CHAPTER 12

Concentrations of heavy metals (Cd, Cu, Pb, Ni & Zn) and organochlorine contaminants (PCBs, DDT, DDE & DDD) in the blubber of Cape fur seals *Arctocephalus pusillus pusillus* off the Eastern Cape coast of South Africa

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ABSTRACT

The concentration of heavy metals (Cd, Cu, Pb, Ni and Zn) and organochlorine contaminants (PCBs, DDT, DDE and DDD) in the blubber of 12 adult male Cape fur seals, *Arctocephalus pusillus pusillus*, inadvertently caught in trawl nets off the Eastern Cape coast of South Africa during commercial fishing operations between May 1993 and October 1994, was investigated. The median and range of concentrations for each metal were, in µg/g wet weight: Cd, 0.4 (<0.04–0.53); Cu, 2.6 (2.17–7.43); Pb, 0.7 (0.54–0.99); Ni, 17.7 (9.39–23.18) and Zn, 11.5 (3.14–16.65). Dry weights were: Cd, 0.5 (<0.04–0.59); Cu, 2.9 (2.47–8.45); Pb, 0.6 (0.54–1.14); Ni, 17.0 (10.79–28.22) and Zn, 12.8 (3.61–20.26). Concentrations of Cd, Pb and Zn were in the limits of reported values; however Cu and Ni levels were considerably higher. There is no evidence that the elevated levels of Cu and Ni reported in this study would pose a serious threat to the health of individual animals; however, high concentrations of these metals may be sufficient to result in some additional stress to animals when they mobilise their lipid reserves during illness or starvation. Nickel and Cd concentrations appeared to increase with age; however, small sample size prevented statistical analysis. Concentrations of organochlorines (µg/g wet weight) were below the limit of detection.

INTRODUCTION

Organochlorine contaminants, particularly polychlorinated biphenyls (PCBs) and the DDT group of insecticides are persistent environmental contaminants. These lipophilic compounds are known to accumulate in the fatty tissue of pinnipeds and other marine mammals (Risebrough, 1978). Pinnipeds are ideal repositories for high concentrations of organochlorines because they are long lived top predators which have large fat reserves in relation to their body size (Holden, 1972, 1978). In wild pinniped populations, the detrimental effects of organochlorines are difficult to establish; evidence is mostly circumstantial. However, high concentrations of certain organochlorines have been associated with premature births in California sea lions, *Zalophus californianus* (DeLong *et al.*, 1973); decreased reproductive rates and reproductive abnormalities in harbour seals, *Phoca vitulina* (Duinker *et al.*, 1979; Reijnders, 1980, 1982, 1986); suppression of natural killer cell activity in harbour seals (Ross *et al.*, 1997); and pathological changes of bony tissue and reproductive organs in Baltic grey seals, *Halichoerus grypus,* and ringed seals, *Phoca hispida* (Helle *et al.*, 1976; Olsson 1978; Bergman & Olsson, 1986, 1989; Bergman *et al.*, 1986, 1992; Olsson *et al.*, 1994).

Other pollutants which pose a potential threat to the future status of pinniped populations are the heavy metals. High concentrations of certain metals are a potential source of clinical disease and stress in marine mammals (Eisler, 1981; Wagemann & Muir, 1984; Thompson 1990; Skoch, 1990; Olsson *et al.*, 1992; Law, 1996). Of the metals which are considered to be toxic, Hg, Pb and Cd are thought to represent the greatest health risk to pinnipeds (Thompson, 1990). The toxic effects of these metals have been summarised by Skoch (1990).

The Cape fur seal, *Arctocephalus pusillus pusillus,* is the only indigenous breeding pinniped in southern Africa. It breeds at 25 colonies from Black Rocks (lat. 33° 50'S, long. 26° 15'E) on the south-east coast of South Africa, to Cape Cross (lat. 21° 46'S, long. 13° 57'E), Namibia. Current population size is estimated to be 1.5 to 2 million (Butterworth & Wickens, 1990). On the south-east coast, where two breeding colonies occur (Seal Island, Mossel Bay; Black Rocks, Algoa Bay), population levels are declining (SFRI, unpubl. data; Stewardson, unpubl. data), underlying the immediate need to document the biology of these top predators and evaluate potential threats.

DDT, dieldrin and PCBs have been used extensively in South Africa primarily as insecticides, fire retardants or heat absorbents; however, few studies have examined the occurrence of chlorinated hydrocarbon residues in the resident seal population (Henry, unpubl. report; Cockcroft & Ross, 1991). Furthermore, industrial development along the coast of southern Africa has resulted in an increase in the presence of toxic metals in the marine environment, particularly in inshore waters (Allan Connell, pers. comm.). The effects of industrialisation on the health of resident pinnipeds is not known.

Here we investigate the concentrations of heavy metals (Cd, Cu, Pb, Ni and Zn) and organochlorine contaminants (PCBs, DDT, DDE and DDD) in the blubber of 12 healthy adult male Cape fur seals from the Eastern Cape coast of South Africa. The results are compared with concentration ranges reported in the literature for other species of pinnipeds, and the toxic significance of these concentrations discussed. Age accumulation effects are also considered.

MATERIALS AND METHODS

Collection of samples

Twelve adult male Cape fur seals were included in this study (Table 12.1). These animals were inadvertently drowned within trawl nets during commercial fishing operations off the Eastern Cape coast (Fig. 12.1), between May 1993 and October 1994. Routine necropsies were performed on the fresh carcasses and biological parameters recorded based on recommendations of the Committee on Marine Mammals, American Society of Mammologists (1967). Blubber thickness was used as an index of physical condition. Specimens were examined for gross abnormalities (histopathological studies were not conducted). Blubber samples of approximately 20 g were removed from the anterior end of the sternum, wrapped in aluminium foil and stored at –20˚C for subsequent analysis. Upper canines were collected for aging purposes following Oosthuizen (1997), assuming a birth date of December 1 (Shaughnessy & Best, unpubl. report).

Gas chromatography

Thawed samples of blubber (15 g) were mixed with anhydrous sodium sulphate and subject to soxhlet extraction with hexane for 4 h. Fat extract (0.3–0.4 g) was cleaned up using alumina and silica gel as adsorbents. Concentrations of polychlorinated biphenyls (PCBs-57 in total) and DDT and its metabolites (DDE and DDD), were estimated using high resolution capillary gas chromatography equipped with a 30 m fused silica column (0.32 mm i.d.), coated with SPB5 as a liquid phase (0.22 mm) and ^{63}Ni electron capture detection (ECD). The detector temperature was 320˚C. The oven was programmed at a rate of 10˚C. min^{-1} from 50˚C to 180˚C (1 min), and then at 2˚C. min^{-1} to 220˚C, and at 4˚C. min^{-1} to 260˚C. The limits of detection of the residues represent amounts giving at least 2.5% full scale detection on the chart reader. The limits were DDE 0.5 pg/µl; DDD 0.5 pg/µl; DDT 0.75 pg/µl. Detection limits for a 10 g sample with a fat content of 0.5% was 500 pg/g for the PCBs. Full details of procedures are given in de Kock (1990).

The chlorinated hydrocarbon concentrations were determined by comparing the peak characteristics and retention times obtained from the samples with those of calibration range of standards injected daily. Compounds were quantified with standards obtained from the National Research

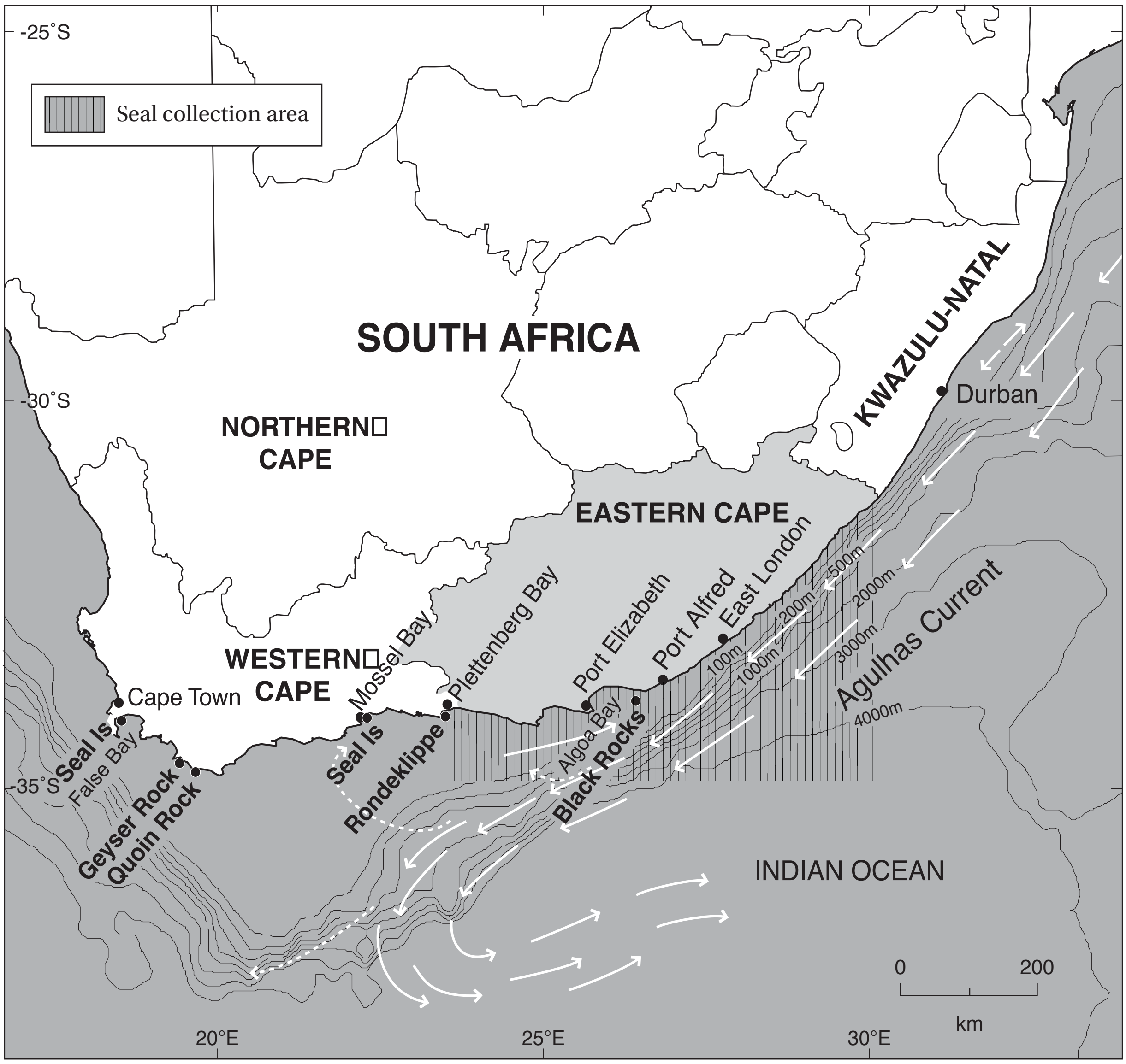

Fig.12.1 The breeding range of Cape fur seals along the south coast of southern Africa.
Seals (n = 12) were collected from the Eastern Cape coast.

Council, Marine Analytical Chemistry Standards Program (MACSP).

Atomic absorption spectroscopy

Thawed samples of blubber (2.5–3.0 g) were dried at 90˚C for 24 h, cooled in a desiccator, brought to room temperature and weighed to obtain dry weight. The dried samples were digested with concentrated nitric acid and the sediments with a 4:1 mixture of nitric and perchloric acids. Concentrations of Cd, Cu, Pb, Ni and Zn were determined by atomic absorption spectroscopy (single-element hollow cathode lamp and a deuterium lamp background corrector). The limits of detection for each metal were Cd, 2 µg/l (10 µg/l); Cu, 3 µg/l (30 µg/l); Pb, 10 µg/l (100 µg/l); Ni, 10 µg/l (70 µg/l) and Zn, 1 µg/l (8 µg/l). Suggested working concentrations are given in parentheses. Full details of procedures are given in Watling (1981). Compounds were quantified using MERK standards.

Concentrations are expressed as µg/g wet weight and µg/g dry weight. The median and range were used rather than the mean and standard deviation because the data are skewed and there are extreme data whose exact values are unknown (T. Prvan, pers. comm.). In pinnipeds, Cd, Cu and Zn concentrations tend to decrease in the order kidney/liver > muscle/blubber (Thompson, 1990). Therefore, we compare the results of the present study with concentrations from the blubber/muscle tissue of other pinnipeds.

RESULTS AND DISCUSSION

Details of the 12 male specimens are presented in Table 12.1. Animals were in good physical condition with an average blubber thickness of 29 ± 8 mm. Apart from high parasite burdens in some animals (Stewardson & Fourie, 1998), post-mortem examination showed no gross abnormalities.

Table 12.1 ***Details of 12 adult male Cape fur seals caught inadvertently within trawl nets during commercial fishing operations off the Eastern Cape coast of South Africa between May 1993 and October 1994***

Accession no.[a]	Date of collection	Age (yrs)	Body length (cm)	Girth (cm)	Blubber thickness[b] (mm)
2047	20 May 1993	7	167	106	24
2048	20 May 1993	8	157	95	18
2053	28 June 1993	7	153	103	25
2055	29 June 1993	8	179	122	27
2056	29 June 1993	8	139	92	27
2252	22 August 1994	9	172	122	26
2253	27 August 1994	NR	152	97	33
2254	27 August 1994	NR	146	95	33
2256	17 September 1994	NR	198	144	45
2257A	19 September 1994	6	142	93	17
2257B	7 October 1994	9	170	120	40
2258	8 October 1994	8	186	131	30

[a] Port Elizabeth Museum, seal accession number.
[b] Blubber thickness taken at the base of the sternum (index of physical condition).
NR, not recorded.

Cadmium (Cd), lead (Pb) and zinc (Zn)

Concentrations of Cd (0.4 wet wt.), Pb (0.7 wet wt.) and Zn (11.5 wet wt.) were in the limits of reported values for the blubber and muscles of other pinnipeds (Table 12.2, 12.3). However, seven seals showed Cd concentrations towards the upper limits of this range. It is thought that diet plays an important role in determining Cd concentrations in pinnipeds, with those species that feed predominantly on cephalopods or euphausiids showing higher concentrations of Cd than those that feed on fish (Hamanaka & Mishima, 1981; McClurg, 1984; Pena *et al.*, 1988; Thompson, 1990). Considering that Cape fur seals feed on both cephalopods (17%) and teleost fish (75%) (David, 1987; Lipinski & David, 1990), and have a comparatively long life-span of approximately 20 years (Wickens, 1993), we would also expect to find higher Cd concentrations in these animals than in strictly fish eating species.

The highest Cd concentrations (0.5 µg/g wet wt.) were found in the two largest males (PEM2258 and PEM2256), supporting reports that Cd accumulates in pinniped tissue with increasing age (Roberts *et al.*, 1976; Drescher *et al.*, 1977; Hamanaka *et al.*, 1982; Thompson, 1990; Malcolm *et al.*, 1994). There is no evidence in the literature to suggest that Pb and Zn concentrations increase with increasing age (Roberts *et al.*, 1976; Drescher *et al.*, 1977; Helle, 1981; Hamanaka *et al.*, 1982; Goldblatt & Anthony, 1983; Honda & Tatsukawa, 1983; Wagemann *et al.*, 1988).

Copper (Cu)

Copper concentrations in the blubber of Cape fur seals ranged from 2.17–3.21 µg/g wet wt., and 2.47–4.17 µg/g dry wt., with the exception of one animal (PEM2055) that had a very high concentration of 7.44 µg/g wet wt. and 8.45 µg/g dry wt. (Table 12.2). Most of these concentrations were outside the range of reported values for the blubber and muscle of other pinnipeds (Table 12.3).

Copper is an essential element and is therefore presumably under close physiological regulation (Thompson, 1990). In humans, high concentrations of Cu (above 50 µg/g body weight) can cause cirrhosis of the liver and, in extreme cases, death (NHMRC/ARMCANZ, 1996). Localised anthropogenic sources of Cu may result in deleterious effects to marine life (Thompson, 1990).

As with Cd, diet is thought to play an important role in determining Cu concentrations in seals, with those species that feed predominantly on cephalopods having higher levels of Cu than fish-eating species (McClurg, 1984). High levels of Cu found in the present study presumably reflect the relatively high levels of metal in squid. Copper concentrations in marine vertebrates do not appear to have a geographical bases (Thompson, 1990).

Table 12.2 ***Heavy metal concentrations in the blubber of 12 adult male Cape fur seals from the Eastern Cape coast, South Africa.*** **Concentrations of metals are given in µg/g wet wt. and µg/g dry wt.**

Accession	**Cd**		**Cu**		**Pb**		**Ni**		**Zn**	
no.[a]	**wet**	**dry**	**wet**	**dry**	**wet**	**dry**	**wet**	**dry**	**wet**	**dry**
2047	<0.04	<0.04	2.17	2.49	0.54–0.81	0.54–0.81	9.39	10.79	3.14	3.61
2048	<0.04	<0.04	2.85	3.51	0.54–0.81	0.54–0.81	12.73	15.64	4.83	5.93
2053	<0.04	<0.04	3.21	4.14	0.54–0.81	0.54–0.81	11.97	15.42	6.30	7.90
2055	<0.04	<0.04	7.44	8.45	0.54–0.81	0.54–0.81	11.98	13.61	6.30	7.15
2056	<0.04	<0.04	2.78	3.23	0.54–0.81	0.54–0.81	12.03	13.97	4.81	5.59
2252	0.44	0.51	2.48	2.90	0.88	1.03	21.17	24.72	14.70	17.16
2253	0.46	0.52	2.19	2.47	0.72	0.81	16.25	18.35	12.06	13.62
2254	0.49	0.55	2.55	2.85	0.87	0.97	21.77	24.37	14.24	15.95
2256	0.50	0.57	2.36	2.70	0.99	1.14	17.74	20.29	11.62	13.30
2257A	0.42	0.46	2.60	2.88	0.71	0.79	20.26	22.45	14.09	15.62
2257B	0.42	0.52	2.75	3.35	0.93	0.11	23.18	28.22	16.65	20.26
2258	0.53	0.59	2.41	2.71	0.86	0.97	14.67	16.47	11.40	12.79
Median[b]	0.4	0.5	2.6	2.9	0.7	0.6	17.7	17.0	11.5	12.8
Range	<0.04 –0.53	<0.04 –0.59	2.17– 7.44	2.47– 8.45	0.54– 0.99	0.54– 1.14	9.39– 23.18	10.79– 28.22	3.14– 16.65	3.61– 20.26

[a] Port Elizabeth Museum, seal accession number.
[b] The midpoint of the interval 0–0.04 was used to calculate the median for < 0.04; the midpoint of the interval 0.54–0.81 was used to calculate the median for 0.54–0.81.

Nickel (Ni)

The range of concentrations for Ni in the blubber of Cape fur seals was 9.39–23.18 µg/g wet wt. and 10.79–28.22 µg/g wet wt. (Table 12.2). These values are unusually high considering that the concentrations of Ni in marine mammals tend to be less than 0.5 µg/g wet wt. (Thompson, 1990) (Table 12.3). Although contamination of samples with Ni during laboratory analysis should not be discarded, retesting of all samples using new equipment and chemicals did not suggest that values were inaccurate. Elevated concentrations of Ni have been recorded in the liver of Ross seals from Antarctica (4.8 µg/g dry wt.) (McClurg, 1984), and the blubber of a vagrant leopard seal, *Hydrurga leptonyx,* from South Africa (8.39 µg/g wet wt.) (Stewardson, unpubl. data).

In terrestrial mammals, high levels of Ni (over 100 µg/g body weight per day) can cause liver and kidney toxicity, alter body weights and affect the immune system (NHMRC/ARMCANZ, 1996). However, little is known of the effects of Ni toxicity in marine mammals (see Law, 1996).

On the east coast of South Africa, Ni is used in the electroplating industry, chemical marine industries and in oil refining (NHMRC/ARMCANZ, 1996), and was exported from the Port Elizabeth harbour throughout the 1900s, until 1984. Therefore, industrial activity may be a possible source of contamination. However, the origin is probably geological; Ni concentrations in bivalves from unpolluted and polluted regions of the Cape south coast are considerably higher than values considered high by the US 'Mussel Watch' programme (Gardner *et al*., 1985).

For the range of values calculated in the present study, there is a suggestion that blubber Ni concentrations increase with increasing age, i.e., the highest concentrations (21.17 and 23.18 µg/g wet wt.) were found in animals 9 years of age (PEM2252 and PEM2257B).

Organochlorines

In the present study, chlorinated hydrocarbon residue concentrations in adult male Cape fur seals were below the limits of detection (Table 12.4). Although there is no baseline contaminant data for comparative purposes from healthy pinniped tissue in this area, earlier studies of beach-stranded (partially emaciated) animals from the east coast (Cockcroft & Ross, 1991), and healthy animals from the south-west Cape and Namibia (Henry, unpubl. report), suggest that pollutant levels have declined since the 1970s (Table 12.4).

Table 12.3 ***Heavy metal concentrations in the blubber and muscle of pinnipeds from different geographical locations: comparison of results of this work with values from the literature.*** **Concentrations of metals are given as the range (or mean ± SD) in µg/g wet wt.**

Species	Tissue	Cd	Cu	Pb	Ni	Zn	Area
Cape fur seal *Arctocephalus p. pusillus*	B	<0.04–0.53 [12]	2.17–7.44 [12]	0.54–0.99 [12]	9.39–23.18 [12]	3.14–16.65 [12]	Eastern Cape(1) (South Africa)
South American fur seal *Arctocephalus australis*	M	0.40 ± 0.10 [8]	1.70 ± 0.10 [8]	NR	NR	28.20 ± 15.40 [8]	Argentine Sea(2)
Steller's sea lion *Eumetopias jubatus*	M	<0.10–0.20 [15]	NR	NR	NR	24.30–39.10 [15]	Hokkaido(3) (Japan)
Grey seal *Halichoerus grypus*	B	<0.06 [1]	<0.10 [1]	<0.60 [1]	<0.50 [1]	4.70 [1]	Cardigan Bay(4) (West Wales)
	M	<0.06 [1]	2.50 [1]	<0.60 [1]	<0.50 [1]	43.00 [1]	Cardigan Bay(4) (West Wales)
Harbour seal *Phoca vitulina*	B	<0.01–0.02 [3]	0.9–3.0 [3]	<0.50–1.00 [3]	NR	3.00–14.00 [3]	Dutch Wadden Sea (West)(5)
	M	NR	NR [12]	1.20 ± 0.30	NR	NR	Britian(6)
Ringed seal *Phoca hispida*	M	<0.10–0.40 [29]	1.00–1.60 [29]	0.20–0.10 [29]	NR	14.20–39.50 [29]	Greenland(7) (West)
Harp seal *Phoca groenlandica*	M	0.10 [56]	1.80 [50]	0.03 [56]	NR	NR	Gulf of St Lawrence(8)
Ribbon seal *Phoca fasciata*	M	<0.10–0.30 [16]	NR	NR	NR	NR	Okhotsk Sea(9)
Weddell seal *Leptonychotes weddellii*	M	<0.10–0.30 [2]	0.90–1.00 [2]	NR	NR	33.70–39.60 [2]	Antarctic(10)
Leopard seal *Hydrurga leptonyx*	B	0.12 [1]	NR	0.34 [1]	NR	NR	Australia(11)
	B	0.54 [1]	2.30 [1]	0.51 [1]	8.39 [1]	2.33 [1]	South Africa(12)
	M	NR	NR	0.07 [1]	NR	NR	Australia(11)
	M	<0.10 [15]	0.40–1.20 [15]	NR	NR	14.80–49.30 [15]	Antarctic(10)
Elephant seal *Mirounga leonina*	M	0.40 [1]	NR	7.11 [1]	NR	35.60 [1]	Antarctic(10)

B, blubber. M, muscle. [], sample size. NR, not recorded.

References: (1) present study; (2) Gerpe *et al.,* (1990); (3) Hamanaka *et al.,* (1982); (4) Morris *et al.,* (1989); (5) Duinker *et al.,* (1979); (6) Roberts *et al.,* (1976); (7) Johansen *et al.,* (1980); (8) Ronald *et al.,* (1984); (9) Hamanaka *et al.,* (1977); (10) Thompson (1990); (11) Kemper *et al.,* (1994); (12) Stewardson (unpubl. data).

In South Africa, DDT was withdrawn from the market as an agriculture remedy in 1976; however, it is still used for malaria control. In March/April 1998, the government announced the phasing out of all stocks. There is no official limit on PCBs in South Africa. It was conceded that international market forces would eventually determine their use and availability. Although it would take a considerable amount of time before restrictions and prohibitions on the production and use of organochlorines will take effect in this region, a significant decline in t-DDT has already been observed in inshore waters, e.g., t-DDT concentrations in the inshore bottlenose dolphin, *Tursiops truncatus,* declined significantly from 1980 to 1987 (de Kock *et al.*, 1994). Recent studies of fish and bivalves in the Durban outfalls region confirm that DDT and PCBs are slowly disappearing (EPC, 1998). Only dieldrin and heptachlor are found with any regularity (EPC, 1998).

CONCLUSION

The interpretation of the significance of observed concentrations of heavy metals and organochlorine compounds in the blubber of the Cape fur seal is difficult because the coverage of samples has been very limited and our understanding of pollutants in pinnipeds is still in its infancy. Information on contaminants in healthy pinnipeds is sparse, therefore, authors frequently compare their results with terrestrial laboratory animals or with those from emaciated (beached) pinnipeds.

Considering that pinnipeds differ anatomically and physiologically from terrestrial mammals, pollutants will not have the same toxicity, thus comparisons between the two groups should be made with caution (Skoch, 1990). Even within

Table 12.4 ***Chlorinated hydrocarbon residue concentrations in the blubber of adult Cape fur seals from Southern Africa, 1974–1995.*** **Concentrations are given as the mean and range in μg/g wet wt.**

Date	No.	PCB	DDE	TDE	DDT	t-DDT	Area
1974–75	9	0.13	1.25	0.09	0.04	1.38	Namibia[(1)]
		ND–1.17	0.02–7.69	ND–0.54	ND–0.28	–	
1974–75	8	2.79	1.45	0.36	1.21	3.02	South Africa[(1)]
		0.37–5.88	0.17–3.52	ND–1.26	0.14 –3.39	–	(south west coast)
1978–80	4*	1.80	9.50	ND	2.40	11.30	South Africa[(2)]
		0.39–3.49	2.23–23.03	ND	0.09–7.90	–	(east coast)
1993–95	12	ND	ND	ND	ND	ND	South Africa[(3)]
							(east coast)

* males and females greater than 1.3 m in length.
ND, not detected.
tDDT = DDT + DDE + TDE.
References: [(1)] Henry (unpubl. report); [(2)] Cockcroft & Ross (1991); [(3)] Present study.

different groups of marine mammals there are significant differences in the ability to metabolise contaminants (Wells *et al.*, 1997). Interpretation can be further complicated by factors such as the seal's age, sex, reproductive condition, size, health condition, feeding habits and geographic location, all of which may influence the total contaminant burden (Reijnders, 1980; Eisler, 1981; Storr-Hansen *et al.*, 1995; Wells *et al.*, 1997).

Information derived from emaciated pinnipeds may also be misleading because metals tend to leach from decomposing tissue of stranded animals (Skoch, 1990), and, if there is a decline in body condition prior to stranding, absolute concentrations of chlorobiphenyl congeners may increase, while some metabolisable chlorobiphenyls may decrease (Boon *et al.*, 1994). Furthermore, comparisons with other data-sets may be erroneous due to methodological differences.

With these limitations in mind, we conclude that the levels of toxic contaminants in the blubber of seals from the Eastern Cape coast of South Africa were generally low compared with those reported from species in other geographic locations, with the exception of Cu and Ni. There is no evidence that the elevated levels of Cu and Ni reported in this study would pose a serious threat to the health of individual animals; however, high concentrations of these metals may be sufficient to result in some additional stress to animals when they mobilise their lipid reserves during illness or starvation. Nickel and Cd concentrations appeared to increase with age; however, small sample size prevented statistical analysis.

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