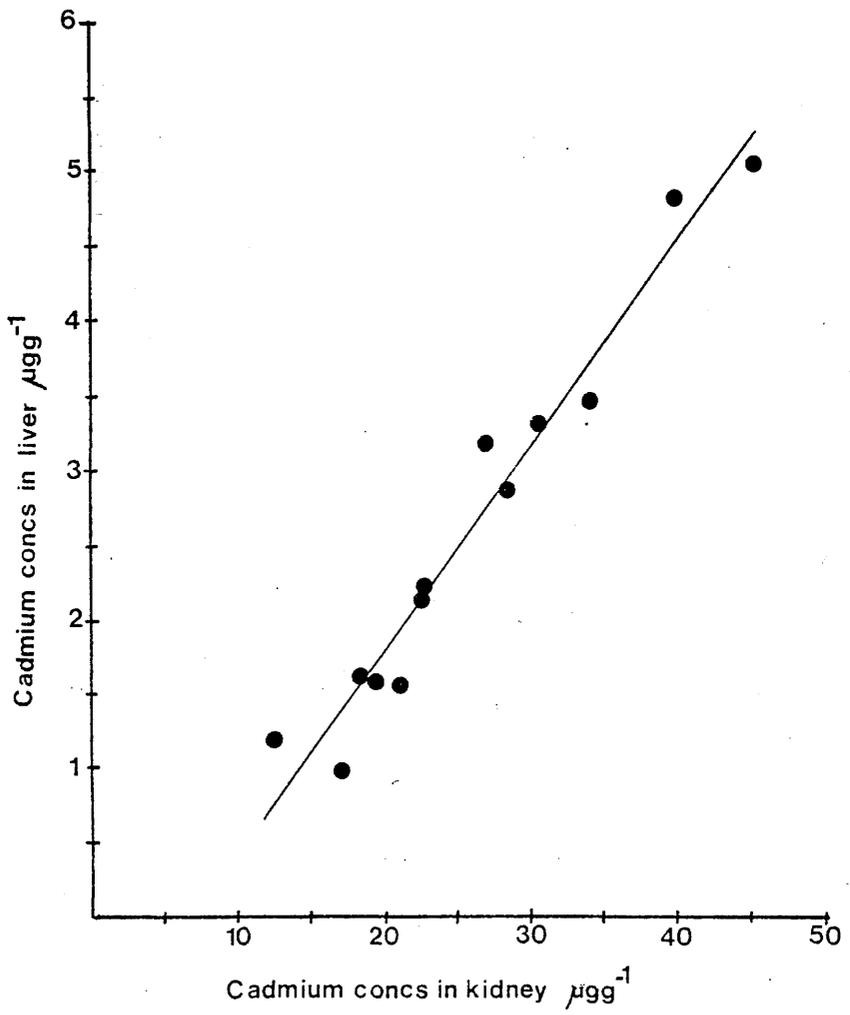


Table 7.3 Relationships between cadmium concentrations in the liver
and kidney of the North and South Atlantic Great Skuas and
Procellariiformes

SPECIES	n	KIDNEY v LIVER	
		r	r _s
South Atlantic Great Skua	13	0.978 ^{***}	0.962 ^{***}
North Atlantic Great Skua	47	0.847 ^{***}	0.839 ^{***}
Sooty Albatross	8	0.144	0.238
Yellow-nosed Albatross	9	0.453	0.767 [*]
Great Shearwater	12	0.373	0.392
Atlantic Petrel	13	0.783 ^{**}	0.857 ^{***}
Little Shearwater	13	0.577 [*]	0.582 [*]
Soft-plumaged Petrel	18	0.675	0.395
Kerguelen Petrel	14	0.733 ^{**}	0.680 ^{**}
Broad-billed Prion	31	0.376	0.422 [*]
Common Diving Petrel	17	0.322	0.679 ^{**}
Grey-backed Storm Petrel	8	0.002	-0.143
White-bellied Storm Petrel	8	0.239	0.252
Rockhopper Penguin	12	0.525	0.571
Fulmar	25	0.902 ^{***}	0.841 ^{***}
Leach's Petrel	13	0.786 ^{**}	0.786 ^{**}

it may be expected that there is a relationship between zinc in the kidney and the liver and this is in fact the case, although it is a much weaker ($r=0.673$, $p<0.05$; $r_s=0.621$, $p<0.05$). For the North Atlantic Great Skua a highly significant relationship was found between cadmium concentrations in the liver and kidney (Fig 7.16), but no relationship was found between zinc concentrations in the liver and kidney as found in the South Atlantic Great Skua.

A positive but non-significant relationship was found for the cadmium concentrations in the liver and kidney of the British Storm Petrel ($r=0.745$, $r_s=0.786$) although a much weaker relationship was found between liver and kidney zinc concentrations ($r=0.284$).

A significant correlation was found for cadmium concentrations in the liver and kidney of Leach's Petrel ($r=0.786$, $p<0.01$; $r_s=0.758$, $p<0.01$), and for zinc between the liver and kidney ($r=0.566$, $p<0.05$).

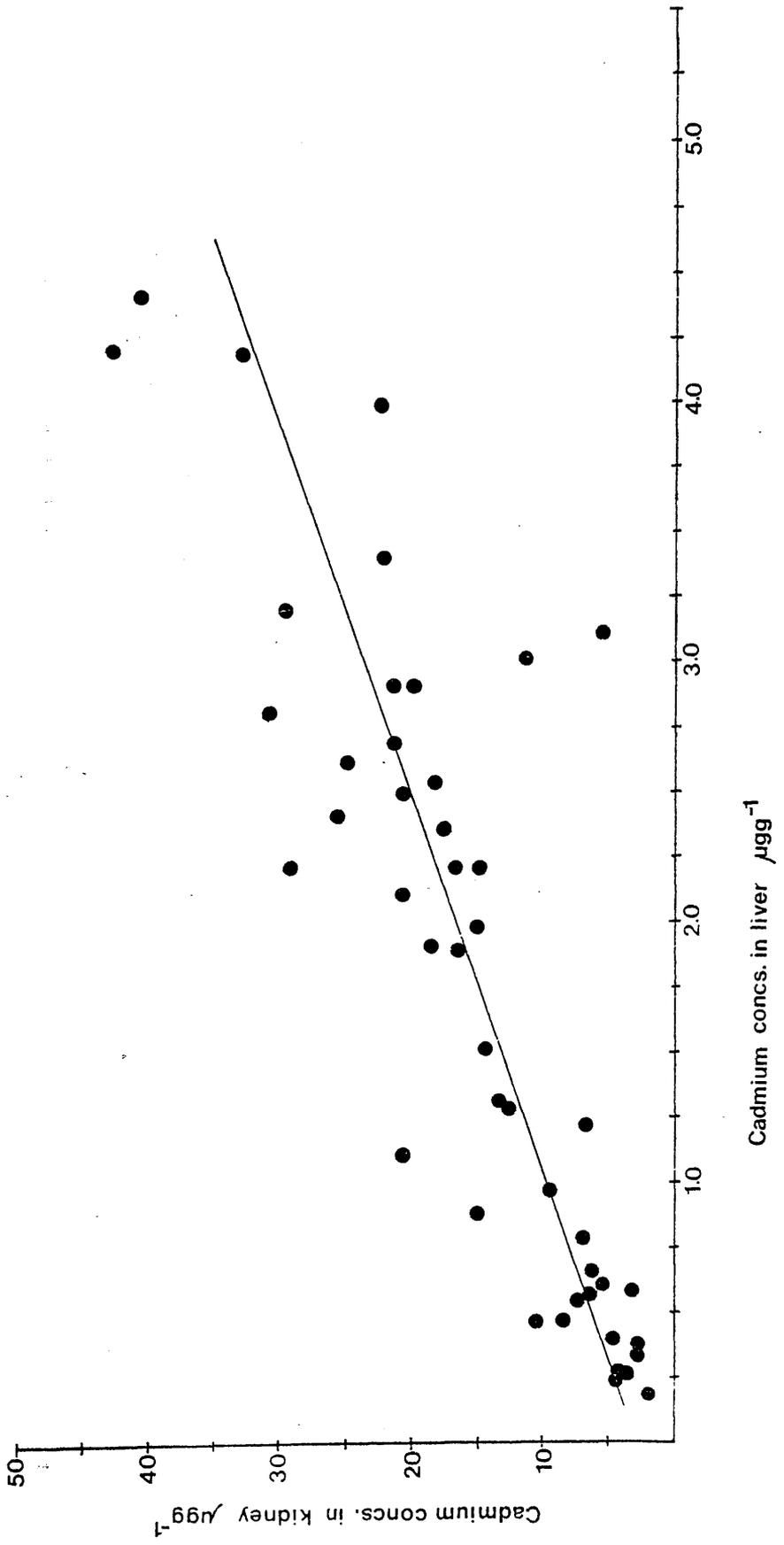
Cadmium concentrations in the liver and kidney of the Fulmar were highly significantly correlated ($r_s=0.841$, $p<0.001$), while the relationship for zinc concentrations was only weak ($r=0.500$, $p<0.05$).

The relationship between cadmium concentrations in the liver and kidney of the Rockhopper Penguin was not significant ($r=0.525$, $r_s=0.571$), but the relationship was significant for zinc ($r=0.776$, $p<0.01$).

Cadmium kidney and liver concentrations showed no significant relationships in the White-bellied Storm Petrel and Grey-backed Storm Petrels, but were significantly correlated in the White-faced Storm Petrel ($r_s=0.823$, Table 7.3). For the Common Diving Petrel, liver and kidney cadmium concentrations were significantly correlated when using Spearman's rank correlation and log-transformed data as appropriate ($r_s=0.679$ $p<0.001$; log-transformed data $r=0.537$, $p<0.05$).

The Broad-billed Prion showed a significant but weak relationship between cadmium concentrations in the liver and kidney ($r_s=0.422$,

Fig 7.16 Relation between cadmium concentrations ($\mu\text{g g}^{-1}$, wet weight) in the liver and kidney of the North Atlantic Great Skua Catharacta skua skua ($r=0.845$, $y=6.98x + 2.83$, $n=47$).



$p < 0.05$). Zinc concentrations in the liver and kidney were more significantly correlated ($r = 0.517$, $p < 0.01$).

A significant relationship was found between kidney and liver cadmium concentrations for the Soft-plumaged Petrel (Fig 7.17) and the Kerguelen Petrel (Fig 7.18). The relationship between cadmium liver and kidney concentrations were highly significant (Fig 7.19) for the Atlantic Petrel but this species showed no other significant relationships between metals in the liver or kidney. Zinc concentrations in the liver and kidney, although positively correlated, were not significant ($r = 0.496$).

Cadmium concentrations in the kidney and liver of the Little Shearwater were positively correlated at the 5% level (Fig 7.20), but in the Great Shearwater no significant correlations were found between cadmium or zinc in the liver and kidney.

The relationship for cadmium in the liver and kidney of the Yellow-nosed Albatross was only weakly significant at the 5% level for Spearman's rank correlation ($r_s = 0.767$, $p < 0.05$) and no relationship was found between liver and kidney zinc concentrations ($r = 0.464$). There was no relationship between cadmium in the liver and kidney of the Sooty Albatross, though a more positive relationship was found between liver and kidney zinc concentrations ($r = 0.639$, $n = 8$).

7.5 RELATIONSHIPS BETWEEN COPPER AND ZINC IN LIVER AND KIDNEY TISSUE OF NORTH AND SOUTH ATLANTIC PROCELLARIIFORMES AND GREAT SKUAS

The strongest relationships between copper and zinc were found in the kidney of the North Atlantic Great Skua (Fig 7.21) and Great Shearwater and White-bellied Storm Petrel, with the relationship in this latter species being strongly negative. In the liver of the Common Diving Petrel a highly significant relationship was found in the liver between copper and zinc. A positive relationship was found for the

Fig 7.17 Relation between cadmium concentrations ($\mu\text{g g}^{-1}$, wet weight) in liver and kidney of the Soft-plumaged Petrel Pterodroma mollis ($r=0.675$, $y=0.38x - 2.34$, $n=18$).

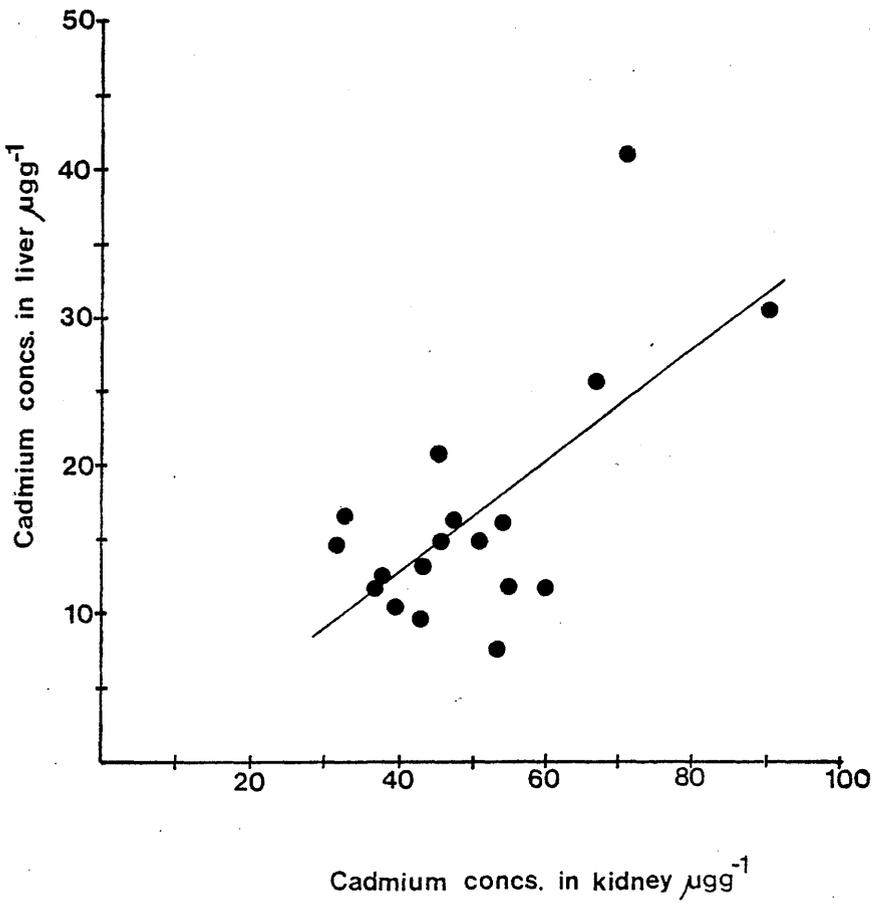


Fig 7.18 Relation between cadmium concentrations ($\mu\text{g g}^{-1}$, wet weight) in the liver and kidney of the Kerguelen Petrel Pterodroma brevirostris ($r=0.733$, $y=0.23x + 5.02$, $n=14$).

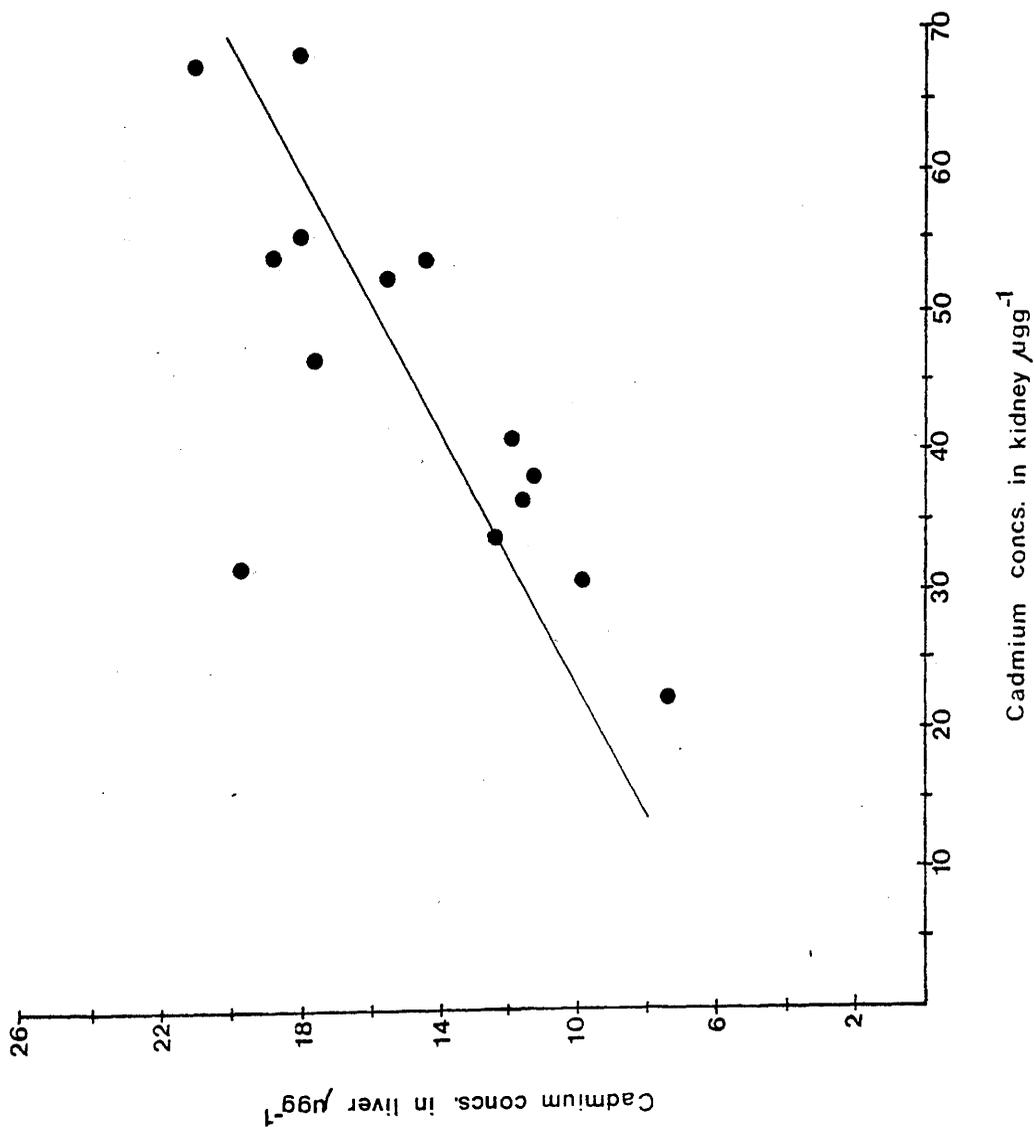


Fig 7.19 Relation between cadmium concentrations ($\mu\text{g g}^{-1}$, log values, wet weight) in the liver and kidney of the Atlantic Petrel Pterodroma incerta ($r=0.835$, $y=1.35x - 1.13$, $n=13$).

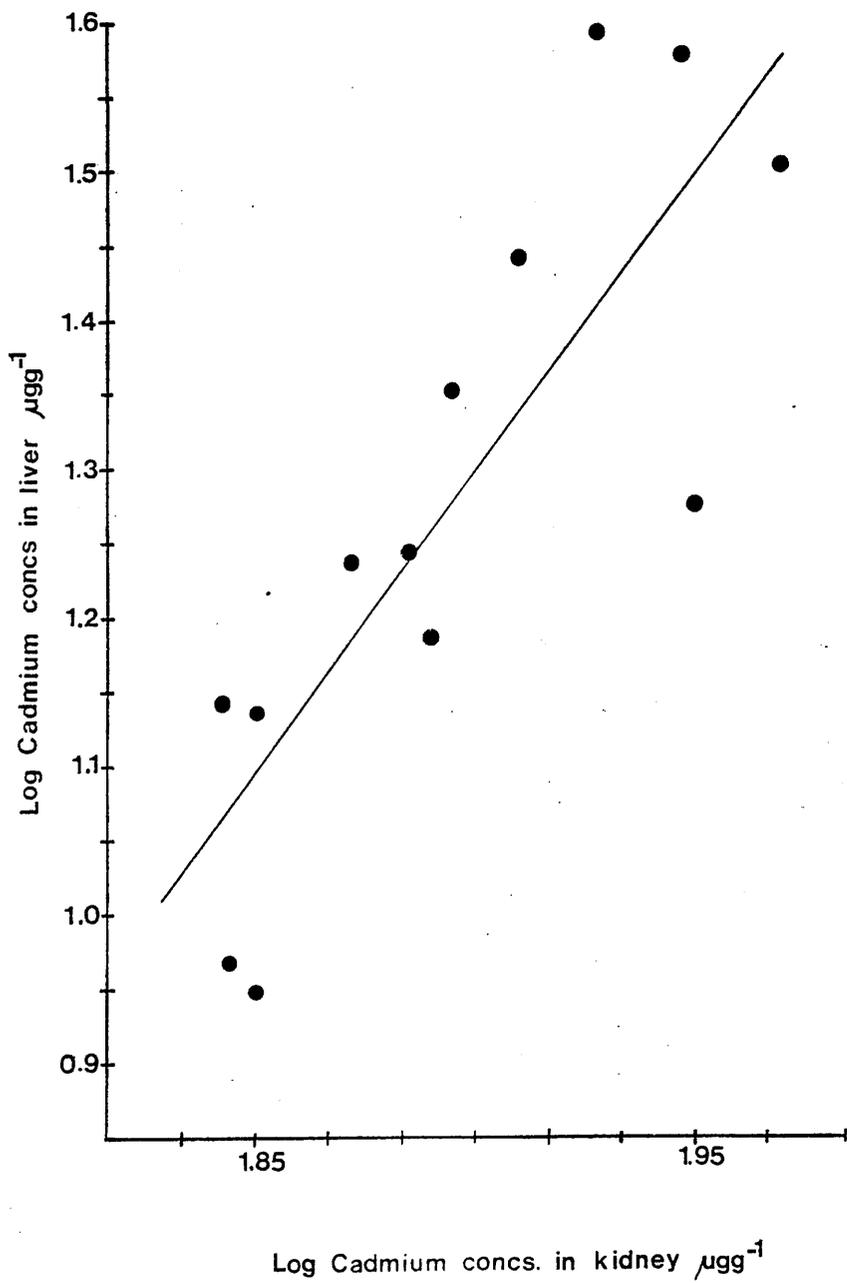


Fig 7.20 Relation between cadmium concentrations ($\mu\text{g g}^{-1}$, log values, wet weight) in the liver and kidney of the Little Shearwater Puffinus assimilis ($r=0.728$, $y=1.04x - 0.55$, $n=13$).

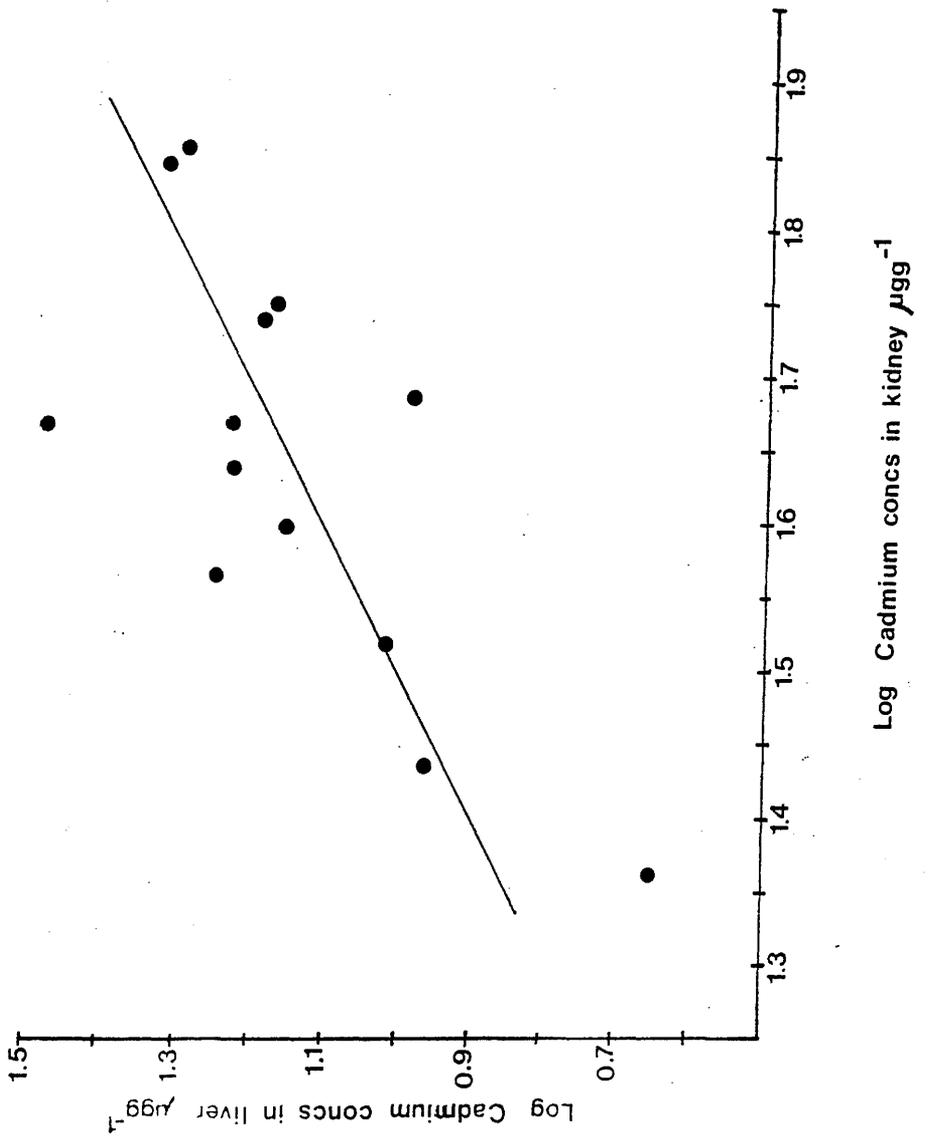


Fig 7.21 Relation between copper and zinc concentrations ($\mu\text{g g}^{-1}$, wet weight) in the kidney of the North Atlantic Great Skua Catharacta skua skua ($r=0.748$, $y=6.70x + 6.85$, $n=47$).

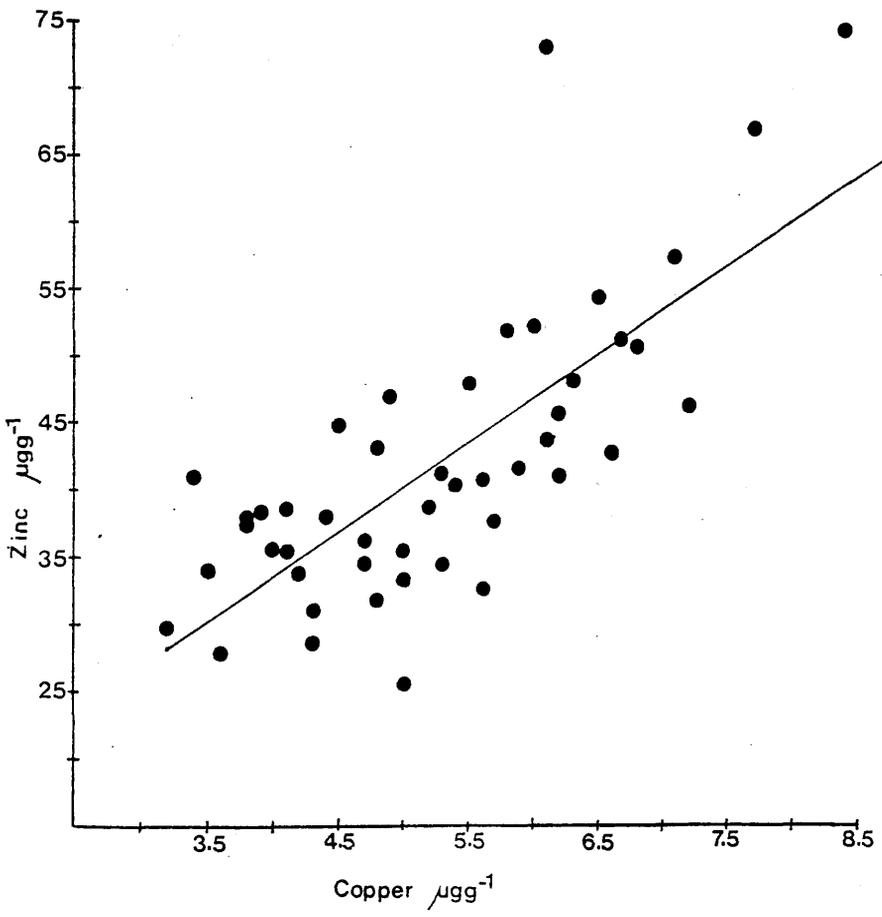


Table 7.4 Relationships between copper and zinc in the liver and kidney of North and South Atlantic Great Skuas and

Procellariiformes

SPECIES	n	KIDNEY		LIVER	
		r	r ^S	r	r ^S
South Atlantic Great Skua	13	0.173	0.322	-0.174	0.396
North Atlantic Great Skua	47	0.748 ^{***}	0.718 ^{***}	0.008	0.041
Sooty Albatross	8	-0.081	-0.156	0.417	0.538
Yellow-nosed Albatross	9	0.658	0.494	0.413	0.310
Great Shearwater	12	0.685 [*]	0.837 ^{***}	0.610 [*]	0.400
Little Shearwater	13	0.493	0.433	0.621 [*]	0.537
Atlantic Petrel	13	0.318	0.369	0.002	0.332
Soft-plumaged Petrel	18	0.243	0.230	0.294	0.625
Kerguelen Petrel	14	0.230	0.501	-0.059	0.498
Broad-billed Prion	31	0.179	0.272	0.469 [*]	0.339
Common Diving Petrel	17	0.578 [*]	0.590 [*]	0.818 ^{***}	0.870 ^{***}
White-faced Storm Petrel	7	0.001	0.162	0.723	0.451
Grey-backed Storm Petrel	8	0.527	0.619	-0.282	-0.611
White-bellied Storm Petrel	8	-0.776 [*]	-0.881 ^{**}	0.850 ^{**}	0.802 [*]
Rockhopper Penguin	12	0.245	0.465	0.258	0.448
Northern Fulmar	25	0.144	0.113	0.391	0.561 ^{**}
Leach's Petrel	13	0.265	0.209	0.541	0.311
British Storm Petrel	7	0.731	0.811 [*]	0.115	0.180

Little Shearwater (Fig 7.22) and in the kidney of the British Storm Petrel (Fig 7.23) and White-bellied Storm Petrel (Fig 7.24) between copper and zinc .

None of the other species showed significant relationships between copper and zinc in the liver and kidney tissue (Table 7.4)

7.6 RELATIONSHIPS BETWEEN METALS IN THE MUSCLE TISSUE OF PROCELLARIIFORMES AND THE NORTH ATLANTIC GREAT SKUA

No correlations were found between any of the metals for muscle tissue (Table 7.5). Many of the values were close to zero, indicating that no trends exist between the metals in the this tissue.

Table 7.5 Relationships between the metals copper, zinc and cadmium in the muscle tissue of Procellariiformes and the North

Species	n	<u>Atlantic Great Skua</u>			
		Cu v Cd	Cu v Zn		Cd v Zn
		r ^S	r	r ^S	r ^S
North Atlantic Great Skua	47	0.117	-0.205	-0.207	-0.114
Fulmar	25	0.346	-0.261	-0.262	0.163
Leach's Petrel	13	0.196	-0.117	-0.093	-0.068
British Storm Petrel	7	0.000	0.343	0.536	-0.357
White-bellied Storm Petrel	8	0.108	-0.320	-0.168	-0.191
Grey-backed Storm Petrel	8	0.359	0.062	-0.133	-0.133

7.7 RELATIONSHIPS BETWEEN MERCURY, CADMIUM AND SELENIUM IN MUSCLE, LIVER AND KIDNEY

In a sample of twenty North Atlantic Great Skuas mercury and selenium concentrations were measured, and the results (Table 7.6) show significant relationships between mercury and selenium in the liver (Fig 7.25) and the muscle. No relationships were found to exist

Fig 7.22 Relation between copper and zinc concentrations ($\mu\text{g g}^{-1}$, log values, wet weight, in the liver of the Little Shearwater Puffinus assimilis ($r=0.728$, $y=0.17x + 1.56$, $n=12$).

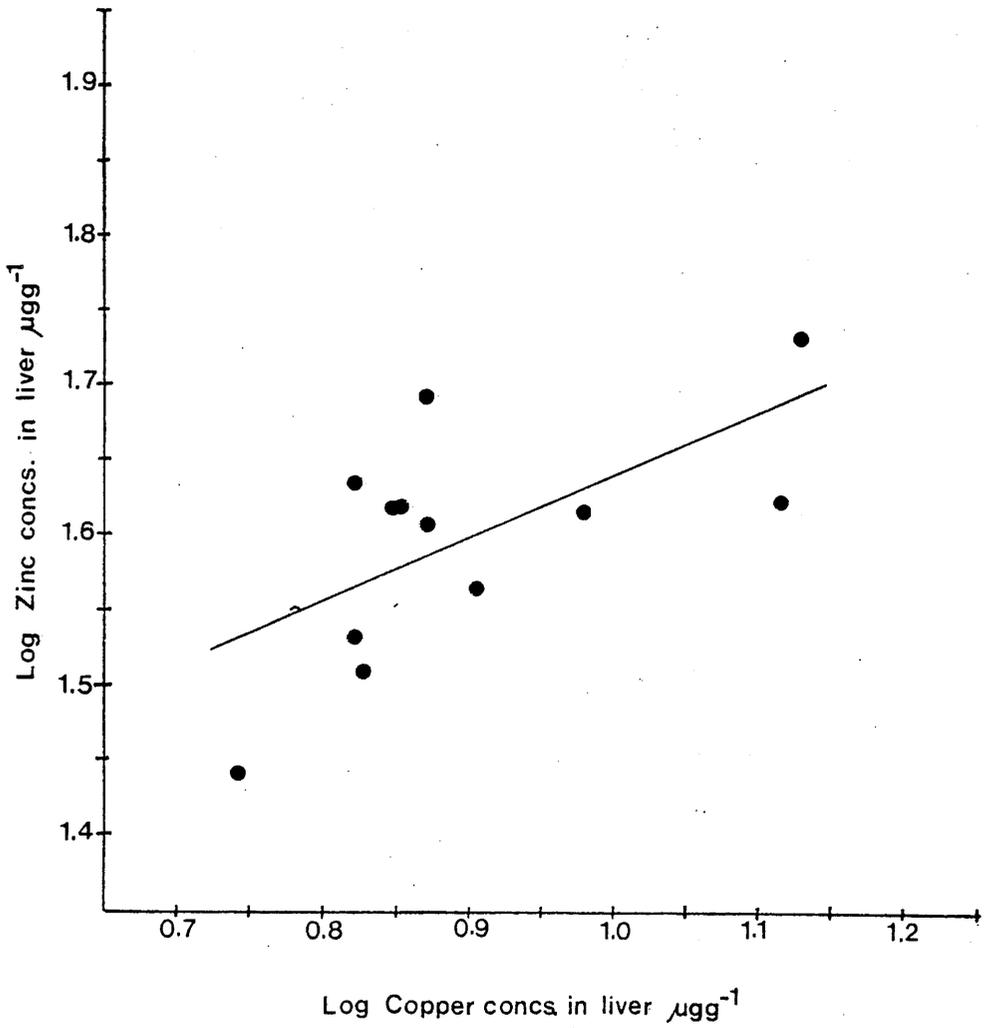


Fig 7.23 Relation between zinc and copper concentrations ($\mu\text{g g}^{-1}$, wet weight in the kidney of the British Storm Petrel ($r=0.731$, $y=1.94x + 15.16$, $n=7$)).

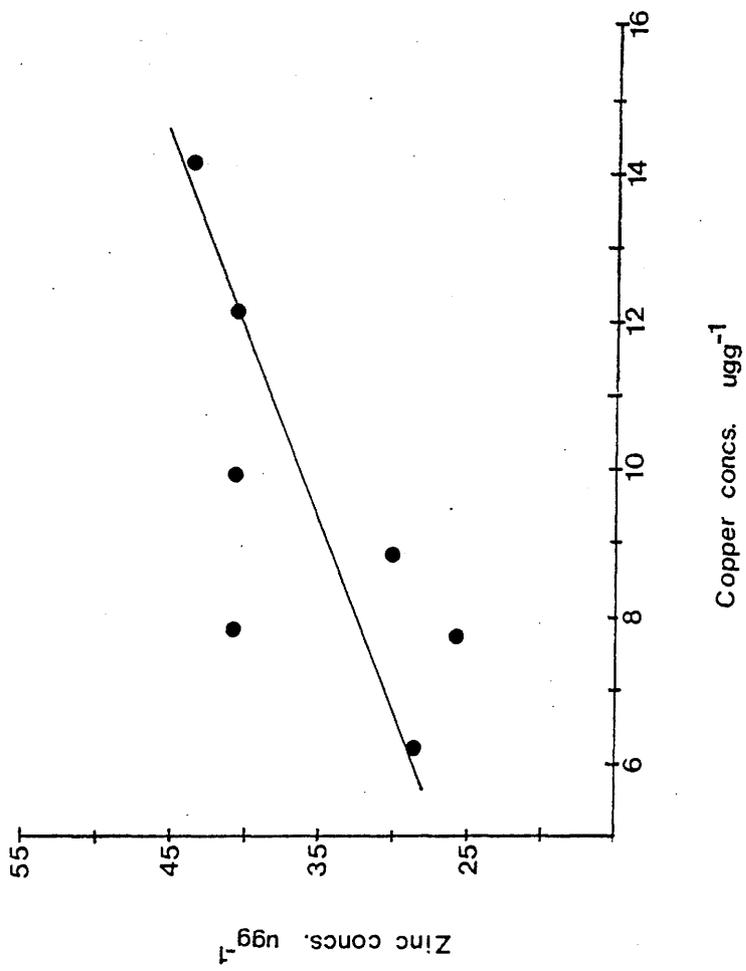


Fig 7.24 Relation between zinc and copper concentrations ($\mu\text{g g}^{-1}$, log values, wet weight in the kidney of the White-bellied Storm Petrel Fregetta grallaria ($r=-0.805$, $y=-0.69x + 2.14$, $n=8$).

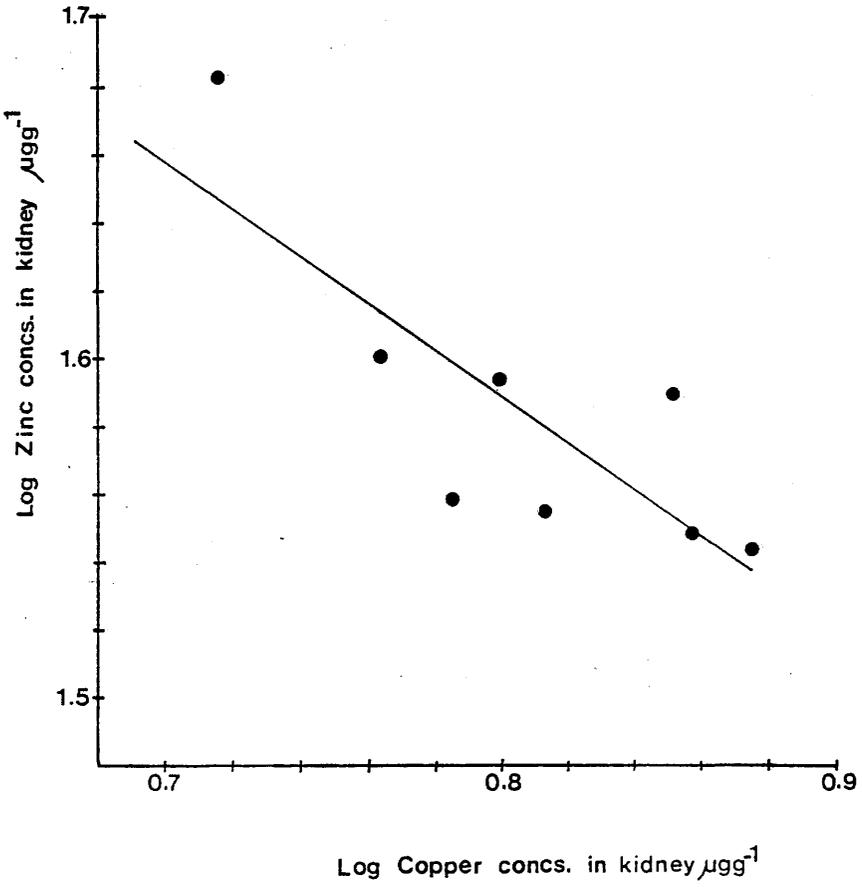
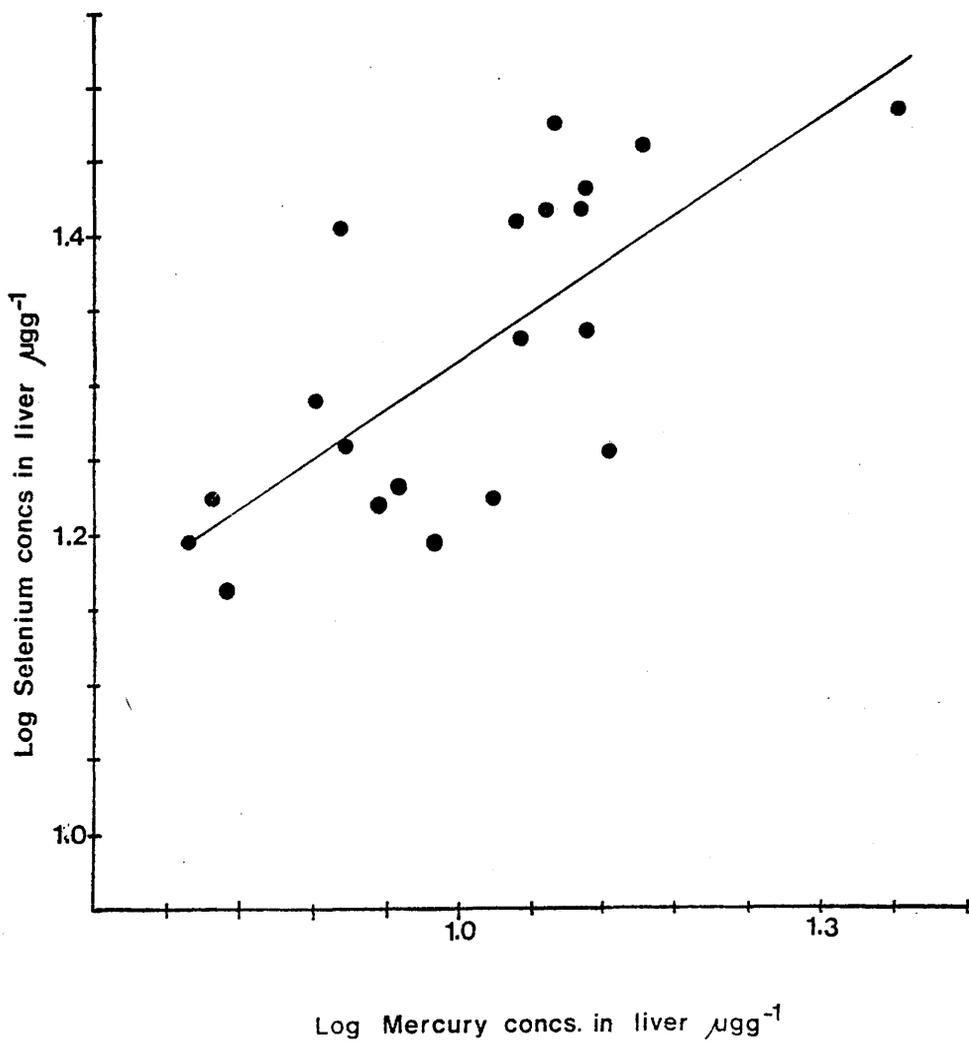


Fig 7.25 Relation between mercury and selenium concentrations ($\mu\text{g g}^{-1}$, log values, wet weight in the liver of the North Atlantic Great Skua Catharacta skua skua ($r=0.726$, $y=0.33x + 0.99$, $n=20$).



between cadmium and selenium or mercury.

Table 7.6 Relationships between cadmium, mercury and selenium in muscle, liver and kidney of the Great Skua

Tissue	Hg v Se	Se v Cd	Cd v Hg
n=20	r_s	r_s	r_s
Kidney	0.353	0.221	-0.247
Liver	0.731 ^{***}	-0.323	0.059
Muscle	0.603 ^{**}	0.231	-0.086

For the Little Shearwater no significant correlations were found between selenium and mercury or cadmium ($r_s = -0.192$ and $r_s = 0.222$, respectively, $n=7$). Mercury showed no significant relationships with the other metals for any of the study species except the Soft-plumaged Petrel and Atlantic Petrel. A highly significant correlations was found between cadmium and mercury in the liver for this latter species ($r = 0.870$, $p < 0.001$; $r_s = 0.718$, $p < 0.02$, $n=11$). The relationship in the liver for the Soft-plumaged Petrel was also significant ($r_s = 0.629$, $p < 0.01$). In the liver of the Soft-plumaged Petrel a positive relationship was found between mercury and selenium but this was not significant, possibly due to the small sample size ($r = 0.767$, $r_s = 0.464$).

7.8

DISCUSSION

The results show a high degree of variability in the relationships between the various metals in the tissues and between the liver and kidney. Some species show strong positive correlations between the metal concentrations and others weak or non-existent correlations, although some of the latter may be because of small sample sizes for

several species. Zinc and cadmium concentrations were found to be significantly correlated in the hepatic tissue of Rockhopper Penguin, Yellow-nosed Albatross and Great Shearwater. Such correlations have also been found in liver tissue of Black-backed Gull Larus dominicus, Red-billed Gull Larus novaehollandiae scopulinus, South Island Pied Oystercatcher Haematopus ostralegus finischi, Pied Stilt Himantopus himantopus leucocephalus, and Pukeko Porphyrio porphyrio melanotus (Turner et al., 1978). Actual cadmium concentrations were higher in the kidney than in the liver, but if zinc is involved in the detoxification of cadmium (see below), it may be that this is taking place in the liver rather than the kidney in these species.

The North and South Atlantic Great Skuas showed significant positive relationships in the liver and kidney between zinc and cadmium, though in the liver the relationship was much weaker. Other studies have also found kidney zinc and cadmium concentrations to be significantly positively correlated, in the Great Skua, Herring Gull and Oystercatcher (Furness and Hutton, 1979; Hutton, 1981). The parallel increase of zinc and cadmium in the kidney has also been found in horses and humans, and the zinc is considered to have a protective role against cadmium toxicity (Friberg et al., 1974; Elinder et al., 1981).

In the tissues of the seabirds studied, few statistically significant correlations were found between the concentrations of any one metal in the different tissues or between the levels of different metals in the same tissue. Positive correlations were found between the liver and kidney cadmium concentrations in nine of the sixteen species examined. In horse kidney a significant relationship was found between zinc and cadmium, but this was not found in deer (Holterman et al., 1984). In the Herring Gull a strong correlation was found between

zinc and cadmium concentrations in the kidney, but the Puffin showed very few statistically significant correlations between the metals in various tissues (Osborn et al., 1979). The differences found between species suggest, therefore, that direct comparisons between species are difficult to justify.

The uptake of cadmium both antagonizes and is antagonized by certain essential metallic ions (Zn^{2+} , Cu^{2+} , Fe^{2+} and Ca^{2+}) and these metals have been implicated in the detoxification of cadmium (Webb, 1975). Most interest has centered on the interaction between zinc and cadmium, as the toxicity of cadmium has been alleviated by zinc supplementation (Bremner, 1978). It has been demonstrated that a prior administration of zinc salts had a marked effect in preventing lesions typical of acute cadmium toxicity in rats. This included the prevention of testicular damage and alterations in the hepatic and pancreatic function (Bremner, 1978; Webb, 1972).

The toxicity of cadmium may result, in part, from disturbances in zinc metabolism and it was suggested that there may be isomorphous replacement of the metals (Bremner, 1978). However, concentrations of zinc are often increased in cadmium-treated animals, which would be unlikely to occur if cadmium ions were displacing zinc from binding sites on the proteins (Bremner, 1978). A complex relationship also apparently exists between copper, zinc and cadmium which may vary between species and with age. Zinc and cadmium have been found to antagonize copper, especially in the liver, when zinc and cadmium concentrations are elevated (Denton et al., 1980). With these various interactions, it becomes impossible to predict a critical value of cadmium in the diet that would cause acute toxicity. Zinc concentrations do appear to be elevated in the tissues of the pelagic seabirds in this study and in some cases this is paralleled by an accumulation of cadmium, suggesting the existence of a relationship of

biological significance. This relationship has been linked to the presence in the liver and kidney of a low molecular weight protein, metallothionein, which is thought to be involved in the detoxification of cadmium, and possibly mercury (Margoshes and Vallee, 1957; Webb, 1972; Bremner, 1978). This protein has been isolated from the kidney cytosol of the Great Skua and Fulmar (Osborn, 1978; Hutton, 1981) and metallothioneins may therefore be present in other pelagic seabirds.

Metallothionein is not, however, a specific cadmium-binding protein as it is also known to bind copper, mercury, silver and zinc. The protein may have a physiological role in the homeostatic control of zinc and copper metabolism (Evans et al., 1970; Bremner, 1978) whilst the binding of non-essential elements is a possibly fortuitous consequence of the chemical similarities of the metals to zinc and copper (Bremner and Davies, 1975). Metallothioneins which contain no mercury or cadmium, but contain copper and zinc have been isolated and characterized from the liver of the horse (Kagi et al., 1960), calves and humans (Bremner and Davies, 1975).

The role of metallothionein has not been clearly identified, but if it is involved in the detoxification of metals it could play an important role in preventing cadmium toxicity due to the high concentrations found in the renal and hepatic tissues of the South Atlantic Procellariiformes.

Nevertheless, Webb (1972) and Friberg et al. (1971) suggested that metallothionein acts as a defence mechanism against certain heavy metals, and Squibb and Cousens (1974) substantiated this idea by showing that the synthesis of a low molecular weight protein took place in rats with increased exposure to cadmium. White and Finley (1978) also found that exposure to cadmium in Mallards caused the synthesis of a cadmium-binding protein, i.e. metallothionein, but free

cadmium tended to accumulate mainly in the liver, while metallothionein-bound cadmium was mostly found in the kidney. This was characterized by the high uptake and long retention time of cadmium in the kidney (White and Finley, 1978). In the Mallards, 97% of the cadmium was found to be present in either the renal or hepatic tissue, and the results for the seabirds where muscle tissue was analysed together with kidney and liver tissue, suggest that cadmium is mainly concentrated in the liver and kidney.

In the pelagic seabirds it appears that the liver and kidney are the main concentrating organs for cadmium, and this may be because these two organs have more metal-inducible high affinity binding sites than other tissues. The binding of cadmium in the liver and kidney may be more important than for mercury because of its apparent inability to cross the 'blood-brain' barrier or enter eggs or feathers (Parslow and Jefferies, 1977; Osborn et al., 1979). The correlations between cadmium and zinc in the liver and kidney are relatively few, so that the existence of parallel accumulation of cadmium and zinc, and the involvement of metallothionein as a mechanism for detoxification of the metals, may be in question for these seabirds.

The Fulmar and Great Skua are known to contain metallothionein in the kidney cytosol but they also contain relatively low amounts of cadmium. In the South Atlantic species, concentrations of cadmium are very high and may 'overload' the system involving metallothionein such that some unknown mechanism comes into operation. This may even take the form of metabolic regulation, as cadmium concentrations appear to be normally distributed in the kidney of some of the Procellariiformes, and a similar suggestion was made for Antarctic seabirds (Schneider et al., 1985). The Atlantic Petrel, for example, shows no relationships between cadmium and zinc in the kidney or the liver, but does show parallel accumulation of cadmium with mercury in

the liver. The Rockhopper Penguin shows highly significant zinc/cadmium correlations, but, as a member of a completely different family, a different mechanism may have evolved to that of the Procellariiformes.

Many of the South Atlantic birds contained concentrations of cadmium comparable to the concentrations found in Mallards which had been fed on a diet containing $200\mu\text{g g}^{-1}$ of cadmium over a period of 90 days. In the kidney, the latter showed several lesions (White et al., 1978), and seabirds from St. Kilda, with a mean kidney concentration of $100\text{--}200\text{mg kg}^{-1}$ dry weight, had structural lesions of a nephrotoxic type. Birds from the Isle of May, however, with mean kidney concentrations of $5\text{--}15\text{mg kg}^{-1}$ showed few such lesions (Nicholson and Osborn, 1983).

Many of the pelagic seabirds studied had levels of cadmium in the kidney comparable to and higher than these, but no obvious damage to the breeding population was visible, although the population of the Wandering Albatross is declining (R.W. Furness, pers. comm.). Nicholson and Osborn (1983) suggest that, despite the apparent damage, metallothionein may still play a role in reducing potential damage to the kidney in the St. Kilda birds, but further experimental and biochemical studies are required to verify this.

The long-term consequences of kidney damage are difficult to estimate as many of the long-term effects of cadmium are unknown (Nicholson et al., 1984), although a large quantity of data has been collected to suggest that metallothionein is able to limit cadmium toxicity (Webb, 1972). However, the difficulty of obtaining samples of seabirds other than during the breeding season, may obscure seasonal changes in metal concentrations in response to physiological requirements such as moult and breeding. Therefore there may be

changes in the toxicological significance of these metals, and the type of binding sites available as the seasonal cycles in enzyme activity and protein composition proceed (Osborn, 1979).

The two populations of Great Skua had very similar correlations between the metals, concentrations of zinc and cadmium being highly correlated in the kidney, but only weakly correlated in the liver. The results may illustrate that cadmium in the kidney is bound to a metallothionein which has stronger binding and retention affinities than that in the liver. The very similar correlations between the two subspecies suggest that the development of possible detoxifying mechanisms may be genus specific, and that the same mechanisms may not necessarily be applicable to different genera.

In the North Atlantic Great Skua a weak correlation was found between cadmium and copper which may be associated with the antagonistic action of cadmium towards the copper ion (Bremner, 1978). Significant correlations were also found between cadmium concentrations in the kidney and liver in the North and South Atlantic Great Skuas, as was found for skuas sampled in 1976 (Furness and Hutton, 1979). Furness and Hutton (1979) also found significant correlations between cadmium and zinc and between cadmium, mercury and selenium in the liver and kidney. In this study no correlations in either liver or kidney were found for cadmium and selenium. A significant correlation was, however, found for selenium and mercury in the liver and muscle tissue, although Stoneburner *et al.* (1981) found no significant correlations between mercury and selenium in the tissues of the Sooty Tern.

Selenium is an essential micro-nutrient, although it is toxic in large quantities. Fish have been found to accumulate quite large amounts of selenium and may form an important dietary source of this element in marine mammals and birds. Marine fish accumulate levels of

selenium in parallel with mercury (Ganther and Sunde, 1974; Mackay et al., 1975). A strong correlation between mercury and selenium concentrations has been found in the livers of several marine mammals and a 1:1 ratio reported (Koeman et al., 1975). Although mercury and selenium are correlated in the liver of the Great Skua there does not seem to be the strong 1:1 relationship between the two metals as found in marine mammals, and a weaker relationship has been found to exist between the metals in birds (Koeman et al., 1975).

Selenium has been implicated in a detoxifying mechanism for mercury, and to a lesser extent for cadmium (Parizek, 1957; Koeman et al., 1973; Ganther and Sunde, 1974; Stoewsand et al., 1974; Chen and Ganther, 1975; Kosta et al., 1975; Mackay et al., 1975; Berlin, 1978; Kari and Kauranen, 1978; Luten et al., 1980; Chang and Suber, 1982).

The mechanism of the antagonistic interaction between mercury and selenium is not fully understood (Berlin, 1978). One possible mechanism is the formation of a mercury-selenium compound of low biological availability and activity (Beijer and Jernelov, 1978). In the liver of Cuvier's Whale Ziphius cavirostris storage granules of mercuric selenide were located, and this was thought to be another detoxification mechanism (cited in Bryan, 1984). Therefore it may be of interest to examine the livers of the seabirds for such granules, as both mercury and selenium concentrations are elevated in some species.

To a small degree the formation of metallothionein may take place, but it also appears that selenium specifically detoxifies mercury (Bryan, 1984), evidence of which is the 1:1 molar ratio found in marine mammals. This coaccumulation could be thought of as occurring as a result of compensatory uptake by the organism of physiologically essential levels of selenium, as mercury is

accumulated and linked to selenium already present, in a normal homeostatic regulation (Beijer and Jernelov, 1978). Chang and Suber (1982) suggested that glutathione peroxidase, a selenoprotein, may alleviate the toxicity of methyl-mercury through antioxidative mechanisms.

In birds, most of the mercury is believed to occur as methyl-mercury (Osborn et al., 1979), as found in fish. In mammals, however, some form of demethylation mechanism appears to be in action, as mercury in the liver was found to be mainly in the inorganic form. Additionally, the 1:1 ratio is not found in the prey of marine mammals and must therefore develop in the animal itself (Van de Ven et al., 1979; Reijnders, 1980). The tentative conclusion was therefore put forward that if at least a molar equivalent of selenium is necessary to give protection against mercury, then in fish and marine mammals observed selenium concentrations would be expected to be sufficient to give a protective effect against methyl-mercury (Luten et al., 1980). Since the selenium concentrations in the pelagic seabirds in this study were greater than the mercury concentrations, then the same principle may also apply.

In birds of prey and Antarctic seabirds the percentage of total mercury present as methyl-mercury has been found to be relatively low in the liver but not in the muscle tissue, suggesting that there may be some form of demethylation mechanism in operation as in mammals (Reijnders, 1980). Further confirmation is needed, but considering the high concentrations of mercury found in the liver of some of the Procellariiformes it would appear a reasonable suggestion, because of the high toxicity of methyl-mercury.

The protective action of selenium has also been found to extend to cadmium (Parizek, 1978). Selenium appears to divert cadmium from a low molecular weight protein to a larger cadmium-binding protein,

although several other mechanisms may be plausible. These include the incorporation of selenium into a metallothionein and the promotion of polarisation of this metalloprotein, or incorporation of selenium into a large pre-existing protein as a sulphur-selenium bond, which may have a higher affinity for cadmium. Alternatively, selenium could be inducing a conformational change in the large molecular weight protein causing it to have a greater affinity for cadmium (Chen et al., 1975).

Despite elevated cadmium concentrations in the tissues of the Great Skua and Soft-plumaged Petrel no correlation was found between cadmium and selenium. This suggests that selenium may not be involved in the detoxification of cadmium as suggested by Furness and Hutton (1979). In the Common Shrew selenium was found to be present in the hepatocytes in a 1:1 ratio with cadmium in 'inclusion bodies' which are incorporated into the metallothionein. The formation of these inclusion bodies may involve selenium, and the minimization of the possibly toxic effects of free-cadmium metallothionein in the cytoplasm (Hunter, 1984).

In sampling wild birds other factors such as seasonality, condition of the bird, and the diet must be considered. The form in which the metal is ingested is also of importance, for example methyl-mercury is more toxic than inorganic mercury. Even though laboratory studies have proved that the metal interactions exist, the outcome may be influenced by the physico-chemical forms used, the route of administration, the time-lapse between administrations and the actual levels and ratio of concentrations used (Lucu and Skreblin, 1981).

It has been suggested that most of the significant correlations between different metals or between the same metal in different tissues can be explained by changes in the metal concentrations with age, especially as cadmium has a long biological half-life and tends

to accumulate in certain tissues (Van de Ven and Koeman, 1979; Denton et al., 1980). However, in seabirds this does not appear to be the case, as no correlations were found between metal concentrations and age. The results obtained also show much interspecific variations and an overall trend is difficult to ascertain. Detoxifying mechanisms may well exist in the tissues of seabirds, especially in the liver and kidney, and possibly take the form of some of those described, but further research is required to clarify the synergistic and antagonistic effects of metals at the biochemical level.

CHAPTER 8

CONCENTRATIONS OF METALS IN THE FEATHERS OF ATLANTIC GREAT SKUAS AND PROCELLARIIFORMES

8.1

INTRODUCTION

Feathers, due to their durability compared to other tissues, can be used to examine present day mercury concentrations in birds and changes over time to give an indication of historic mercury contamination in the environment (Borg, 1958; Berg et al., 1966; Furness and Hutton, 1979; 1980; Appelquist et al., 1985). Birds accumulate mercury in their tissues through their diet, and due to the long biological half-life of mercury much of this accumulates in the soft tissues. During feather formation birds eliminate their 'stored' mercury into the feather over the period of feather growth. Many of the fish-eating birds are at the top of the food chain and are subject to the biomagnification of mercury through the food chain. Therefore they may act as indicators of mercury contamination in the environment.

Samples of primary and body feathers have been analysed for the metals mercury, selenium, zinc, copper and cadmium, and museum specimens have been analysed for mercury in order to investigate any possible changes over time in the mercury concentrations in the environment. Primary feathers were used in order to examine their suitability as indicators of environmental mercury concentrations, and also because it has been suggested that changes in mercury concentration occur throughout the moulting sequence. The feathers were washed to remove external contaminants before use and although washing of feathers may alter the mineral profile (Edwards and Smith, 1984) this is unlikely to affect mercury as it strongly bound to the disulphide bonds of keratin (Crewther et al., 1965), and is not affected by vigorous treatments (Appelquist et al., 1984).

8.2.1 Mercury and Selenium

Five sets of primaries were analysed for mercury and two for selenium. The results are given in Appendix 3. The correlation coefficients for the relationship between primary number and mercury content of the feather show a general trend of decreasing mercury content with increasing primary number. However as the two samples HW62293 and HW02039 illustrate, this does not always occur (Table 8.1)

Table 8.1 Correlation Coefficients for the Relationship between Primary Number and Mercury Concentration

Ring Number	'r'	p
HW46816	-0.612	p<0.1
HW16414	-0.507	n.s
HW60882	-0.839	p<0.05
HW02039	0.275	n.s
HW62293	0.672	p<0.05

The concentrations of mercury in the primary feathers were not exceptionally high (2.3-10ug g⁻¹ dry weight) which is as to be expected from the relatively low tissue concentrations (see Chapters 6 and 7). Levels of mercury in the back and belly feathers corresponded most closely to the levels in primary 10. Primary 10 quite often contained slightly higher concentrations than primary 9.

Selenium concentrations in the feathers were much lower than those of mercury, the opposite situation to that in the tissues and ranged from 0.40 to 2.47ug g⁻¹ dry weight in the nineteen primaries analysed. Although the selenium concentrations in the primaries did not show a correlation with primary number there was a significant correlation

with mercury concentration. The sample was unfortunately small but this correlation was significant at the 2% level ($r=0.545$, $n=19$).

8.2.2 Zinc, Copper and Cadmium

In the two sets of primaries analysed zinc concentrations were found to be high (Appendix 3; range $85-177\text{ug g}^{-1}$ dry weight), but zinc is known to be required for feather growth (Sunde, 1972). Concentrations of copper in the feathers were comparable to tissue levels, though primary 3 of bird HW69379 showed unusually high concentrations of copper (39ug g^{-1} dry weight) and zinc (175ug g^{-1}). In other body feathers zinc concentrations were similar to kidney concentrations. In most of the feather samples analysed cadmium concentrations were below the limit of detection and in the samples of head and belly feathers levels were detectable but very low (0.18 and 0.47ug g^{-1} dry weight).

8.3 PROCELLARIIFORMES and Catharacta skua hamiltoni

For each of the five South Atlantic species only one set of primaries was available for analysis. The concentrations of mercury in the Atlantic Petrel and South Atlantic Great Skua were higher than in the North Atlantic Great Skua and the Soft-plumaged Petrel. The Kerguelen Petrel and Great Shearwater contained much lower levels of mercury in their primaries (Appendix 3). The correlations between primary number and mercury content were highly significant (Table 8.2). In the Procellariiformes concentrations in the coverts tended to correspond with levels in primary 5, while in the South Atlantic Great Skua the level was closer to that of primary 7. Variation in mercury levels in feathers is considerable and different moulting patterns may also influence the feather mercury concentrations.

Table 8.2 Correlation Coefficients for the Relationship between Primary Number and Mercury Content in South Atlantic Procellariiformes and the South Atlantic Great Skua.

Species	'r'	p
South Atlantic Great Skua	-0.975	p<0.001
Soft-plumaged Petrel	-0.855	p<0.005
Atlantic Petrel	-0.870	p<0.005
Kerguelen Petrel	-0.939	p<0.001
Great Shearwater	-0.983	p<0.001

Table 8.3 Mercury Concentrations in the Primary Feather (Mean) and Mean Liver Concentration

Species	Hg ug g ⁻¹	Hg ug g ⁻¹
	Primary Feather	Liver (dry weight)
North Atlantic Great Skua	5.3	11.9
South Atlantic Great Skua	14.1	22.9
Kerguelen Petrel	2.5	13.9
Soft-plumaged Petrel	7.9	51.4
Atlantic Petrel	17.1	85.6
Great Shearwater	1.9	6.4

There also appeared to be a weak relationship between mercury concentrations in the feathers and the liver, although the sample size was small (Table 8.3). This relationship may in any case be an artifact, since for each species mean levels in the feathers have been related to a mean derived from livers of a different set of individuals.

8.4 CONCENTRATIONS OF MERCURY IN FEATHERS OF MUSEUM SPECIMENS

The concentrations of mercury in feathers of Catharacta skua skua show no differences between present day and museum samples (Mann-Whitney U-test Present day U-statistic=104, n=11 and museum U-statistic=83, n=17, not significant) (Appendix 3). Certain concentrations in the feathers are extremely high, for example birds caught in the Faeroes on the 17th August 1873 and 17th August 1886. This is probably due to the use of mercury in the preservation process and these results have therefore been excluded from the analysis. Many of the Icelandic and Faeroese birds contain quite high concentrations of mercury in the body feathers, which, because of collection and storage at the same time as the Shetland and Orkney birds, may not necessarily be caused by the use of mercury preservative. A significant difference was found in the concentrations of mercury between the Icelandic and Faeroese populations of Great Skuas and those from Orkney and Shetland (Mann-Whitney U-test, Iceland and Faeroes U-statistic =121, n=8 and Orkney and Shetland U-statistic=23, n=18, $p < 0.05$).

There was no difference in the feather concentrations of male and female birds Catharacta skua skua, (Mann-Whitney U-test males U-statistic=81, n=20, females U-statistic=79, n=8, not significant).

Concentrations of mercury in museum feathers of Catharacta skua hamiltoni were low ($1.9-6.3 \mu\text{g g}^{-1}$) and these levels corresponded with those found in present day body feathers and higher numbered primaries. Concentrations in the body feathers of the museum specimens of the other subspecies of skua (Table 8.4) were very similar to those in Catharacta skua hamiltoni. Some anomalous results were found, for example a concentration of $21.6 \mu\text{g g}^{-1}$ in a female South Polar Skua taken in 1873, and $19.4 \mu\text{g g}^{-1}$ in a Chilean Skua female taken in 1912.

These varying levels could be caused by differences in the pattern of natural accumulation or contamination during preservation.

Abnormally high values were excluded, in case of contamination, from the Mann-Whitney U-test used to determine if there were any differences in the mercury concentrations of feathers from male and female birds. In the South Atlantic Great Skua a significant difference was found between the sexes.

Table 8.4 Mean concentrations and ranges of Mercury in Feathers of Museum Skua Specimens

Species	n	Mean Hg ug g ⁻¹	Range Hg ug g ⁻¹
<u>Catharacta</u> <u>maccormicki</u>	6	3.0	0.90-7.0
<u>Catharacta</u> <u>skua</u> <u>hamiltoni</u>	11	3.3	1.9-6.3
<u>Catharacta</u> <u>skua</u> <u>antarctica</u>	11	4.6	0.53-21.6
<u>Catharacta</u> <u>skua</u> <u>lornbergi</u>	6	2.5	1.4-4.3
<u>Catharacta</u> <u>chiliensis</u>	9	5.8	0.79-19.4
<u>Catharacta</u> <u>skua</u> <u>skua</u>	26	9.6	3.0-22.9

8.5

DISCUSSION

The concentrations of the metals zinc, cadmium and copper in the feathers are comparable to those found in Crested Terns (Howarth et al., 1982), and Manx Shearwater, Fulmar and Puffin (Osborn et al., 1979); copper levels alone in the Lesser Snow Goose Anas caerulescens (Hanson and Jones, 1968), and zinc alone in Wild Turkey Meleagris gallopavo (Scanlon et al., 1979) and the Great Skua (Hutton, 1981). In Sooty Terns the Pacific group had lower cadmium levels in the feathers (Stoneburner and Harrison, 1981) than the Foula Great Skua but the Atlantic group of Sooty Terns contained much higher levels of cadmium in the feathers. Stoneburner and Harrison (1981) suggested that this

may be due to differences encountered in the pelagic food chain.

Zinc and copper are found in typical tissue concentrations in the Great Skua, probably because these are essential metal ions, and because zinc is important in feather formation (Sunde, 1972). Cadmium is a non-essential element and was probably found at low concentrations in feathers because of the inability of charged cadmium ions to cross the membranes between the blood and feather as found for eggs (Parslow and Jefferies, 1977) and the brain (Osborn et al., 1979). Therefore no major excretion process for this metal takes place through the feather.

Such an observation was not true for mercury, partly because methyl-mercury, which is lipid soluble, can be transported across the membranes between the blood and feather, egg or brain. The levels in the primary feathers of the Great Skua were of the same order as those found in Great Skua feathers by Furness and Hutton (1979) and the Puffin (Osborn et al., 1979), but higher than those of the Manx Shearwater and Fulmar (Osborn et al., 1979). Similar levels of mercury to those in skua primaries have been found in the primary feathers of Great Blue Herons, Black-crowned Night Herons Nycticorax nycticorax and Great Egrets Casmeradius albus (1.1-7.3 μ g g⁻¹ dry weight) (Hoffman and Curnow, 1979).

The levels of mercury in the primary feathers appears to decrease from primary 1 to 10 in the Great Skuas and Procellariiformes. This result is verified by studies on Kittiwake, Fulmar and Manx Shearwater primary feathers (Furness et al., 1986). The Great Skua does not show a strong correlation of mercury with primary feather number compared to the other species considered. In one case the correlation is reversed ($r=0.672$, $p<0.05$) and this was also found in one set of primaries analysed by Woodburn (1985) ($r=0.753$ $p<0.1$). These two birds may have been exposed during their moulting period to higher mercury

concentrations perhaps by passing relatively close to polluted coastal waters while on migration. Despite these two anomalous results there does appear to be a general decrease in the mercury concentration of the feather with increasing primary number. This pattern has also been found in Osprey (Johnels et al., 1967), Peruvian Boobies (Gochfield, 1980), Sparrowhawks (Buhler and Norheim, 1982), Pergrines (Lindberg and Odjso, 1983), Black Guillemots and Guillemots (Appelquist et al., 1984). In many cases this pattern has been linked to short-term dietary changes after Johnels et al. (1967), but considering that the eight species studied came from both the North and South Atlantic, have different moulting patterns and that the Great Shearwater is a trans-equatorial migrant, the pattern may be related to the physiology of moult and mercury storage rather than short-term changes in the dietary intake of mercury.

The pattern observed may therefore be caused by an accumulation of mercury in the body between moults as the birds are unable to excrete mercury rapidly from the body tissues. The formation of a feather requires a massive degradation and synthesis of muscle and bone tissue (Hanson and Jones, 1968) and changes in liver protein (Osborn et al., 1979), which may cause mobilisation of mercury into the bloodstream and hence to the feather. Mercury is also found to be absent from the liver during moult (Osborn, 1979), suggesting that it is located elsewhere in the body. The mercury level in the feather has been related to the concentration of methyl-mercury in the blood at the time of feather formation (Berg et al., 1966; Westermarck and Johnels, 1969). As the primaries are moulted in the order of 1 to 10 a decrease in the body pool of mercury would occur as the moult progresses. Data from this study, Woodburn (1985) and Furness (unpubl) suggest that the above hypothesis is strengthened by three further points:-1)The

mercury concentrations in the secondaries from the Great Skua and Kittiwake are similar to levels in the last four or five primaries grown, which would be expected as secondary feather replacement starts when about half the primaries have been shed (Ginn and Melville, 1983).

2) Mercury levels in the tail feathers tend to be higher than those in the secondaries but less than in the primaries. Tail moult starts after primary moult but before secondary moult.

3) Concentrations in the head and neck feathers tend to be higher and more variable than in other body feathers. Both the Great Skua and the Kittiwake undergo a partial nuptial moult in early spring. During this moult some but not all of the head and neck feathers may be replaced, while very few, if any of the body or flight feathers are replaced. This limited spring moult may allow mercury accumulated since the last moult to be placed in the new head and neck feathers (Furness et al., 1986).

Teijning (1967) found that feathers contain up to 60% of the body load of mercury, suggesting that the feather acts as a source of waste elimination. Primaries therefore appear to be inadequate for use as indicators of mercury concentrations in the environment and body feathers should be used instead (Furness et al., 1986).

Seasonal changes in both the tissue and feather concentrations must be taken into account, for example the Fulmar was found to contain the highest liver concentrations of mercury, but the Puffin had the highest feather concentrations of three species studied on St Kilda (Osborn et al., 1979). This apparently anomalous finding is probably related to the moulting sequence of the birds and the primary feathers sampled.

Seasonal changes in the concentrations of toxic metals do occur and mercury and cadmium levels in liver and kidney have been observed

to increase near the time of moult (Haarakiangas et al., 1974, Osborn, 1979). Osborn et al. (1979) suggested that as zinc is needed for moult (Sunde, 1972) some toxic metals may accumulate in tissues at times when the birds are also accumulating zinc. This uptake may also be affected by the number of intracellular binding sites available for the toxic metals (Osborn, 1979). Evidence for this suggestion comes from an examination of the moulting pattern of the Puffin, Fulmar and Manx Shearwater (Osborn et al., 1979). The Puffin had the lowest liver concentrations of mercury and moulted in the spring, the Manx Shearwater, which moults only after it has migrated to the South Atlantic, had intermediate concentrations and the Fulmar, which moults in early autumn, had the highest liver mercury concentrations (Osborn et al., 1979). However, this does not fully explain what happens to the high concentrations of mercury in the liver since the Fulmar had the lowest feather concentrations amongst the three species suggesting that the mercury is not necessarily excreted to the feather, although liver and feather mercury concentrations have been found to correlate (Furness and Hutton, 1979). It is unlikely that the primary feathers formed in the year preceding the spring sampling have undergone much leaching as this appears to be of minor importance (Appelquist et al., 1984). The Puffin, which contained the highest feather mercury concentrations, may have a more efficient detoxifying mechanism for metals as suggested for PCB's (Harris and Osborn, 1980).

No significant relationships were found between mercury concentration in the feathers and age, which corresponds to the other data available on Great Skuas (Furness and Hutton, 1979; Woodburn, 1985). Furness and Hutton (1979) found in the Great Skua a correlation between mercury concentrations in the liver and the feather but no significant correlation was found in this study ($r=0.490$, $n=10$). A

significant correlation was found for mercury concentrations in the liver and feather of the Great Blue Heron and in New Zealand Oystercatchers, Pied Stilts and Pukekos (Turner et al., 1970) but not in Great Egrets and Black-crowned Night Herons (Hoffman and Curnow, 1979) or Black Guillemots (Appelquist et al., 1985). Similarly no correlation was found between the mercury concentrations in the feather and muscle tissue of the Ring-necked Pheasant Phasianus colchius (Huckabee et al., 1972).

Two sets of primaries that were analysed for mercury were also analysed for selenium by neutron activation analysis. A significant correlation was found to exist between the feather concentrations of mercury and selenium ($r=0.555$, $p<0.05$, $n=19$). Mercury concentrations in the liver correlate with those of selenium possibly due to a detoxifying mechanism. The mercury and selenium are thought to be bound in a metallo-protein, and as mercury is absent from the liver near the time of moult (Osborn, 1979) this metallo-protein may be mobilised into the bloodstream and then to the feathers. However it is interesting to note that the levels of selenium in the feather are much lower than the mercury concentrations, a situation which is reversed in the liver. Selenium may either be retained as an essential element or it may not easily pass across the blood-feather barrier.

The feathers used had been thoroughly washed to remove any external contamination, as a study on Dunlin Calidris alpina alpina illustrated external contamination of the feathers with selenium from the preen glands (Goede and De Bruin, 1985). After formation feathers lose all their vascular and nervous connections to soft tissues, becoming physiologically isolated (Goede and De Bruin, 1984). Any increase in metal concentrations over time must therefore be caused by external contamination. In the Dutch Waddenzee an increase in Dunlin feather selenium concentration was seen over the winter. An increase

in the intake of dietary selenium was therefore reflected in the feather via the preen gland, but no correlation was found with mercury concentrations (Goede and De Bruin, 1985).

Despite the levels of mercury in the feathers and liver of the Great Skua showing no significant correlation, when the average liver concentration of the South Atlantic samples were correlated with the mean primary feather concentration there appeared to be a relationship between the two ($r=0.773$, $p<0.1$). The primaries of the birds with high liver concentrations tended to have high feather concentrations of mercury suggesting that the feather is used as a means of excreting the mercury, although the Soft-plumaged Petrel was anomalous in this respect.

The mercury levels in the lower primaries of the Atlantic Petrel were within the range of concentrations found in the feathers of White-tailed Eagles found dead with suspected mercury poisoning (Jensen et al., 1972). Johnels and Westermarck (1969) suggested natural background feather mercury concentrations of $4.6\mu\text{g g}^{-1}$ in birds of prey, but seabirds tend to carry higher concentrations of mercury and a value of $10\mu\text{g g}^{-1}$ was suggested (Doi et al., 1984). Some of the South Atlantic birds carried feather burdens higher than $10\mu\text{g g}^{-1}$ and due to a lack of knowledge concerning diet few firm conclusions can be drawn on this aspect of the work.

The mercury concentrations in the South Atlantic birds are very high (Chapter 7), many above the $10\mu\text{g g}^{-1}$ level found to cause mortality in White Leghorn chicks (Fimreite, 1970), suggesting that the birds must have some adaptive mechanism to cope with these high concentrations. Hakkinen and Hanson (1980) suggested that the excretion of mercury via the growing feathers is a most important factor in preventing severe mercury toxicity. Only the mercury levels

in the Great Shearwater and Kerguelen Petrel feathers are comparable to the levels found in feathers of four species of petrel from the Antarctic area (Anderlini et al., 1972).

Bird feathers are well known as a good index of environmental exposure to mercury and this aspect has been especially studied by Swedish investigators in relation to an increase in the mercury input into the environment via alkyl-mercury seed dressings (Berg et al., 1966; Johnels et al., 1969). The relationship between mercury content of the feather and time has been examined in a number of species using present-day and museum specimens (Berg et al., 1966; Johnels et al., 1969; Lindberg and Mearns, 1982), due to the great stability of mercury in the feather keratin (Appelquist et al., 1984).

Johnels and Westermark (1969) measured mercury in feathers of Goshawks, Ospreys and Great-crested Grebes collected in Sweden between 1815 and 1966. They concluded that the natural or background level was about 3-4ug g⁻¹ dry weight. Berg et al. (1966) reported that mercury levels in feathers from Peregrines collected between 1834 and 1940 was 2.6ug g⁻¹, whereas after 1940 levels in the feathers rose to 15-20ug g⁻¹. In this study of Catharacta skua skua no significant difference was found in the mercury concentration in body feathers from 1873-1940 and more recently collected feathers (1978-1984). Samples exceeding concentrations of 25ug g⁻¹ were excluded from the analysis as the samples may have been contaminated through the painting of the bird skins with a sublimate solution (HgCl₂) (Berg et al., 1966).

In the six sub-species of skua examined the levels of mercury in the museum body feathers appear to be highest in the North Atlantic Great Skua with low levels in the closely related South Atlantic Great Skua. Since in the present day feathers high concentrations of mercury were found in the lower primaries, it may be that the South Atlantic birds are more efficient at excreting the body burden of mercury.

The museum specimens from Iceland and Faeroes contain significantly higher concentrations of mercury in the feathers than samples from Orkney and Shetland. These differences appear to unlikely to be caused by contamination as all the samples came from the British Museum and were collected over similar time periods. Differences in mercury levels in feathers with location have been found in Peregrines (Parrish et al., 1983) and Black Guillemots (Appelquist et al., 1985). In the former example the differences found were due to differences in the natural background levels and in the latter were due to differences between polluted and non-polluted environments. Diet may be the cause of the historical differences found. In Black Guillemots differences in the mercury concentrations found in the feathers have been related to dietary preferences of the individual Black Guillemot (Appelquist et al., 1985).

Higher mercury levels were also found in the feathers of Peregrines from northern Sweden as compared to southern Sweden, and this difference was related to the diet of the northern Peregrines. These birds fed mainly on migrant waders which were more highly contaminated with mercury than resident species. The mercury was probably accumulated in the wintering grounds on relatively polluted estuaries (Lindberg and Mearns, 1982; Lindberg and Odjso, 1983). Dietary differences may therefore exist between the two populations of Great Skuas. Hickey (1975) suggested that many of the Icelandic Great Skuas fed on birds and regurgitates from kleptoparasitism, whereas the Shetland population feed mainly on fish.

Catharacta skua skua feathers from the present and the past show no significant differences in mercury concentrations between the sexes, though this does not appear to be the case for the pooled sample of other skua subspecies. The lower levels in the female may be

due to their ability to excrete mercury into the eggs.

The mercury content of the individual feathers can vary widely in one bird (Buhler and Norheim, 1981) and it appears that mercury accumulated in the body is excreted via the feather over the period of feather growth (Teijing, 1967, Buhler and Norheim, 1981), as shown by the sequential decrease in mercury levels from primary 1 to 10 for most species. Body feathers appear to give a good indication of the mercury intake of the bird (Furness et al., 1986) and they may have advantages as environmental monitoring aids in that they are light and durable (Gochfield, 1980) allowing historical comparisons to be made (Appelquist et al., 1984) and using feathers does not require killing the study specimen, which is of especial importance with rare species. However, in using feathers as indicators of environmental contamination by mercury, the timing of the moult, pattern of moult, the nutritional condition of the bird and its migratory habits must all be taken into account before a viable conclusion may be formulated on the levels of mercury in the bird's environment (Osborn, 1979; Gochfield, 1980).

DISCUSSION

9.1

INTRODUCTION

The pelagic seabirds studied occupy the open ocean and areas of upwelling, rather than inshore areas. It is in these latter areas that the main sources of pollution are found, often affecting only a local resource, but it is in the open ocean that pollution problems could have long-term consequences. The open ocean may be polluted by synthetic chemicals, metals, petroleum hydrocarbons and radioactivity, and it is the increasing concentrations of these in the ocean and its biota which may indicate dangerous trends. The long-term effects of pollution depend upon the residence time of the pollutant, which, in the cases above, is often for a very long period. As coastal areas become increasingly polluted it is important to understand the baseline concentrations of metals in species that occupy the open ocean. Though the birds studied are pelagic they spend much of their time on the continental shelf and in areas of upwelling, areas which provide 99% of man's fish catch, and as species occupying the upper levels of the food chain, they could provide useful indicator species in identifying the presence or absence of a pollutant.

9.2

ORGANOCHLORINES

Organochlorines are extremely persistent chemicals which have been found to readily bioaccumulate through the food chain (Addison, 1976). They are also ubiquitous in the marine environment, entering it either directly through coastal discharges or by aerial transport. Organochlorine concentrations were examined in the Great Skua in order to determine levels, to see if they reached levels that might be detrimental to the bird.

In the tissues of the Great Skua no significant relationship was found between the lipid concentrations of DDE and PCB's and the percentage lipid content of the tissues. However, DDE concentrations were significantly positively correlated between muscle and liver tissue, whilst neither of these was correlated with concentrations in the fat. The correlations between PCB concentrations in the three tissues were more pronounced than for DDE. The correlations between PCB and DDE concentrations in each of the tissues for both the whole tissue and lipid values were highly significant and particularly strong for muscle tissue, suggesting that these two substances are coaccumulated.

The concentrations found in the tissues of the Great Skua and Fulmar were comparable to those found in Icelandic birds (Sproul et al., 1975), but were lower than those found in Herring Gulls from south-western Finland (Lemmetyinen et al., 1982). The concentrations were highest in the fat tissues, as expected from the lipophilic nature of organochlorines, and this was also found for Adelle Penguins (Subramanian et al., 1986).

The correlations between tissue concentrations and body burden of DDE and PCB's have only been examined at one particular season. During the breeding season the adult Great Skuas utilise their fat reserves, which may result in a percentage decrease in fat DDE and PCB concentrations and slight increases in other tissues and organs. Such a situation has been found to exist for Adelle Penguins and Sparrowhawks (Bogan and Newton, 1977; Subramanian et al., 1986). Changes in the PCB or DDE concentration or tissue volume of any one tissue will therefore result in a corresponding change in the concentration in all tissues. In Adelle Penguins it was found that the concentrations of these compounds increased simultaneously in the fat

reserves as well as in other tissues because of a drastic decline in fat deposits during starvation. Once the fat reserves decline to a critical level the percentage of these compounds in other organs is increased (Subramanian et al., 1986). Therefore if organochlorine concentrations are sufficiently high, the mobilisation of reserves may have deleterious effects on the birds and eggs. From comparison with other species, organochlorine concentrations in the Great Skuas may not be detrimental to the population (Bourne and Bogan, 1972; Bogan and Newton, 1977). An abnormal number of chick deformities have, however, been noted for the Great Skua (Furness and Hutton, 1980), but as the population in recent years has successfully increased in numbers it appears unlikely that DDE and PCB's are having a severe effect on the birds.

No differences were found in the accumulation of DDE and PCB's between male and female Great Skuas, although this was considered a possibility as the female may be able to excrete some of her organochlorine burden into the egg. Also, despite the persistence of organochlorines in body tissues, in considering birds that were from 4 to 15 years old no significant correlations were found to exist between the age of the bird DDE or PCB concentrations.

The DDE:PCB ratios in the Great Skua tissues were high, but comparable to those found for Great Skuas sampled in 1972 (Bourne and Bogan, 1972). The DDE:PCB ratios were lower for the Fulmar (mean=2.2) possibly indicating that these birds feed further out into the Atlantic than the Great Skuas, for the ratio has been found to increase from west to east across the Atlantic (Sproul et al., 1975). It may also be that the Great Skua is wintering in a more contaminated environment than the Fulmars. It has been suggested that migratory species which breed in northern regions may pick up organochlorines in their wintering areas in southern Europe or Africa, where

organochlorines such as DDT are still used (Burgers et al., 1986).

Over the years 1971 to 1983, DDE levels in Great Skua tissues and eggs appear to have declined, although this was not the case for PCB's. The ban on the use of DDT was implemented in many European countries in the early 1970's, but for PCB's, despite the ban on their manufacture in some countries, are still stockpiled and manufactured in a number of others. PCB's may still be entering the environment in quite large quantities. Significant decreases in DDE levels and DDE:PCB ratios were observed in Herring Gull eggs between 1969 and 1979-81, but similar decreases were not seen for PCB's (Mosknes and Norheim, 1986), which is a similar situation to the results found for the Great Skua.

Seabirds are long-lived and able to carry residues for a decade or more (Sproul et al., 1975), and changes immediately apparent at the points of discharge may show a time-lag effect before declining in the oceanic environment. Great Skua ringing recoveries indicate that a number of birds winter in the western Mediterranean and these birds may acquire a heavy body burden of organochlorines from this relatively polluted region, thus possibly accounting for some of the variability between individuals.

The eggs of the Golden Eagle from Rhum contained high concentrations of DDE and PCB's. The Great Skua eggs contained lower concentrations of DDE, and the Fulmar eggs lower PCB concentrations. The levels of DDE in the Golden Eagle eggs appear to have declined since 1969, but PCB concentrations have increased. Bogan and Newton (1983) found that eagle eggs from coastal sites had the highest levels of PCB with a mean of 270 ug g^{-1} lipid, which is similar to the results in this study. The results are analogous to the situation for coastal Peregrines which were found to contain higher concentrations

of organochlorines than inland birds and did not reflect the decline in the levels seen in inland populations. These results may be related to diet, as bioconcentration values for organochlorines have been found to increase with trophic level (Subramanian et al., 1986). The Golden Eagle at Rhum mainly feeds on seabirds, which may contain high concentrations of DDE and especially PCB's (Sproul et al., 1975), while the Great Skua and Fulmar tend to concentrate on fish, young birds and plankton (Furness and Hislop, 1983; Furness and Todd, 1984).

9.3 METALS IN ATLANTIC GREAT SKUAS AND PROCELLARIIFORMES

The concentrations of the essential metals copper and zinc in the tissues of the pelagic seabirds were comparable to concentrations found in other species (Osborn et al., 1979; Parslow et al., 1982). However, zinc concentrations were very variable in the liver, kidney and muscle of many species, whilst copper concentrations were found to cover a much smaller range of values. The metals did not always show a normal distribution, which may have resulted from antagonism from other metals.

The concentrations of cadmium and mercury in the kidney and liver of the Wandering Albatross are possibly the highest yet reported for apparently healthy seabirds. Concentrations of cadmium and mercury were also very high in the Sooty Albatross, but concentrations in the Yellow-nosed Albatross were significantly lower. In many of the other Procellariiformes and the Rockhopper Penguin, although cadmium concentrations were very high, mercury liver levels were much lower, as found in Cory's Shearwater (Renzoni et al., 1986).

All the South Atlantic Procellariiformes contained much higher concentrations of cadmium in the kidney and liver than the North Atlantic Procellariiformes, which suggests that the cadmium accumulations are of natural rather than anthropogenic origin. The

Great Skua and many of the South Atlantic Procellariiformes stored proportionally more cadmium in the kidney than in the liver when compared to the Herring Gull, Oystercatcher and five other pelagic seabirds (Bull et al., 1977; Hutton, 1981). This interorgan distribution was suggested to result from a sensitivity to the toxic effects of cadmium, as the kidney is the main excretory organ for this metal. The normal distribution of cadmium concentrations in some of the tissues of the Atlantic species suggests that some form of metabolic regulation is in operation. Schneider et al. (1985) concluded that cadmium may be metabolically regulated, due to the similarities in cadmium concentrations between species from Antarctica. If the diet of these species contains high quantities of cadmium, which is potentially toxic, then metabolic regulation of this metal may have evolved to reduce cadmium toxicity.

The South Atlantic Procellariiformes are at or near the top of the food chain and they all show a definite enrichment in cadmium tissue concentrations, compared to background levels. The concentrations of cadmium in the kidney appeared to be related to the amount of squid in the diet. Cadmium concentrations were thus highest in those species feeding almost entirely on squid and lowest in the seabirds feeding primarily on euphausiids or copepods. For the larger Procellariiformes and Rockhopper Penguin, squid may be the main source of dietary cadmium, if the concentrations in the South Atlantic squid are similar to those found in the three species of Pacific squid investigated by Martin and Flegal (1975).

Concentrations of cadmium in the kidney of the South Atlantic Great Skua were significantly higher than in the North Atlantic Great Skua, though this was not the case for liver mercury concentrations. The difference in cadmium concentrations appeared to be related to

diet, as the South Atlantic skua feeds primarily on seabirds with elevated cadmium levels and the North Atlantic Great Skua's diet comprises mainly fish, which were found to contain low cadmium levels. Mercury concentrations in these dietary items were more comparable, perhaps explaining the similarity between liver mercury concentrations in the two populations of skuas.

The variability in mercury and cadmium concentrations between individual North Atlantic Great Skuas may relate to the winter location of some individuals. The winter diet of the Great Skuas is unknown but is unlikely to show a dramatic change from the summer. Some Great Skuas winter off the coast of Iberia and in the western Mediterranean. This latter location is relatively polluted and the skuas may take up, through the diet, higher body burdens of cadmium and mercury. Significant differences were found for mercury liver concentrations between Cory's Shearwaters found in the Atlantic and Mediterranean (Renzoni et al., 1986).

In relating tissue concentrations to diet, a certain amount of data is available on the concentrations of metals in North Atlantic fish because of their importance as a food source for man. Although metal levels may vary geographically (cited in Forstner and Wittman, 1983), the effect is not highly significant. From results of analysis of metal levels in Atlantic and Pacific marine teleosts it appears unlikely that South Atlantic Procellariiformes are accumulating significant concentrations of cadmium and mercury from this source. Squid and euphausiids are a more important component of the diet, but few data are available on concentrations of metals in these groups.

The source of mercury in the South Atlantic is more difficult to ascertain as no measurements appear to have been made for the common prey items and the results for British coastal squid were less than $1 \mu\text{g g}^{-1}$. The accumulation of mercury in the South Atlantic

Procellariiformes appears to be different to that of cadmium. Concentrations of mercury are relatively low compared to cadmium, in squid-feeders and others, except for two species, the Wandering and Sooty Albatrosses. Mercury concentrations in the liver have been found to correlate with mercury intake in several studies (Fimreite, 1979; Hutton, 1981; Parslow et al., 1982; Delbeke et al., 1984; Norheim, 1984), so it can be presumed that these albatrosses have an elevated level of mercury in their diet.

Concentrations of both cadmium and mercury were much lower in the North Atlantic Procellariiformes. These species feed primarily on zooplankton and, in the case of the Fulmar, on fish offal. From analyses of fish offal the Fulmar would be unlikely to accumulate cadmium and mercury to the same extent as the South Atlantic Procellariiformes. The metal content of some items in the zooplankton are known to vary seasonally and may reach $16\mu\text{g g}^{-1}$ of cadmium, although $5\mu\text{g g}^{-1}$ was the average (Knauer and Martin, 1972). However, these concentrations could give rise to the slightly elevated levels found in North Atlantic Procellariiformes.

Differences in metal accumulation between sexes may be evident if female birds were able to excrete metals via the egg. However, metal accumulation may also be affected by the breeding season and moult (Ward, 1978). Sexual differences were found for liver mercury concentrations in the Rockhopper Penguin and Kerguelen Petrel, with lower concentrations being present in the female. For cadmium, differences were found in concentrations between male and female Rockhopper Penguins, Broad-billed Prions and South Atlantic Great Skuas, again with concentrations being lower in the female than the male. None of the North Atlantic species showed statistically significant differences in metal concentrations between male and female

birds.

There was considerable variation in the concentrations of the metals and the relationships between them, both in and between the various tissues. The correlations between the concentrations of the metals copper and cadmium were only found to be highly significant in the renal tissue of the North Atlantic Great Skua. Weakly significant relationships were found in the renal tissue of the Yellow-nosed Albatross and Broad-billed Prion, and in the hepatic tissue of Leach's Petrel, the Common Diving Petrel and the North and South Atlantic Great Skuas. Fewer correlations were found between copper and zinc.

Cadmium and zinc are known to antagonize copper metabolism by displacing copper from sulfhydryl binding sites on metallothioneins (Evans et al., 1970) but the inconsistencies in the results here suggest that this may not be taking place. However, the copper concentrations are low, compared to ducks and geese (Parslow et al., 1982) perhaps indicating that cadmium and zinc are antagonising copper. It may also be that copper concentrations are genus specific.

Considerable interest has been shown in the interactions between cadmium and zinc, since it was demonstrated that prior or simultaneous administration of zinc salts had a marked effect against cadmium toxicity (Webb, 1972; Parizek, 1978). Squibb and Cousens (1974) suggested that the increase in the synthesis of a low molecular weight protein in rats increased on exposure to cadmium, and that the binding of the cadmium to the protein was a mechanism of detoxification.

Highly significant correlations were found between the concentrations of zinc and cadmium in the kidney of seven of the sixteen species studied, with three other species showing weakly significant relationships. Significant relationships were also found between zinc and cadmium in the liver of ten species, although significant relationships in the liver did not always coincide with

those in the kidney.

The parallel increase in zinc renal concentrations with cadmium is thought to be caused by the protective influence of zinc against cadmium toxicity (Friberg et al., 1974; Elinder et al., 1977). It is possible, therefore, that the observed accumulation of zinc in the study species may influence the toxicological significance of the cadmium present, the process perhaps involving a metal-binding protein such as metallothionein. Hutton (1981) isolated from the kidney cytosol of the Great Skua a protein with similar properties to metallothionein and this protein was also isolated from Fulmar kidney (Osborn, 1979). As both of these species contained elevated cadmium concentrations in their tissues it was suggested that metallothionein was involved in the detoxification of cadmium.

The variations between the species, however, for the cadmium/zinc relationship were sufficiently great as to throw doubt on the validity of using this as an explanation for the detoxification of cadmium in the liver and kidney of all the species studied. More work would be required to explore the possibilities of other detoxification mechanisms and the possibilities of metabolic regulation. The normal distribution of cadmium in the tissues of some of the species also suggests the existence of metabolic regulation which may alter the significance of zinc to the amelioration of the toxic effects of cadmium. However, it has been suggested that the accumulation of cadmium and zinc parallel's that of zinc, and so there may be seasonal changes in cadmium and mercury levels with zinc, as related to the individual's physiology (Ward, 1978).

Damage to the kidney structure in the North Atlantic Fulmar, Puffin and Manx Shearwater was thought to be caused by the high metal concentrations in the tissues (Nicholson and Osborn, 1983). These

birds appeared, as do the South Atlantic birds, outwardly healthy with no obvious signs of physiological damage. It was suggested that the elevated concentrations of zinc in the tissues were indicative of disturbances in essential metal homeostasis. Nicholson and Osborn (1983) suggested that in the long-term there may be times in the life cycle, for example moult and breeding, when the demands on metal metabolism are high and damage to the kidney becomes critical. This damage was also found below the concentrations considered safe for humans by the World Health Organisation (Nicholson et al., 1983). If this renal damage exhibited itself in South Atlantic seabirds it may be that only a small anthropogenic input would cause more serious damage, to the detriment of the species.

Correlations were also found between cadmium concentrations in the liver and the kidney for nine of the sixteen species. The correlations between the metals appear to be most pronounced for the species with lower metal concentrations, perhaps suggesting that at very high concentrations other mechanisms of detoxification are used.

The contamination of seabirds has been linked to the importance of fish in the diet, as fish-eating seabirds contain higher levels of pollutants than most other avian species (Fimreite, 1979), but in this study high concentrations of cadmium and mercury appear to result from a squid and possibly zooplankton diet rather than from fish diet. The cadmium is probably of natural origin and the seabirds may have evolved a detoxification mechanism whereby cadmium is bound to a specific protein and is subsequently retained and excreted by the kidney. This efficient binding of cadmium may prevent cadmium transfer to the feather or egg (Renzoni et al., 1986).

Mercury is also known to have deleterious effects on reproductive physiology and on the birds themselves. The mercury concentrations were greatest in the Wandering and Sooty Albatrosses, Atlantic and

Soft-plumaged Petrels. Only the latter two species of the sixteen examined showed correlations between mercury and cadmium levels in the liver. None of the other metal levels showed any correlations with mercury levels except for selenium.

The concentrations of mercury in the Wandering and Sooty Albatrosses exceeded the levels found to cause symptoms of mercury poisoning in Goshawks (symptoms appear at concentrations of 100ug g^{-1} , wet weight in the liver (Borg et al., 1970), and this is apparently one of the more resistant species. Concentrations of total mercury may not, however, be the best indicators of the levels likely to cause damage as many dosing experiments have used toxic methyl-mercury compounds (Borg et al., 1969; Fimreite and Karstad, 1971). Fimreite (1974), in a Canadian study of scavengers and fish-eating birds, found concentrations of mercury up to 100ug g^{-1} in the liver, but in the Mergansers only 12% of this was in the form of methyl-mercury.

In the liver of several birds of prey Norheim and Frosliie (1978) found that the percentage total mercury present as methyl-mercury was lower in the liver and kidney compared to the muscle tissue. It was also found that there was an inverse relationship between the total mercury concentrations and the percentage of methyl-mercury in the organs (Norheim and Frosliie, 1978). This agrees with the results for Canadian birds (Fimreite, 1974) and may be a possible explanation for the tolerance of the very high concentrations in the livers of the Wandering and Sooty Albatrosses. The Canadian birds contained lower percentages of methyl-mercury in their tissues relative to their prey, which led to the suggestion that a demethylation mechanism was in operation. A similar relationship was found for Antarctic species (Norheim et al., 1982).

In the marine environment, mercury uptake is often accompanied by

selenium in many species of bird, mammal and fish, a relationship which may be the result of normal homeostatic regulation (Beijer and Jernelov, 1978). It therefore appears that selenium will protect against mercury toxicity in the marine environment, decreasing its detrimental effects on reproduction, behaviour and growth of organisms. Beijer and Jernelov (1978) also suggested that the increased retention of mercury caused by selenium may lead to higher biomagnification of mercury in the food chain and a higher body burden in the individual.

The Great Skua showed a highly significant relationship between mercury and selenium in the liver and muscle tissue, but not in the kidney. Of the few samples analysed for selenium from the South Atlantic birds, the relationship between mercury and selenium was positive in the Little Shearwater and Soft-plumaged Petrel. The samples for the Atlantic Petrel and Broad-billed Prion were too small to make any inferences concerning mercury/selenium relationships. The selenium concentrations were very variable for all these species.

The parallel accumulations of mercury in the kidney and liver, and mercury and selenium in the liver of the Great Skua were similar to those reported for Cory's Shearwater (Renzoni et al., 1986), the livers of marine mammals (Koeman et al., 1973) and the Great Skua (Hutton, 1981). A detoxification mechanism based on the demethylation of methyl-mercury and the complexation of mercury and selenium to form a non-toxic compound in the liver cells has been suggested as an explanation (cited in Renzoni et al., 1986). Such a mechanism would seem appropriate for South Atlantic seabirds. However, no significant relationship was found between mercury and selenium in the liver of Guillemots, Razorbills and Sooty Terns (Koeman et al., 1975; Stoneburner et al., 1980). Berlin (1978) concluded that selenium and mercury were metabolised very differently in different species, and

therefore that extrapolation between species was not possible. There may also be a threshold limit to levels below which detoxification mechanisms are prevented from operating.

The ability of selenium compounds to decrease the toxic action of both organic and inorganic mercury has been established in experimental animals, but such a relationship has also been suggested for cadmium (Chen et al., 1975; Mackay et al., 1975). In this study no significant relationship between cadmium and selenium was found to exist in the Great Skua, although Furness and Hutton (1979) found a cadmium/selenium relationship in the kidney of the Great Skua. The detoxifying action of selenium on cadmium may act either through the incorporation of selenium into a low molecular weight cadmium binding protein, or selenium could be incorporated into a large molecular weight pre-existing protein as a sulphur-selenium bond which may have a high affinity for cadmium (Chen et al., 1975).

A possible source of mercury excretion in the bird is via the feather. Feathers are formed during a relatively short period of juvenile life and during moult in adult birds. The mercury present in feathers has been shown to be related to the level of mercury present in the blood at the time of feather formation (Johnels and Westermark, 1969; Westermark, 1975). The mercury concentrations in the feather have been found to be 7-8 times that in the breast muscle although this ratio may vary (Hakkinen and Hanson, 1980). Unfortunately this aspect could not be closely examined in Great Skuas and South Atlantic Procellariiformes as the bird feathers analysed did not have the corresponding tissue available. From the mean liver concentrations for the Great Skuas and Procellariiformes and the mercury content of the feathers there appeared to be some form of relationship, those birds with the highest mercury feather concentrations also having the

greatest liver concentrations.

The concentrations of mercury in feathers from different parts of the bird's body may be very variable (Solonen and Lodenius, 1984; Woodburn, 1985; Furness, unpubl.) and this variability is extended to both species and individuals of the same species (Osborn et al., 1979; Furness, unpubl.; this study).

A lot of the work initiated by Swedish investigators has been carried out to determine historical differences in the mercury concentrations in the feather and hence in the environment generally. The Swedish studies found historical differences in mercury concentrations of feathers primarily because of the use of alkyl-mercury seed dressings (Berg et al., 1966; Westermark, 1975). For the Great Skua, no such historical differences were found although, due to possible differences in dietary habits, a significant difference in mercury concentration was found between birds from Shetland and Orkney and the Faeroes and Iceland. For the South Atlantic species, only one set of present day feathers were available for analysis and the levels found in the feathers do not differ from those in the museum feathers. The sexual differences in mercury feather concentrations for the South Atlantic species may reflect the ability of the female to excrete mercury via the egg.

Feathers are regarded as a possible indicator of levels of mercury in the environment. The use of feathers instead of tissues is advantageous in that reliable analyses can be performed on feathers, the bird does not have to be killed, and due to the keratin content of the feathers they are durable. There are pitfalls, however, in the use of feathers, firstly in the considerable variation in the mercury content of the feathers and secondly because they may become externally contaminated, and therefore have to be thoroughly washed (Goede and de Bruin, 1984).

Primaries have been shown to be less appropriate as indicators of mercury contamination since their content is probably not directly related to the diet at the time of moult, but is related to the stored mercury accumulated in the tissues since the previous moult. This would explain the decrease in mercury content of the feathers from primary 1 to 10. It therefore appears that the body feathers are the best indicators of mercury contamination of the environment. In using feathers of birds to indicate mercury concentrations in the environment, the migratory, feeding and moulting habits of the species should be fully understood (Osborn et al., 1979).

In both feathers and tissues no clear accumulation of mercury or cadmium was seen with age for the Great Skua as found in Black Guillemots (Applequist et al., 1985) and Wood Ducks (Lindsay and Dimmick, 1983). The Great Skua provided a unique opportunity to study the accumulation of metals with age, especially for cadmium and mercury which are non-essential metals with long biological half-lives. The results for the 27 birds of known age contrasted with those of Furness and Hutton (1979), for reasons previously explained (Chapter 6). No birds younger than four years were available for analysis and since chicks tend to have low concentrations, accumulation must occur at a young age. The accumulation of metals may vary between species, and may be dependent both upon the level of exposure and the subsequent metabolism of the metals.

The most important pollutants are those which are persistent in the environment and are readily stored and absorbed into animal tissue. The organochlorine compounds and certain heavy metals are particularly important in this context. They may, through various mechanisms, produce irreversible changes in the physiology, morphology and behaviour of animals exposed to toxic levels.

The man-made organochlorines are now ubiquitously distributed throughout the world's oceans. Levels in the Great Skua do not appear to be detrimental to the birds and the concentrations of DDE appear to be declining over time, but as persistent organochlorines are still evident in the environment and different species show different degrees of susceptibility to organochlorines, further monitoring and recording of the fate of these chemicals is required.

In this study, gross concentrations of metals have been analysed and elevated concentrations of mercury and cadmium found in an ecosystem apparently free from major anthropogenic contamination. The high concentrations of mercury and cadmium in the tissues appear to be related to dietary intake, especially for cadmium, as confirmed by the differences in kidney concentrations and diet of the two sub-species of Great Skua.

The seabirds may be able to detoxify or metabolically regulate these potential pollutants, but, ideally, to understand these mechanisms their mode of action should be fully elucidated at the biochemical level. Such investigations should also take into account the potential for the mechanisms to change seasonally with seasonal factors, such as migration, breeding and moult. The high concentrations found may be finely balanced within the seabird's environment, and between detoxification and toxicity in the birds. This study therefore provides a useful baseline as a guide to natural accumulation in the marine environment. It may only require a small anthropogenic input of metals to cause severe problems for pelagic seabirds.

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APPENDIX 1

NORTH ATLANTIC SEABIRDS

Great Skua	<u>Catharacta skua skua</u>
Fulmar	<u>Fulmarus glacialis</u>
Leach's Petrel	<u>Oceanodroma leucorhoa</u>
British Storm Petrel	<u>Hydrobates pelagicus</u>

SOUTH ATLANTIC SEABIRDS

Broad-billed Prions	<u>Pachyptila vittata</u>
Common Diving Petrel	<u>Pelcanoides urinatrix</u>
White-faced Storm Petrel	<u>Pelagodroma marina</u>
Grey-backed Storm Petrel	<u>Garrodia nereis</u>
White-bellied Storm Petrel	<u>Fregetta grallaria</u>
Kerguelen Petrel	<u>Pterodroma brevirostris</u>
Soft-plumage Petrel	<u>Pterodroma mollis</u>
Atlantic Petrel	<u>Pterodroma incerta</u>
Little Shearwater	<u>Puffinus assimilis</u>
Great Shearwater	<u>Puffinus gravis</u>
Yellow-nosed Albatross	<u>Diomedea chlorochynchus</u>
Wandering Albatross	<u>Diomedea exulans</u>
Sooty Albatross	<u>Phoebetria fusca</u>
Rockhopper Penguin	<u>Eudyptes chrysocome</u>
Tristan or Great Skua	<u>Catharacta skua hamiltoni</u>

APPENDIX 1

NORTH ATLANTIC FISH SPECIES

Sandeels	<u>Ammodytes marinus</u>
Haddock	<u>Melanogrammus aeglefinus</u>
Cod	<u>Gadus morrhua</u>
Whiting	<u>Merlangius merlangius</u>
Grey Gurnard	<u>Eutrigla gurnadus</u>
Red Gurnard	<u>Aspitrigla cuculus</u>
Long Rough Dab	<u>Hippoglossoides platessoides</u>
Dab	<u>Limanda limanda</u>
Plaice	<u>Pleuronectes platessa</u>
Lenon Sole	<u>Microstomus kitt</u>

APPENDIX 2

Table 1

Concentrations of Copper, Cadmium, Zinc Mercury and Selenium in
kidney and liver of the Broad-billed Prion (Pachyptila vittata)

Values for individual birds

KIDNEY			LIVER				
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight			
Cu	Zn	Cd	Cu	Zn	Cd	Hg	Se
4.9	45	40	7.7	41	19	0.14	12.3
3.4	32	29	5.7	50	14	0.28	-
3.5	29	29	3.6	31	9	0.43	-
4.2	38	30	5.2	40	11	0.54	-
4.9	41	42	6.8	54	19	0.23	-
4.6	45	72	7.5	46	26	0.52	-
4.8	45	34	6.0	46	17	0.37	-
3.8	43	29	6.1	59	11	0.44	-
3.7	39	40	4.6	42	18	0.34	-
4.7	40	41	5.9	49	24	0.49	-
3.5	37	30	5.5	50	16	0.48	-
4.0	39	39	5.7	51	26	0.33	2.0
5.2	44	48	7.2	55	13	0.27	-
3.5	37	26	5.3	37	14	0.60	-
6.0	39	27	5.2	35	10	0.23	-
4.3	35	25	6.3	31	11	0.44	-
4.2	32	40	7.5	43	13	0.52	-
5.4	39	46	6.5	39	18	1.06	-
4.8	32	31	6.1	40	16	0.46	-
3.6	30	28	7.5	54	14	0.20	-

Table 1 cont.

KIDNEY			LIVER				
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight			
Cu	Zn	Cd	Cu	Zn	Cd	Hg	Se
5.6	29	28	7.6	30	11	0.25	9.2
5.1	26	29	6.8	44	22	0.29	-
4.0	31	26	5.9	37	11	0.15	-
4.3	31	35	6.3	38	18	0.15	19.3
4.3	37	25	7.9	49	17	0.40	-
4.4	39	51	6.0	31	12	0.33	-
4.5	33	46	7.0	53	18	0.21	-
4.5	39	29	7.5	57	16	0.14	13.1
4.3	47	28	8.4	75	31	0.91	14.8
5.4	31	35	5.9	42	14	0.32	-
3.2	29	19	6.2	43	15	0.14	1.09

Table 2 Concentrations of Copper, Cadmium, Zinc and Mercury in
kidney and liver of the Common Diving Petrel (Pelcanoides
urinatix)

Values for individual birds

KIDNEY			LIVER			
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		
Cu	Zn	Cd	Cu	Zn	Cd	Hg
5.1	49	38	7.4	50	8.1	0.50
8.0	78	74	7.5	43	6.0	1.54
5.6	51	36	6.2	38	12	0.47
5.1	38	24	5.9	28	3.5	0.19
4.5	49	30	5.3	30	3.9	0.55
4.8	46	28	6.8	39	6.6	0.55
4.3	38	29	6.2	32	6.7	0.25
5.2	49	32	7.1	35	7.8	0.44
5.3	45	35	6.1	35	6.1	0.71
5.5	36	17	5.3	31	3.0	0.41
5.6	46	32	6.2	42	7.6	0.47
5.5	44	31	5.7	29	5.7	0.35
2.8	35	23	6.3	33	4.5	0.50
4.3	33	33	7.4	39	7.5	0.53
9.9	48	32	9.4	46	4.3	0.17
6.0	52	44	10.2	48	13.6	0.40
5.3	45	32	8.9	51	8.3	1.18

Table 3 Concentrations of the Metals Copper, Zinc, Cadmium and Mercury in Kidney and Liver of the Wandering Albatross (Diomedea exulans), Sooty Albatross (Phoebetria fusca) the Yellow-nosed Albatross (Diomedea chlororhynchos)

Values for individual birds

KIDNEY			LIVER			
ug g ⁻¹ wet weight			ug g ⁻¹ wet weight			
Wandering Albatross						
Cu	Zn	Cd	Cu	Zn	Cd	Hg
4.7	45	127	8.4	57	41	271
5.6	52	148	4.9	49	24	266
Sooty Albatross						
4.7	42	63	8.5	64	27	80
4.8	59	81	5.4	74	25	93
4.7	61	80	6.5	86	22	177
4.4	56	89	6.5	63	29	141
4.2	47	71	4.1	47	17	128
4.6	62	77	5.9	62	23	118
4.3	65	92	7.0	81	33	227
5.3	53	58	6.4	63	32	164

Table 3 cont.

Yellow-nosed Albatross

KIDNEY			LIVER			
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		
Cu	Zn	Cd	Cu	Zn	Cd	Hg
3.4	36	33	4.6	48	9.4	9.0
2.9	33	21	4.3	39	4.5	5.0
3.1	35	24	4.9	49	8.7	4.8
2.4	31	15	4.6	29	3.1	5.7
3.3	36	18	3.9	51	7.6	5.6
3.3	33	24	3.5	57	10.4	7.6
2.8	40	21	5.1	44	6.7	5.0
4.9	42	23	6.8	59	17.0	21.0
3.8	34	46	7.0	59	11.0	21.0

Table 4 Concentrations of Copper, Cadmium, Zinc and Mercury in the Liver and Kidney of Rockhopper Penguin (Eudyptes chrysocome)

Values for individual birds

KIDNEY			LIVER			
ug g ⁻¹ wet weight			ug g ⁻¹ wet weight			
Cu	Zn	Cd	Cu	Zn	Cd	Hg
3.4	75	60	4.1	53	20.0	3.7
3.1	73	109	5.7	28	3.9	3.2
3.9	67	88	3.7	52	16.0	2.2
2.7	42	40	3.1	27	9.2	2.1
2.7	62	71	3.8	41	16.0	3.6
4.4	86	112	4.2	42	25.0	1.8
2.7	41	32	3.0	27	6.7	1.3
3.7	54	54	2.8	33	9.0	0.97
6.1	55	73	5.8	36	16.0	1.5
4.1	47	52	3.4	33	10.0	1.5
4.5	82	112	5.1	61	26.0	2.8
3.8	78	62	4.6	44	16.0	2.9

Table 5 Concentrations of Copper, Zinc, Cadmium and Mercury in
Kidney and Liver of the Great Shearwater (Puffinus
gravis)

Values for individual birds

KIDNEY			LIVER			
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		
Cu	Zn	Cd	Cu	Zn	Cd	Hg
5.5	42	82	5.1	35	14	6.5
5.1	49	38	5.3	39	22	1.0
5.1	45	85	5.5	37	12	1.5
4.2	27	43	5.5	33	5.6	1.2
5.9	50	87	6.0	38	17	0.8
8.1	52	62	6.1	33	7.4	1.0
5.6	49	55	6.6	40	13	1.1
5.4	45	77	8.4	45	18	1.4
7.1	56	96	4.6	37	15	1.3
11.0	56	99	5.1	41	27	3.7
4.7	38	88	6.5	43	18	3.1
5.3	48	74	5.6	40	15	1.6
10.9	88	161	-	-	-	-

Table 6 Concentrations of Copper, Zinc, Cadmium, Mercury and Selenium in Kidney and Liver of the Little Shearwater (Puffinus assimilis)

Values for individual birds

KIDNEY			LIVER				
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight			
Cu	Zn	Cd	Cu	Zn	Cd	Hg	Se
2.8	50	71	13.4	54	20	1.29	-
5.7	59	69	6.6	43	21	1.25	-
6.0	61	39	6.6	34	14	1.52	50
5.5	45	48	8.0	37	10	1.56	56
5.9	41	37	7.4	50	18	0.93	-
4.9	46	43	9.5	42	17	1.47	59
10.4	49	54	7.4	41	16	0.88	-
3.7	34	23	5.5	28	4.5	0.60	-
4.2	46	27	7.0	42	9.2	1.60	5.0
24.0	66	56	7.1	42	15	0.94	-
3.9	48	33	6.7	32	10	1.45	8.0
5.2	57	46	-	44	17	1.00	46
7.0	49	46	13	42	30	1.45	1.3

Table 7 Concentrations of Copper, Zinc, Cadmium, Mercury and Selenium in Kidney and Liver of the Atlantic Petrel (Pterodroma incerta)

Values for individual birds

KIDNEY			LIVER				
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight			
Cu	Zn	Cd	Cu	Zn	Cd	Hg	Se
7.2	67	57	4.5	48	18	20	48
4.5	50	42	4.1	45	14	23	38
5.7	68	43	4.3	40	9	14	-
4.7	64	68	4.6	57	28	29	34
5.7	57	59	13.0	43	15	27	-
5.1	71	87	5.5	64	38	38	-
6.3	61	45	4.5	36	9	-	-
6.4	56	45	3.6	40	14	24	-
4.6	59	52	5.2	45	17	29	-
7.5	71	61	4.5	57	23	34	6.3
9.3	65	102	4.3	43	32	-	-
7.3	65	76	5.3	33	40	53	-
7.0	57	89	3.9	41	19	20	-

Table 8 Concentrations of Copper, Zinc, Cadmium, Mercury and Selenium in Kidney and Liver of the Soft Plumage Petrel (Pterodroma mollis)

Values for individual birds

KIDNEY			LIVER				
ug g ⁻¹ wet weight			ug g ⁻¹ wet weight				
Cu	Zn	Cd	Cu	Zn	Cd	Hg	Se
5.4	50	43	4.7	31	13	103	61
6.2	64	53	4.3	32	7.6	6.1	30
5.6	44	47	4.6	44	16	26	-
4.7	36	32	4.5	41	15	15	18
5.4	68	60	5.1	43	12	16	-
8.0	44	37	4.1	41	12	17	-
4.1	41	38	3.8	30	13	6.8	-
7.2	46	55	3.5	33	12	10	-
6.1	44	33	5.1	49	17	39	-
5.4	56	71	6.1	56	41	26	-
6.7	50	43	5.1	36	9.6	7.1	-
6.6	66	90	4.8	50	31	43	-
5.8	45	40	12.0	36	11	3.6	-
4.0	47	51	5.5	47	15	7.6	3.9
6.6	49	54	4.5	30	16	-	-
6.6	39	45	4.7	39	21	14	35
4.4	44	46	4.5	32	15	13	-
6.5	78	67	7.1	110	26	20	2.9

Table 9 Concentrations of Copper, Zinc, Cadmium and Mercury in
Kidney and Liver of the Kerguelen Petrel (Pterodroma
brevirostris)

Values for individual birds

KIDNEY			LIVER			
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		
Cu	Zn	Cd	Cu	Zn	Cd	Hg
4.9	52	67	5.9	52	21	5.9
4.7	45	34	6.2	41	12	6.3
4.5	47	41	5.1	39	12	6.8
4.5	38	32	3.4	43	20	5.8
4.5	36	22	17.0	35	7.4	4.3
6.1	50	54	6.6	81	19	2.0
8.4	43	36	5.1	29	12	5.3
5.0	54	54	6.6	48	14	5.7
5.0	51	46	5.0	31	18	4.1
4.7	44	52	6.5	51	16	4.3
3.8	49	55	5.5	44	18	3.9
3.8	38	38	5.2	37	11	1.9
5.2	47	68	5.3	42	18	4.7

Table 10 Concentrations of Copper, Zinc and Cadmium in Kidney, Liver, and Muscle of the White-bellied Storm Petrel (Fregetta grallaria)

Values for individual birds

KIDNEY			LIVER			MUSCLE		
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		ug g ⁻¹	wet weight	
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
7.5	35	18	5.8	34	11	5.5	15	2.7
7.2	35	20	8.0	41	10	7.1	13	1.8
7.1	39	22	8.1	46	15	5.6	14	0.59
6.3	39	23	6.0	41	13	5.7	17	1.4
6.5	36	21	6.0	39	12	7.2	14	0.84
5.8	40	20	3.4	28	10	7.3	17	1.7
6.1	36	19	7.2	38	11	6.5	14	1.4
5.2	48	26	6.2	41	10	5.6	19	0.54

Table 11 Concentrations of Copper, Zinc and Cadmium in Kidney,

Liver and Muscle of the Grey-backed Storm Petrel

(Garrodia nereis)

Values for individual birds

KIDNEY			LIVER			MUSCLE		
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		ug g ⁻¹	wet weight	
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
7.5	46	-	6.4	40	13	6.5	16	0.46
6.8	26	36	6.4	50	13	6.4	14	1.84
8.3	31	22	7.1	48	11	6.4	14	0.51
5.5	27	18	5.9	77	14	8.8	11	0.52
4.7	15	21	14.5	41	18	6.7	9.8	2.03
8.1	29	21	7.2	29	10	9.1	33	3.60
4.5	21	22	7.7	34	13	7.5	13	1.25
6.5	49	21	8.1	33	8	16.3	13	1.35

Table 12 Concentrations of Copper, Zinc and Cadmium in Kidney, Liver and Muscle of the White-faced Storm Petrel (Pelagodroma marina)

Values for individual birds

KIDNEY			LIVER			MUSCLE		
ug g ⁻¹ wet weight			ug g ⁻¹ wet weight			ug g ⁻¹ wet weight		
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
7.3	38	32	8.9	44	12	6.3	16	0.62
7.7	39	32	9.9	34	7.6	6.6	15	1.68
8.4	37	30	8.3	34	7.1	6.8	16	0.82
6.4	38	25	6.0	20	5.7	6.6	17	0.39
6.6	46	26	8.9	43	7.1	6.3	14	0.38
6.6	44	54	9.1	40	7.8	-	-	-
6.2	30	30	8.7	31	7.6	-	-	-

Table 13 Concentrations of Copper, Zinc and Cadmium in Kidney,

Liver and Muscle of the British Storm Petrel

Hydrobates pelagicus

Values for individual birds

KIDNEY			LIVER			MUSCLE		
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		ug g ⁻¹	wet weight	
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
15.0	43	12	6.3	32	4.6	6.3	10.3	0.71
11.0	41	27	6.5	25	6.1	7.0	13.0	0.80
8.7	26	15	6.0	26	2.6	7.7	11.0	0.50
13.0	41	30	6.1	16	8.3	6.6	9.9	0.76
9.8	30	16	6.3	28	4.9	5.6	10.5	0.55
8.8	41	7	3.5	21	3.5	6.9	12.0	0.35
7.2	28	22	4.0	28	9.6	7.3	11.0	0.75

Table 14 Concentrations of Copper, Zinc and Cadmium in Kidney,

Liver and Muscle of Leach's Petrel Oceanodroma
leucorhoa

Values for individual birds

KIDNEY			LIVER			MUSCLE		
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		ug g ⁻¹	wet weight	
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
8.5	21	37	7.7	20	13	6.8	7.1	2.0
8.1	20	33	6.9	17	13	6.1	6.6	0.66
9.7	24	29	8.2	29	12	5.7	7.5	0.62
6.1	16	19	5.1	19	6.6	6.8	8.1	1.02
8.6	14	26	7.7	18	11	6.4	7.0	1.05
6.8	15	21	5.9	18	8.0	5.6	7.0	1.70
8.4	18	23	6.1	18	6.9	5.9	7.2	0.60
5.8	19	25	4.8	19	6.8	5.7	7.5	1.50
6.6	24	29	6.4	21	14	6.6	8.0	1.75
5.7	19	27	5.0	20	7.2	5.7	7.8	0.80
4.2	19	22	6.3	16	4.5	5.2	7.2	1.20
5.0	15	22	5.2	19	7.7	5.2	8.5	0.90
6.5	17	23	7.8	23	9.8	5.8	9.2	0.90

Table 15 Concentrations of Copper, Zinc and Cadmium in Kidney, Liver and Muscle of Fulmars (Fulmarus glacialis) from the islands of St Kilda, Outer Hebrides and Foula, Shetland.

Values for individuals

KIDNEY			LIVER			MUSCLE		
ug g ⁻¹	wet weight		ug g ⁻¹	wet weight		ug g ⁻¹	wet weight	
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
St Kilda Fulmars								
3.9	30	6.0	4.7	27	1.9	3.0	17	0.14
3.4	22	5.5	4.4	27	1.4	2.8	18	0.10
3.9	36	7.4	4.3	32	2.6	4.6	17	0.22
3.4	35	19.0	4.4	29	5.0	3.6	17	0.21
3.8	27	2.8	5.2	40	0.65	4.0	20	0.22
4.4	32	11.7	6.8	35	2.6	3.3	28	0.21
3.9	28	8.9	3.8	25	2.0	3.9	26	0.22
3.2	34	14.0	5.5	28	2.9	4.4	24	0.20
Foula Fulmars								
3.5	30	5.5	6.4	43	2.0	4.2	27	0.70
3.5	35	5.9	5.1	73	1.4	3.7	22	0.70
3.4	49	25.0	7.0	79	7.7	3.8	24	0.66
4.2	46	15.0	6.5	38	1.9	5.0	22	0.46
2.9	33	5.0	4.8	-	1.6	4.4	26	0.43
3.3	39	7.3	4.7	79	1.4	4.3	19	0.28
3.1	36	6.8	4.8	29	1.6	3.7	22	0.18

Table 15 cont.

KIDNEY			LIVER			MUSCLE		
ug g ⁻¹		wet weight	ug g ⁻¹		wet weight	ug g ⁻¹		wet weight
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
Foula Fulmars								
3.1	38	14.0	5.2	39	4.5	4.6	16	0.92
3.8	38	11.7	4.7	34	2.4	3.5	24	0.32
2.3	35	7.1	5.5	36	1.3	4.4	22	0.45
1.2	30	2.3	5.0	32	0.52	3.4	24	0.25
2.3	40	13.0	3.3	28	3.1	3.7	17	0.36
3.2	86	5.0	5.4	38	0.77	3.9	23	0.35
4.9	55	14.0	5.2	32	3.1	4.3	12	0.34
3.9	44	6.7	11.2	-	0.74	4.9	16	0.24
3.9	47	12.0	6.9	-	4.2	5.0	13	0.29

Table 16 Concentration of Copper, Zinc, Cadmium and Mercury in
Kidney and Liver of the South Atlantic Great Skua
(Catharacta skua hamiltoni)

Result as $\mu\text{g g}^{-1}$ wet weight

KIDNEY			LIVER			
Cu	Zn	Cd	Cu	Zn	Cd	Hg
4.4	34	31	4.5	22	3.33	15.1
3.4	28	13	4.3	20	1.18	2.3
5.0	38	23	4.3	20	2.17	7.7
4.0	35	34	4.0	20	3.48	9.6
6.6	32	18	4.4	22	1.61	3.1
4.0	34	17	4.1	18	0.97	3.5
5.2	38	27	4.5	19	3.19	8.6
4.1	31	19	3.6	18	1.58	3.1
4.5	38	28	5.4	22	2.87	6.4
3.6	32	21	3.0	20	1.56	3.4
4.6	53	45	4.8	28	5.08	16.6
5.4	48	40	4.6	23	4.84	0.9
3.3	42	23	3.1	32	2.22	15.7

Table 17 Concentration of Copper, Zinc, Cadmium, Mercury and Selenium in Muscle Tissue of the Great Skua (Catharacta skua skua)

Results as $\mu\text{g g}^{-1}$ wet weight

Cu	Zn	Cd	Hg	Se
4.8	29	ND	0.80	1.32
5.6	24	0.11	0.37	0.61
5.7	21	0.09	0.56	0.79
4.9	19	ND	0.80	0.58
4.7	19	0.09	2.30	1.08
6.0	21	ND	0.74	0.76
5.9	23	0.07	0.76	1.24
6.8	25	0.07	0.58	0.56
4.7	27	0.04	0.43	1.02
5.3	22	ND	0.27	0.59
5.8	20	0.18	0.45	0.82
6.3	22	ND	0.85	1.17
5.0	18	0.22	0.32	0.58
5.6	18	0.19	0.71	0.94
5.1	32	0.13	1.18	1.07
6.0	39	0.13	1.17	1.80
5.2	20	0.09	0.12	-
5.6	28	0.10	0.31	0.80
6.0	23	0.11	0.35	0.79
5.8	24	ND	0.46	0.53

ND = Not Detectable

Table 18 Concentration of Copper, Zinc, Cadmium, Mercury and
Selenium in Liver tissue of the Great Skua
(Catharacta skua skua)

Cu	Zn	Cd	Hg	Se
6.6	33	3.10	4.30	7.6
4.5	28	3.00	2.80	6.0
5.9	28	0.57	5.37	9.7
5.6	30	0.36	13.70	10.5
4.7	30	0.23	4.53	10.1
4.6	39	0.34	4.45	8.8
6.4	28	1.97	2.37	8.8
4.2	32	0.96	5.07	9.0
5.7	27	1.21	1.69	6.2
6.0	22	0.59	2.87	6.0
6.5	42	3.98	4.12	8.9
5.3	32	1.27	3.73	5.6
4.5	31	2.53	5.13	7.5
6.3	40	4.18	5.56	6.2
6.9	33	2.48	3.24	5.5
4.7	30	2.68	6.12	9.9
5.7	34	2.35	1.50	5.5
5.7	35	1.88	1.82	5.4
5.2	28	0.77	2.83	7.3
5.0	32	0.17	2.24	6.9

Results as $\mu\text{g g}^{-1}$ wet weight

Table 19 Concentration of Copper, Zinc, Cadmium, Mercury and Selenium in Kidney Tissue of the Great Skua (Catharacta skua skua)

Results as $\mu\text{g g}^{-1}$ wet weight

	Cu	Zn	Cd	Hg	Se
	4.8	43	5.2	4.1	5.2
	4.2	34	11.1	2.0	4.6
	5.0	36	3.0	3.2	4.2
	4.3	29	2.7	4.6	6.5
	4.2	35	4.2	4.4	7.8
	3.6	28	2.5	2.9	6.3
	4.4	38	14.8	1.8	6.2
	3.2	30	9.3	2.3	7.4
	4.8	32	6.6	1.6	3.8
	3.5	34	5.3	1.3	5.0
	5.3	41	22.2	1.9	4.4
	4.0	36	12.6	1.3	4.2
	4.7	36	18.1	3.0	4.9
	4.9	47	32.6	2.2	5.8
	5.3	-	20.4	2.1	9.6
	4.5	45	21.2	5.2	8.6
	4.1	39	17.4	0.9	7.5
	3.8	38	16.5	1.9	5.1
	5.2	39	6.8	2.4	4.9
	3.8	38	1.7	2.2	4.5

Table 20 Concentration of Copper, Zinc and Cadmium in Kidney, Liver and Muscle Tissue of the Great Skua (Catharacta skua skua)

Results as $\mu\text{g g}^{-1}$ wet weight

KIDNEY			LIVER			MUSCLE		
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
5.2	48	26.2	7.6	35	-	-	-	-
5.4	40	24.8	7.2	26	2.6	-	-	-
6.5	55	20.6	5.6	32	1.1	-	-	-
3.4	41	16.5	6.2	26	2.2	-	-	-
7.2	47	14.9	5.3	21	0.9	-	-	-
6.1	44	20.6	6.6	29	2.1	-	-	-
3.9	38	13.3	5.6	35	1.3	-	-	-
5.7	38	8.3	5.7	23	0.5	5.8	18	0.01
6.2	41	18.4	6.7	26	1.9	5.1	24	0.07
5.6	33	6.5	7.2	24	0.6	6.0	25	0.02
4.2	31	14.4	4.3	28	1.5	4.7	27	0.07
5.0	33	3.6	6.1	25	0.3	5.1	20	0.02
5.0	26	6.1	3.9	21	0.6	5.0	24	0.03

Table 21 Concentration of Copper, Zinc and Cadmium in Kidney ,
Liver and Muscle Tissue of the Great Skua (Catharacta
skua skua)

Results as $\mu\text{g g}^{-1}$ wet weight

KIDNEY			LIVER			MUSCLE		
Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
7.7	67	42.8	6.6	26	4.2	6.2	18	0.23
5.3	34	4.1	5.9	22	0.3	5.2	16	0.04
5.9	42	14.7	6.4	22	2.2	6.0	17	0.05
5.6	41	4.4	6.1	24	0.4	5.3	19	0.04
6.0	52	25.4	5.4	73	2.4	5.8	16	0.06
6.7	51	21.1	6.1	26	2.9	6.4	19	0.05
7.1	58	28.9	6.4	25	2.2	6.0	19	0.07
6.8	51	19.6	7.0	27	2.9	6.1	16	0.08
8.4	75	40.6	8.2	33	4.4	6.1	19	0.10
6.6	43	10.4	5.7	22	0.4	5.9	16	0.05
5.8	52	30.5	7.2	27	2.8	5.9	15	0.14
4.1	36	7.2	4.4	21	0.5	6.0	24	0.08
6.2	46	29.4	6.8	28	3.2	-	-	-
6.1	73	-	7.7	31	0.2	6.2	19	0.03
6.3	48	22.0	4.7	31	3.4	7.0	17	0.13

Table 22 Concentration of Organochlorines in Muscle Tissue of the
Great Skua (Catharacta skua skua)

Results as $\mu\text{g g}^{-1}$ wet weight

SEX	AGE	%LIPID	DDE		PCB	
			TISSUE	LIPID	TISSUE	LIPID
female	4	6.2	0.45	7	4.2	6.7
"	6	7.1	10.30	145	23.0	322
male	9	8.3	4.50	55	41.0	488
female	13	7.1	0.82	12	12.0	165
male	7	6.4	1.60	25	14.0	226
"	9	7.4	4.30	59	39.0	528
"	5	7.4	6.90	94	45.0	607
female	6	9.8	8.20	84	72.0	738
male	5	10.1	2.96	29	32.0	313
"	5	5.5	0.56	10	6.2	114
"	11	8.2	1.61	20	10.9	133
female	6	8.7	0.60	7	3.4	39
male	15	5.3	1.11	21	10.0	189
female	11	6.7	1.13	17	1.8	27
male	5	8.2	0.85	10	6.2	76
"	12	6.5	3.30	50	16.0	249
"	10	7.0	0.87	12	5.6	79
"	12	7.9	2.57	33	17.0	216
"	13	8.5	1.75	21	22.0	261
female	11	7.7	2.69	35	46.0	569

Table 23 Concentration of Organochlorines in Liver Tissue of the
Great Skua (Catharacta skua skua)

Results as ug g⁻¹ wet weight

AGE	%LIPID	DDE		PCB	
		TISSUE	LIPID	TISSUE	LIPID
4	11	3.14	28	7.6	68
6	12	7.40	63	6.9	59
9	10	7.80	75	44.0	422
13	9	2.11	24	10.2	117
7	10	3.90	38	32.0	323
9	-	-	-	-	-
5	-	-	-	-	-
6	-	-	-	-	-
5	12	1.57	14	12.4	108
5	15	1.08	7	11.1	76
11	15	1.31	9	7.8	54
6	11	0.38	4	1.7	16
15	13	1.80	14	19.0	150
11	13	2.06	16	9.2	70
5	12	1.04	9	14.0	114
12	14	7.20	51	33.0	234
10	11	1.33	12	10.4	93
12	11	5.60	49	28.0	245
13	29	7.50	25	78.0	264
11	15	6.00	41	99.0	668

Table 24 Concentration of Organochlorines in Fat Tissue of the
Great Skua (Catharacta skua skua)

Results as $\mu\text{g g}^{-1}$ wet weight

AGE	%LIPID	DDE		PCB	
		TISSUE	LIPID	TISSUE	LIPID
4	80	9	12	64	81
6	76	24	32	95	125
9	62	6	10	456	741
13	68	39	57	201	297
7	69	45	65	308	447
9	73	84	115	581	793
5	52	81	157	574	1113
6	79	78	101	346	445
5	73	42	58	427	584
5	73	17	24	175	241
11	61	20	33	136	223
6	80	80	100	128	675
15	64	31	98	260	195
11	54	17	32	76	140
5	69	13	19	181	263
12	62	61	99	258	417
10	66	11	17	68	111
12	62	32	52	183	299
13	72	-	-	306	427
- 11	73	-	-	-	-

APPENDIX 3

Table 1 Concentration of Mercury in Feathers from Museum Specimens of McCormick's Skua

LOCATION	DATE OF COLLECTION	SEX	ug g ⁻¹ DRY WT	HG
Palmer	11.4.45	female	2.34	
"	14.11.13	"	0.90	
"	26.2.45	"	7.04	
"	3.4.45	male	2.68	
"	2.4.45	"	2.46	
"	1.4.42	"	2.68	

Table 2 Concentration of Mercury in Feathers from Museum Specimens of Catharacta skua hamiltoni

LOCATION	DATE OF COLLECTION	SEX	ug g ⁻¹ DRY WT	HG
Inaccessible	9.3.51	male	3.50	
Island	16.10.1873	-	6.29	
"	9.5.50	male	1.90	
"	28.5.52	female	3.49	
Gough Is	31.5.22	male	3.65	
"	17.12.55	female	2.92	
"	-. 5.22	"	4.25	
"	21.2.52	male	2.10	
"	12.1.56	"	2.04	
Nightingale	21.5.22	"	2.18	
Tristan da Cunha	28.8.50	female	4.00	

Table 3 Concentration of Mercury in Feathers of Museum Specimens
of the Antarctic Skua

LOCATION	DATE OF COLLECTION	SEX	ug g ⁻¹	HG
Falklands	19.1.32	female	0.69	
"	4.1.31	male	0.53	
"	18.12.30	"	1.75	
"	20.11.21	female	1.29	
"	4.1.31	male	1.05	
"	17.12.30	"	0.85	
"	1894	female	3.85	
"	1894	male	5.26	
"	15.4.1883	-	7.62	
"	1875	-	6.06	
"	1873	female	21.61	

Table 4 Concentration of Mercury in Feathers of Museum Specimens
of Catharacta skua lonnebergi

LOCATION	DATE OF COLLECTION	SEX	ug g ⁻¹	HG
South Shetland	26.12.23	female	4.26	
South Orkneys	18.12.49	male	1.40	
South Georgia	1913	"	1.40	
"	14.11.13	"	2.69	
"	"	"	2.73	
"	25.12.21	"	2.35	

Table 5 Concentration of Mercury in Feathers from Museum Specimens of the Chilean Skua

LOCATION	DATE OF COLLECTION	SEX	ug g ⁻¹ HG
Rio de Janeiro, Brazil	?8.1882	-	5.00
Brazil	?9.1879	male	9.18
Peru	27.9.12	female	19.40
Patagonia	5.2.03	"	1.53
Magellan Strait	?12.1879	male	2.08
Tierra del Fuego	14.3.30	female	3.34
Chile	9.2.03	"	2.03
"	?9.1879	"	9.20

Table 6 Concentration of Mercury in Feathers from Museum Specimens of the Great Skua (Catharacta skua skua)

LOCATION	DATE OF COLLECTION	SEX	ug g ⁻¹ HG
Hoy Orkney	11.8.38	female	5.37
" "	"	male	4.22
" "	22.8.38	"	3.64
Unst Shetland	31.8.07	"	2.98
Scalloway	30.9.11	"	9.94
Hermanness	20.6.14	"	7.77

Table 6 cont.

	LOCATION	DATE OF COLLECTION	SEX	ug g ⁻¹	HG
	Shetland	20.9.32	male	8.44	
	"	29.8.39	"	3.87	
	Lunna	17.8.39	female	4.38	
	Papa Stour	26.8.39	"	3.99	
	Lerwick	21.8.39	male	5.52	
	"	29.7.40	female	3.57	
	Foula	15.9.83	-	3.54	
	Faroes	26.8.1873	male	36.00	
	"	22.7.1873	-	84.00	
	"	25.6.1873	male	22.00	
	"	?8.1877	-	22.00	
	"	12.6.1879	female	14.00	
	"	1879	male	46.00	
	"	26.5.1884	"	16.00	
	"	26.9.1884	"	8.85	
	South Iceland	4.8.07	"	16.00	
	"	"	female	35.00	
	North Iceland	11.8.10	male	4.46	
	"	2.8.11	"	11.90	

Table 7 Concentration of Mercury in Primary Feathers of the
Great Skua (Catharacta skua skua)

Results in $\mu\text{g g}^{-1}$ Hg

PRIMARY	RING NO				
	NO	HW46816	HW02039	HW16414	HW60882
1	10.0	5.4	7.4	4.3	5.6
2	8.8	5.3	6.7	4.0	4.4
3	8.6	4.8	5.9	3.9	4.2
4	6.4	4.1	6.1	2.5	3.5
5	5.9	3.8	4.7	3.3	3.4
6	5.5	4.5	5.0	2.9	4.3
7	3.4	4.5	5.6	2.8	6.3
8	2.4	4.0	6.4	2.8	9.0
9	2.3	5.9	5.0	2.5	7.4
10	9.0	6.7	6.0	2.6	7.3
Back	8.7	8.3	6.1	3.5	7.4
Belly	7.5	6.4	6.1	2.2	7.6

Table 8 Concentration of Mercury in Feathers of Seabirds from the South Atlantic

Results in $\mu\text{g g}^{-1}$ Hg

PRIMARY	SPS	AP	KP	GS	GRS
NO					
1	12.1	24.5	4.2	3.4	28.3
2	12.9	26.7	3.6	3.2	28.8
3	11.3	20.2	4.4	2.5	21.7
4	8.1	18.0	3.2	2.3	20.4
5	7.5	13.0	2.5	1.8	13.8
6	4.2	13.6	1.6	1.8	11.1
7	5.3	15.4	1.5	1.3	6.0
8	6.0	13.7	1.5	1.1	4.1
9	6.7	13.9	1.3	1.0	3.2
10	4.9	11.6	1.0	0.8	3.1
Coverts	7.4	18.3	2.3	2.0	7.4

SPS = Soft-plumaged Petrel

AP = Atlantic Petrel

KP = Kerguelen Petrel

GS = Great Shearwater

GRS = Gough I. Great Skua

Table 9 Concentration of Cadmium, Copper and Zinc in Feathers of
the Great Skua (Catharacta skua skua)

Results in ug g⁻¹

PRIMARY	HW69379			HW03804			
	NO	Cd	Zn	Cu	Cd	Zn	Cu
	1	ND	121	10	ND	97	18
	2	"	112	13	"	93	15
	3	"	175	39	"	92	10
	4	"	88	18	"	94	10
	5	"	82	17	"	91	21
	6	"	85	21	"	97	12
	7	"	88	16	"	87	11
	8	"	97	9	"	93	13
	9	"	91	22	"	100	14
	10	"	89	17	"	95	15
	Back	"	141	15	-	-	-
	Belly	0.18	45	22	-	-	-
	Head	-	-	-	0.47	121	12
	Scapulas	-	-	-	ND	123	15
	Under-tail	-	-	-	"	111	16
	Mantle	-	-	-	"	136	9

ND = Not Detectable

Table 10 Concentration of Selenium in Primary Feathers of the
Great Skua (Catharacta skua skua)

Results in $\mu\text{g g}^{-1}$ Se

PRIMARY	HW46816	HW02039
NO	Se	Se
1	2.47	1.62
2	-	0.99
3	1.81	9.29
4	1.46	1.45
5	1.74	0.40
6	1.68	1.38
7	0.66	1.22
8	1.45	1.26
9	1.91	1.54
10	1.64	1.56

Table 11 Concentration of Mercury in Feathers of the Great Skua
from present day and Museum Specimens

LOCATION	RING NO	ug g ⁻¹	HG	LOCATION	DATE OF COLLECTION	ug g ⁻¹	HG
Foula	HW23722	2.61		Unst	31.8.07	7.8	
"	HW13056	11.12		"	20.6.14	35.1	
"	HW15674	2.75		Noss	26.8.39	11.5	
"	HW47152	6.13		Noss	21.8.39	22.9	
"	HW46981	3.75	Shetland		30.9.11	51.5	
"	HW46145	4.81		"	20.9.32	48.8	
"	HW16414	11.03		"	29.7.40	11.9	
"	HW38024	14.49		"	29.8.39	12.3	
"	HW02039	7.20	Faeroes		17.8.1873	101.0	
"	HW29208	12.67		"	17.8.1886	205.0	

APPENDIX 4

Table 1 Concentration of Copper, Zinc and Cadmium in Gut, Gut Contents, Liver and Flesh of Fish from Shetland waters.

Results in $\mu\text{g g}^{-1}$ wet weight

	GUT			LIVER		
	Cu	Zn	Cd	Cu	Zn	Cd
Whiting n=10						
Mean	4.45	83	0.98	1.60	20	0.16
Range	1.2-12.0	28-163	.20-4.29	.90-3.46	12-38	.08-.48
Cod n=4						
Mean	1.20	25	0.14	2.46	12	0.06
Range	1.09-1.31	18-32	.10-.18	2.0-3.1	9-16	.05-1.00
Haddock n=9						
Mean	2.07	29	0.19	2.42	19	0.08
Range	1.17-3.29	17-46	.04-.31	1.02-4.92	7-38	.04-.12
Dab n=10						
Mean	1.78	19	0.17	2.76	24	0.27
Range	1.10-2.74	14-27	.09-.26	1.23-3.43	21-27	ND-.6
Plaice n=4						
Mean	1.08	17	0.19	1.63	20	0.26
Range	.72-1.68	16-18	.14-.26	1.26-1.99	15-24	.12-.40
Lemon Sole n=10						
Mean	2.26	21	0.29	3.69	28	0.70
Range	1.65-3.60	15-25	.12-.65	.51-5.10	22-33	.29-1.39
Sandeel n=16						
Mean	3.20	25	0.51	1.77H	46H	0.13H
Range	2.10-4.90	22-30	.42-.66	1.60-1.90	43-47	.10-.18

H =Results for Head alone

Table 2 Concentration of Copper, Zinc and Cadmium in Kidney,
Liver and Muscle of Guillemot, Fledgling Kittiwake and
Skua Chick

Results as $\mu\text{g g}^{-1}$ wet weight

	KIDNEY			LIVER			MUSCLE		
	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn	Cd
Skua chick									
	3.2	20	0.03	3.4	22	0.05	1.66	13	ND
Fledgling Kittiwake									
	3.5	23	0.11	3.7	17	0.06	2.94	12	ND
Guillemot chick									
	7.6	22	0.12	6.5	25	0.06	1.48	15	ND
Guillemot adult females									
	4.1	24	3.25	6.7	26	0.77	4.32	10	0.03
	3.4	22	6.70	5.6	25	1.07	3.33	9	0.08
	3.7	22	8.10	5.3	22	1.17	4.13	12	0.03
Guillemot adult male									
	3.3	23	4.70	5.1	19	0.60	3.77	15	0.04

Appendix 5

Diets of South Atlantic Procellariiformes from published and unpublished data of stomach contents and regurgitates

a = unpublished data from stomach contents of birds sampled at Gough Island (Furness and Furness, unpubl).

b = Williams and Imber, 1982

c = Croxall and Prince, 1981

d = Strange, 1982

Rockhopper Penguin

12 samples: stomach contents = 19 squid beaks
50 otoliths

N.B squid beaks are more difficult to digest than otoliths and there may therefore be some bias towards the squid content of the diet (a).

Literature 1) chick is fed on euphausiids, fish and squid (d).

2) adult also feeds on crustaceans (Thysanoessa macrura)

(b)

Wandering Albatross

2 samples: stomach contents = 14 squid beaks

4 regurgitates contained 570 squid beaks and 4 fish

60% of the squid were Histioteuthidae (a)

Yellow-nosed Albatross

9 samples: stomach contents = 30 squid beaks
5 otoliths

Literature 1) 2 pellets contained 5 squid beaks (b)

Sooty Albatross

8 samples: stomach contents = 5 squid beaks (a)

Literature 1) 4 pellets contained only squid beaks, 60% of which came from the family Cranchidae. Many of these squid beaks were Onychoteuthid (b).

Broad-billed Prion

31 samples: stomach contents = 14 contained copepods
2 contained squid beaks
1 contained a fish bone

Over 100 regurgites contained only copepods (a)

Literature 1) 3 regurgites contained copepods (b).

Atlantic Petrel

13 samples: stomach contents = 619 squid beak
1 contained crustaceans

8 regurgites: 7 contained squid, 3 fish and 1 octopus (a)

Literature 1) 13 food samples = 70% squid (Cranchidae:
Histioteuthidae).
17% fish (Mystophidae)
13% crustaceans especially
amphipods (b)

Kerguelen Petrel

13 samples: stomach contents = 123 squid beaks
6 otoliths
30 polychaetae jaws

Literature 1) 22 stomach samples contained: 70% squid
24% crustacea
6% fish (Schramm, 1983)

Soft-plumaged Petrel

18 samples: stomach contents = 433 squid beaks
22 otoliths
13 fish bones (a)

Literature 1) 2 stomachs contained 9 squid beaks (Cranchidae;
Histioteuthidae, Mastogoteuthidae) (b).

2) 9 chicks regurgitated: 89% squid
10% crustacea

1% fish (c)

Great Shearwater

13 samples: stomach contents = 591 squid beaks (a)

Literature 1) 1 stomach sample contained 22 squid beaks, 70% of which were juvenile *Ommastrephidae* and 30% *Histioteuthidae* (b).

Little Shearwater

13 samples: stomach contents = 1504 squid beaks

74 otoliths

2 fish bones

1 stomach contained copepods (a)

Literature 1) 1 stomach contained the beaks of small squid, mostly juvenile *Ommastrephidae* (b).

Common Diving Petrel

19 samples: stomach contents = euphausiids

fishbones (a)

Literature 1) 1 stomach contained 13 euphausiids and 1 hyperiid amphipod (b).

2) 100% crustacea (c)

Grey-backed Storm Petrel

11 samples: stomachs were empty (a)

Literature 1) young stalked goose barnacles *Lepas australis*

(Imber, 1981). Grey-backed Storm Petrel stomachs from

the Chatham Islands contained: 6.8% Amphipoda

7.3% Euphausiacea

85.5% *Lepas australis*

0.1% Isopoda

0.3% Teleostei

(Imber, 1981)

White-faced Storm Petrel

19 samples: stomach contents = 2 squid beaks in 1 stomach
17 fish vertebrae in 1 stomach
4 polychaetae jaws in 1 stomach
copepods in 1 stomach (a)

Literature 1) 30% Teleostei
3.6% Stomatopoda
46.2 Euphausiacea
9.6% Amphipoda (Imber, 1981)

2) stomach samples contained the euphausiid Nematoscelis megalops (Imber, 1984).

White-bellied Storm Petrel

13 samples: stomach contents = 3 squid beaks
7 otoliths (a)

South Atlantic Great Skua

Diet in order of importance 1) Broad-billed Prions
2) Soft-plumaged Petrels
3) Kerguelen and Atlantic Petrels
4) Storm Petrels
5) Common Diving Petrels
6) Yellow-nosed Albatross eggs, Rockhopper Penguin eggs and Chicks, Fur Seal carcasses and afterbirth (a).

APPENDIX 6

Results for Mann-Whitney U-test testing for significant differences between concentrations of zinc in the liver and kidney tissue and between concentrations of cadmium in the same tissues.

	ZINC			CADMIUM		
	n	U-statistic	'p'	U-statistic	'p'	
North Atlantic Great Skua	47	251 stnd 6.45	0.01	65.5 stnd 7.8	0.05	
South Atlantic Great Skua	13	4	0.05	0	0.05	
Wandering and Sooty Albatrosses	10	11	0.05	1	0.05	
Yellow-nosed Albatross	9	k23	0.05	1	0.05	
Broad-billed Prion	31	k226 stnd 3.58	0.01	25.5 stnd 6.41	0.01	
Great Shearwater	12	22	0.05	0	0.05	
Little Shearwater	13	30	0.05	2	0.05	
Common Diving Petrel	17	77.5	0.05	0	0.05	
Atlantic Petrel	13	11	0.05	0	0.05	
Soft-plumaged Petrel	18	93.5	0.05	5	0.05	
Kerguelen Petrel	14	76	n.s.	0	0.05	
White-bellied Storm Petrel	8	k27	n.s.	0	0.05	
Grey-backed Storm Petrel	8	k12	0.05	0	0.05	
White-faced Storm Petrel	7	18	n.s.	0	0.05	
British Storm Petrel	7	6.5	0.05	2	0.05	
Leach's Petrel	13	k71.5	n.s.	0	0.05	
Fulmar	25	254 stnd 0.45	n.s.	30 stnd 5.48	0.01	
Rockhopper Penguin	12	15	0.05	0	0.01	

stnd= standard normal deviate n>19

In all samples kidney metal concentrations are higher than in the liver, except those marked k.