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Toxicology of Marine Mammals

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8 Persistent organic contaminants in Arctic marine mammals

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Introduction

This chapter will address the concentrations and possible effects of selected persistent organic contaminants (POCs) in marine mammals of the Arctic region. Other recent sources of information concerning POCs in Arctic marine mammals include Letcher et al. (1996, 1998), Becker et al. (1997), Bernhoft et al. (1997), Muir et al. (1997), Weis and Muir (1997), Addison and Smith (1998), De March et al. (1998), Norstrom et al. (1998), Wiberg et al. (1998 and 2000), Krahn et al. (1999), O’Hara et al. (1999), Becker (2000), Kucklick et al. (2001) and Seagars and Garlich-Miller (2001). Arctic marine mammals are long-lived, develop large lipid or fat depots, and many occupy high trophic levels in the lipid-rich, Arctic marine food webs. These factors are important in the uptake and magnification of persistent, lipophilic organic contaminants. Bowhead whales (Balaena mysticetus), which feed almost exclusively on copepods, euphausiids and amphipods (Lowry, 1993), account for some of the lowest tissue concentrations of ‘bioaccumulating’ organochlorines (OCs), and correspondingly occupy the lowest trophic level of marine mammals addressed in this chapter (Hoekstra et al., 2000a, b). Pacific walrus (Odobenus rosmarus divergens) and Atlantic walrus (Odobenus rosmarus rosmarus) typically feed on mollusks, but also may occasionally eat ringed seals (Pusa hispida) (Fay, 1960; Lowry and Fay, 1984). Other Arctic marine mammals feed on a combination of invertebrates, fish and/or mammals. One class of POCs, the polycyclic aromatic hydrocarbons (PAHs), are readily metabolized by mammals and do not accumulate in their tissues. Assessing the exposure of marine mammals to these compounds is not as straightforward as is the case for lower vertebrates (e.g., fish) and invertebrates. The latter have little capacity for metabolizing this class of aromatic compounds; therefore PAHs will accumulate in their tissues (Livingstone et al., 1992). Although specific cases of marine mammal response to benzo[a]pyrene exposure will be discussed, we will not address PAHs or petroleum effects in this review. Concentrations of contaminants provided in this chapter are on a wet weight basis, except when noted otherwise.
Persistent organic contaminants of concern

The following chlorinated industrial compounds and pesticides are of concern for marine mammals: polychlorinated biphenyls (PCBs), 2,3,7,8-tetrachlorodibenzo-p-dioxin (dioxin) as a member of the polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDFs), 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane and metabolites (DDTs), chlorinated cycodienes (chlordane, dieldrin, mirex/kepone), chlorinated bornanes (toxaphenes), chlorinated benzenes (including hexachlorobenzene or HCB), chlorinated cyclohexanes (HCHs) and, in very specific cases, benzo[a]pyrene (a PAH). POC exposure and concentrations in tissues are affected by biological factors (age, sex, body condition, reproductive status and season), spatial distribution (habitat or home range, global region) and temporal relationships (i.e. based on historic data, are levels decreasing, increasing or not changing?).

Potential sources and transport mechanisms

Generally, anthropogenic contamination of the Arctic with POCs is thought to be the result of long-range atmospheric transport, with minor contributions from local sources (Wania and Mackay, 1993, 1996). Atmospheric contamination is visible in the form of Arctic haze (Shaw, 1995) and may threaten the health of Arctic residents (Barrie, 1986; Hoff and Chan, 1986; Heintzenberg, 1989; Hoff et al., 1992; Kinloch et al., 1992; Dewailly et al., 1993; Ayotte et al., 1995; Barrie et al., 1997). Many contaminants are transported in the gaseous phase, on particles and in aerosols, and are deposited during precipitation events. These compounds may be trapped by the colder temperatures associated with the Arctic, due to the relatively large surface areas of both the sources and the receiver (the Arctic). Seasonal changes in temperature can also affect atmospheric levels of contaminants (Manchester-Neesvig and Andren, 1989; Hoff et al., 1992; Barrie et al., 1997; Stern et al., 1997) that are delivered to the Arctic in snow (Gregor and Gunner, 1989).

Physical-chemical partitioning of the contaminant is key to the introduction of such compounds into the Arctic food chain. All of the POCs have ringed molecular structures. Positions of the chlorine (or other halogen) atoms on these ring structures, and whether the chlorine is bound to aromatic or aliphatic carbons, are major factors affecting bioaccumulation and toxicity (Boon et al., 1992, 1994). For example, the planar molecules (coplanar congeners) of PCBs and dioxins are the most toxic of these compounds. This characteristic generally holds true for other chlorinated hydrocarbons and for PAHs as well. It should also be stressed that ‘super lipophilic’ ($K_{ow} > 10^5$) agents have a decreased bioaccumulative potential because they have an increased time to effective equilibrium, i.e. dissolution time (Livingstone et al., 1992).
The POCs are well known for their lipophilicity and ability to bioconcentrate, and the concentrations of these compounds are many times higher in biota than in the aqueous and atmospheric media. Persistent OCs bind to organic particles (including detritus, plankton and algae) and enter the base of the food chain. This bioaccumulation (higher concentrations in biota than in water) sets the stage for biomagnification (increased concentrations in the predator versus the prey). The biomagnification factor, or BMF, is commonly expressed as \( [X]_{\text{predator}}/[X]_{\text{prey}} \) (when > 1.0 it is ‘magnified’), where \([X]\) = contaminant concentration in lipid weight. Fish, pinnipeds or baleen whales consume invertebrates, many of which consume organic particles. Arctic cod \((Boreogadus saida)\) appear to play a major role in biomagnification of POCs in the Arctic. This small fish feeds extensively on invertebrates and is a major prey of marine mammals in the Arctic.

PCB Aroclor mixtures (Monsanto Chemical Company) 1221, 1232, 1242, 1248, 1254, 1260 and 1268 contain 21, 32, 42, 48, 54, 60 and 68 per cent chlorine, by weight, respectively, and theoretically contain 209 congeners (O’Hara and Rice, 1996). As heat-stable oils, PCBs were used around the world: in electrical transformers and capacitors, in hydraulic fluids, as flame retardants, as plasticizers in waxes, in paper manufacturing and other uses. PCBs are known to be transported in the atmosphere (Hoff et al., 1992) and to interact with surface waters (Bidleman et al., 1989). PCBs are adsorbed and carried on sediments and particles in water, as well as by migratory organisms in both freshwater and marine systems (O’Hara and Rice, 1996; Ewald et al., 1998). Fish represent a significant dietary source of PCBs to many marine mammals. Adverse effects on fish as prey (decreased reproduction) could have effects on food availability.

Additional classes of POCs that originate from industrial activities are the halogenated dibenzo-p-dioxins and dibenzofurans. Chlorinated or brominated forms of dioxins and furans can result from combustion, the production of other chlorinated organic compounds (e.g. chlorinated pesticides and PCBs) or from industrial processes that mix halogens with organic material (i.e. pulp-mill effluents). These compounds are easily distributed to the aquatic and atmospheric environments. Brominated organic compounds are widely used (i.e. flame retardants) as well, and have been reported in marine mammal tissues (de Boer et al., 1998). The occurrence of brominated fire retardants in biota of the Arctic will require further evaluation.

More than 30 kinds of POCs were developed intentionally for release into the environment as pesticides. These chlorinated pesticides, which have been used worldwide for the past 50 years, include DDT \((o,p^-\text{-} \text{and} \ p,p^-\text{-}\text{forms})\) and associated metabolites \((o,p^-\text{-} \text{and} \ p,p^-\text{-}\text{forms of DDD and DDE})\), chlorinated cyclodienes (chlordane, endrin, dieldrin, mirex/kepone), chlorinated camphanes and boranes (including toxaphene), chlorinated benzenes and chlorinated cyclohexanes (primarily \(\alpha\)-HCH, \(\beta\)-HCH, and \(\gamma\)-HCH, also known as lindane). Industrial- or technical-grade versions of chemicals such as chlordane and toxaphene contain many isomers or chemicals closely
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related to the parent or intended synthesized chemical. A mixture's toxicity is often related to these 'by-products'. Toxaphene is produced by the chlorination of camphene to 67–69 per cent, producing hundreds of congeners. Many studies have shown its wide global distribution and presence in biota (Voldner and Schroeder, 1989; Saleh, 1991; Muir and deBoer, 1995; Wade et al., 1995). Chlorinated pesticides are well known to be of low water solubility and high solubility in oils and organic solvents. They tend to accumulate and to be stored in lipids, are resistant to metabolic breakdown and have relatively long half-lives in tissues of biota (Blus et al., 1996).

Movement of POCs from one medium to another is determined by their vapor pressure, octanol/air partition coefficient, temperature of condensation and octanol/water (o/w) partition coefficient (high lipophilicity = high octanol/water partitioning coefficient) (Bidleman et al., 1989). Compounds such as HCB, dieldrin, HCHs, three-ringed PAHs, and PCB congeners having six chlorine atoms or fewer per molecule have relatively high vapor pressures and relatively low octanol/air partition coefficients. They are therefore easily transported via the atmosphere from lower latitudes to the Arctic where, due to their relatively low temperatures of condensation, they can be preferentially deposited from the atmosphere (Wania and Mackay, 1993, 1996). Other compounds, such as mirex, and octa- and nonachlorinated biphenyls (PCB congeners containing 8–9 chlorine atoms per molecule) have relatively high octanol/air partition coefficients, high temperature of condensation and relatively low vapor pressures, and are not easily transported via the atmosphere. Compounds such as chlordane, DDTs and toxaphene exhibit characteristics mid-way between these two extremes; therefore, preferential deposition and accumulation might be expected in the mid-latitudes rather than in the high Arctic.

The relatively high octanol/water partition coefficients of these POCs explain their accumulation in lipid-rich tissues (adipose, blubber, brain) and partitioning from water to the surfaces of particles and sediments. The kind of lipid also affects the degree of accumulation. For example, accumulation in brain is lower than in blubber or adipose tissue, due to the high phospholipid content of brain. Determination of concentrations of POCs in brains is critical for diagnosis, because the brain is the target organ of acute toxicity. The trophic level of a species determines its respective exposure to these lipophilic agents. Species such as seals, beluga whales (Delphinapterus leucas) and narwhals (Monodon monoceros), that feed at the middle level (i.e. consuming fish) have moderate concentrations in their tissues; and the polar bears (Ursus maritimus), which consume mammals dependent upon fish (i.e. seals), tend to have the highest exposures. Tissue burdens at these higher trophic levels will also depend on the species-specific ability to absorb, metabolize and/or eliminate these compounds. In addition to trophic level, body size and metabolic rate also play a role in the accumulation of POCs. Smaller species can have higher concentration in tissues but sometimes lower total body burdens (Aguilar et al., 1999).
Factors affecting POC concentrations and interpretation of effects

Many biological factors must be considered when interpreting POC concentrations and their possible effects (Aguilar et al., 1999). Parturition and lactation are important excretion mechanisms for sexually mature and active females. However, this also results in exposure of offspring in utero and during lactation at critical phases in the development of neonatal organs (especially the central nervous system (CNS), reproductive and immune systems). In general, POC concentrations are lower in mature females than in mature males for polar bear, ringed seals and bowhead, beluga and narwhal whales (Muir et al., 1992a; b; O'Hara et al., 1999). This reproduction-dependent route of excretion for the adult and exposure for the neonate represents a critical pathway. Although this neonatal exposure may be the highest and most significant for the entire life of the animal, indications of adverse effects may be delayed until later life stages. Dysfunction in the neonate may be expressed acutely, at maturation or in the next generation (transgenerational). Transgenerational effects have only been noted in laboratory animals. Body burdens or concentrations in tissues usually increase with age for both sexes until sexual maturity, when a difference based on gender is usually detected (Boon et al., 1992). However, exceptions have been reported. Stern et al. (1992) found no correlation of DDTs and PCBs with increased age in male belugas from Greenland. Muir et al. (1996a) suggest that this lack of correlation could result from a shift in the diet of older males.

In most cases (the exceptions being marine mammals from highly contaminated areas), males continue to accumulate POCs as they increase in age, whereas concentrations in females reach a plateau and stabilize or decrease (Boon et al., 1992). This sex difference is due to the production of offspring and lactation by the female, as described above. The largest POC mobilization and subsequent excretion is likely to occur during lactation. This varies by compound, with the higher lipophilic compounds probably removed to a lesser degree by lactation (Boon et al., 1992). This should be considered when comparing populations and assessing potential impacts to critical life stages.

Blubber or fat is the main repository for POCs; hence changes in an animal’s nutritional status may affect the concentrations of these compounds in these lipid-rich tissues. However, measurement of nutritional status is difficult, and reliable condition indices have not been developed as part of contaminant studies for most cetaceans (IWC, 1995), pinnipeds or polar bears. Blubber thickness is unreliable as a sole indicator of condition and, instead, the use of blubber weight and lipid content of the blubber in standardized body locations is recommended. Lipid content is important, particularly in emaciated individuals, because lipid mobilization may be coupled with increased water content of blubber, as is known for some pinnipeds (Beck et al., 1993; Gales and Renouf, 1994; Fadely, 1997), and variations in
lipid types could affect partitioning of the POCs. Collecting these biological data is important for the toxicological interpretation of the results (Law, 1994), especially with respect to compounds that are lipophilic and susceptible to changes with change in lipid status of the animal. Seasonal differences are mostly reflective of feeding and reproductive behavior, and can influence the concentrations of POCs (Boon et al., 1992). These can be caused by migratory behavior (differing concentrations in regional prey) or by opportunistic feeding strategies (Boon et al., 1992).

Metabolism or biotransformation of POCs within an animal can affect POC concentration patterns (Boon et al., 1992, 1994). Some PCB congeners may be lower in concentration than expected simply based upon types and concentrations in prey. This indicates possible metabolic elimination (Tanabe et al., 1988, 1994). Research has emphasized the inducible Phase I mixed function oxidase (MFO) system of the liver. The MFO system utilizes cytochrome P450 enzymes (CYP) that occur as many different types (CYP1A, CYP2, etc.). The P450 enzymes are well known for oxidizing many natural (i.e. steroid hormones, PAHs) and some synthetic compounds (some POCs) (Safe, 1990). Cytochrome P450 enzymes have not been studied to any great extent in Arctic cetaceans. Of those whales that have been studied (i.e. odontocetes) mostly CYP1A activity was detected and there was evidence for the CYP3 subfamily, but no evidence for CYP2 (Boon et al., 1992). Hepatic CYP1A1 isozymes have been characterized for use in monitoring POC exposure in Arctic belugas (White et al., 1994). There have been many differences seen in P450 activity with respect to age and sex for each species that has been studied (Boon et al., 1992), thus complicating our understanding of the role of MFOs in eliminating and detoxifying POCs.

Marine mammals can apparently metabolize some PCBs, especially the CYP1A substrates (e.g. PCBs with vicinal H atoms in the $o,m$ positions and a maximum of one $ortho$-Cl); however, odontocetes may lack, or have very low activity of, CYP2B (Boon et al., 1992; Norstrom et al., 1992). Metabolic indices suggest lower levels of PB (phenobarbital or CYP2B)-inducible or MC (3-methylcholanthrene or CYP1A)-inducible enzyme activities in piscivorous cetaceans, seals and marine birds than those of other animals which are not piscivores (Tanabe and Tasukawa, 1992). This phenomenon was noted in both marine and terrestrial organisms and may reflect the evolutionary loss of a specific P450-based oxidative capability (i.e. isozyme) in piscivores. It has been speculated that perhaps this is because herbivorous or non-fish prey may excrete specific types of lipophilic agents (thus need the oxidative capacity), whereas the piscivores (carnivores) had no need to maintain this specific P450 system if the lipophilic agents were not present in the prey (Tanabe and Tasukawa, 1992). Carvan et al. (Chapter 16 in this volume) discuss the cytochrome P450 system and interactions with aromatic hydrocarbons in greater detail.

Physiologic and morphologic measures of exposure or response to contaminants in free-ranging animals are occasionally referred to as 'biomarkers'.
Biomarkers are needed for Arctic marine mammals to better assess impacts of ‘high’ contaminant concentrations. Proposed toxicant biomarkers for cetaceans include an assessment of DNA adducts, induction of the MFO system, plasma hormone levels, immune responses (IWC, 1995) and lesions (i.e. tumors). These biomarkers can show a documentable biological response to measured contaminants. However, sample collection logistics and the multiple biological variables that can affect these systems make interpretation very difficult. This is especially true for non-lethal sampling, where sample size and type are extremely limited (i.e. skin/blubber biopsies, blood samples). Neoplastic lesions are useful gross indicators, considering that PCBs and the related PCDDs and PCDFs are known to cause preneoplastic lesions, neoplastic nodules and hepatocellular carcinomas. Female mammals tend to be more susceptible to these tumorigenic potentials through free-radical generation, Ah-receptor interactions, lipid peroxidation, degeneration of cell defense mechanisms and altered vitamin A metabolism (Livingstone et al., 1992). In vitro immunoassays are being developed for Arctic belugas and St. Lawrence estuary beluga whales (De Guise et al., 1997; Brousseau et al., Chapter 14 in this volume) and other assays (Gauthier et al., 1999, Chapter 15 in this volume) also show promise as biomarkers. Martineau et al. (1999, and Chapter 13 in this volume) and De Guise et al. (1994a) emphasized the use of neoplasia and non-neoplastic lesions (De Guise et al., 1995; Lair et al., 1997) as biomarkers, used for the St. Lawrence estuary beluga whales as examples (Martineau et al., 1988, 1994).

Some POCs have been implicated as endocrine disruptors by affecting sexual or gonadal development in laboratory animals, as early as in utero. Deficiency of the CYP2B activity and low activity of CYP1A in cetaceans may limit their metabolic capabilities and the elimination of POCs, making these animals more susceptible to reproductive derangement (Livingstone et al., 1992). True hermaphroditism has been reported in the beluga whale (De Guise et al., 1994b) and pseudohermaphroditism has been found in the bowhead whale (Tarpley et al., 1995). However, cause-effect relationships for these conditions have not been determined but are discussed further by Reijnders (Chapter 3 in this volume).

Assessment of effects of contaminants has lagged behind analytical chemistry (biotic and abiotic) and to date there has been little progress in determining effects of contaminants in marine mammals. Biomarkers have an important role in health assessments; however, there is still a large gap between determining a ‘biomarker’ response and having a clear understanding of how this really affects the health of an animal or a population. Recognizing the known in utero and neonatal exposures to POCs in marine mammals, several recent reports (IWC, 1995; O’Shea et al., 1999; Reijnders et al., 1999) include recommended measures for assessing their effects (Table 8.1).

No laboratory test can replace a thorough necropsy and/or clinical examination, where one conducts gross (must include life history) and histologic assessments (as complete as possible) to address general health and possible
Table 8.1 Some endpoints for assessing possible effects of known in utero and neonatal exposures to POCs in marine mammals (after IWC, 1995; O’Shea et al., 1999; Reijnders et al., 1999)

<table>
<thead>
<tr>
<th>Endpoints</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thyroid hormone</td>
<td>p, b, l</td>
</tr>
<tr>
<td>Vitamin A</td>
<td>p</td>
</tr>
<tr>
<td>Steroid hormones</td>
<td>p</td>
</tr>
<tr>
<td>Estrogen receptors</td>
<td>o, b, l</td>
</tr>
<tr>
<td>Clinical signs, histopathology + biochemistry</td>
<td>CNS, e, i</td>
</tr>
<tr>
<td>Gross and histopathology</td>
<td>Routine*</td>
</tr>
</tbody>
</table>

p, Plasma; o, ovary; b, brain; l, liver; CNS, central nervous system; e, endocrine glands; i, immune. * for ‘ruling in’ and ‘ruling out’ other disease factors.

Confounding variables related to disease (‘ruling in’ and ‘ruling out’). True examination must provide for long-term interdisciplinary studies to encourage collaboration of multiple perspectives, and report findings in a timely manner (this helps future experimental designs and allows managers to respond). Standardizing field and laboratory protocols, and statistically ‘powerful’ experimental designs will enhance interpretative potential and allow for comparisons. There is great need to link exposure to effects as expressed at the whole animal and population levels (beyond classical biochemical biomarkers) in a ‘dose–response’ manner.

**Persistent organic contaminants in Arctic cetaceans**

Arctic cetaceans are long lived, especially the bowhead whale, which is estimated to live for more than 100 years (George et al., 1999). Bowhead whales feed almost exclusively on copepods, euphausiids and amphipods (Lowry, 1993) and occupy the lowest trophic level of the cetaceans addressed here. The beluga and narwhal feed on invertebrates and fish. The summer diet of the narwhal was investigated on northern Baffin Island, Canada, where Arctic cod and Greenland halibut (Reinhardtius hippoglossoides) made up 51 per cent and 37 per cent (by weight) of the diet, respectively. Squid (Gonatus fabricii) beaks were noted but squid mass could not be quantified. Deep-water fish [halibut, redfish (Sebastes marinus), and polar cod (Arctogadus glacialis)] were found in the stomachs of males and may be from deeper dives than in females (Finley and Gibb, 1982). This high trophic level feeding (piscivory) sets the stage for POC biomagnification.

**Bowhead whales**

Bowhead whales are baleen whales (suborder Mysticeti) and feed mainly on invertebrates in Arctic waters for most of the year. Occasionally, bowhead whales have been known to consume small fish, crabs, mollusks and even
sédiments, but these are likely infrequent and represent insignificant pathways for contaminant exposure (Bratton et al., 1993). The few POC studies in the bowhead whale do not address possible effects of these pollutants, but only pollutant concentrations in tissues at the time of death (Bratton et al., 1993). This hampers assessment of effects, which will require extrapolation from other species. Although the bowhead whale is a mysticete and is assumed to be of low risk for bioaccumulation (O'Shea and Brownell, 1994) as a ‘filter feeder’ (as compared to a ‘fish eater’), we should not be completely unconcerned about biomagnification and potential effects of POCs on this species. Bratton et al. (1993) noted that the bowhead whale is endangered, and the unknown but potential effects of contaminants on their reproduction and on their young (lactational exposure) could be critical. The bowhead whale is also a major subsistence resource for Arctic people. Considering the lack of knowledge about effects of POCs, we point out the documentation of male pseudohermaphroditism in two bowhead whales (Tarpley et al., 1995) for which the cause is unknown. In addition to POCs, exposure of bowhead whales to petrogenic hydrocarbons (PAHs, benzene, etc.) is of great concern considering the exploration and development of oil reserves in the Arctic, especially in northern Alaska. Exposure could be by direct external contact, ingestion or inhalation of volatile components during a spill (Bratton et al., 1993). Petroleum avoidance has been a controversial issue, but oil exposure can affect a variety of systems including the dermis, baleen, eyes, respiratory, gastrointestinal, hematopoietic (blood formation) and hepatic systems. Surprisingly, studies are very limited with respect to petroleum contamination and assessment of potential target organs.

A few reports have described POC concentrations in bowhead whale blubber or liver sampled in Alaska (McFall et al., 1986; O’Hara et al., 1999). Mean concentration of the sum of PCB congeners (ΣPCBs) was 0.212 µg/g (McFall et al., 1986), indicating low concentrations as compared to other marine mammals. Mean concentrations of chlorinated pesticide in blubber were: sum of DDT, DDD and DDE (ΣDDTs) 0.032 µg/g; chlordane, 0.007 µg/g; dieldrin, 0.017 µg/g; heptachlor epoxide, 0.008 µg/g; and lindane, 0.009 µg/g (McFall et al., 1986). Both unsubstituted (parent) and alkyl-substituted PAHs were detected in the blubber at concentrations of 0.028 and 0.025 µg/g, respectively, and would be considered background exposure (McFall et al., 1986). As part of the Alaska Marine Mammal Tissue Archival Project (AMMTAP) liver and blubber have been archived from more than 70 bowhead whales (Becker et al., 1997 and recent sampling efforts) and the POC analyses have been completed on some of these animals (O’Hara et al., 1999; Hockstra et al., 2000a, b). More recent data indicate that concentrations are low compared to some odontocetes, and are similar to concentrations reported by McFall et al. (1986). Female bowhead whales do not accumulate POCs with age, but 7 of 11 POCs that were measured accumulate in males (O’Hara et al., 1999).
The enantiomeric fractions (EFs) of α-HCH and chlordane-related compounds were near racemic (1:1) in water and plankton samples off the coast of northern Alaska. The (+)-α-HCH and (+)-cis-heptachlor epoxide were selectively enriched in bowhead blubber and liver relative to plankton and water samples, and independent of sex, season and age. The EFs of other chlordane-related compounds were near racemic (Hoekstra et al., 2000a). Although previous studies have determined PCB concentrations in tissues of bowhead whales, Hoekstra et al. (2000b) analyzed chiral PCB congeners. Blubber and liver samples were analyzed for several chiral PCB congeners (PCBs 91, 95, 136, 149, 174 and 176) and for many achiral PCB congeners. PCB concentrations in bowhead whales were dominated by penta- and hexachlorobiphenyl congeners and were relatively low (mean: 671 ng/g lipid). Female bowhead whales (regardless of age) and shorter (<13 m) male bowhead whales were characterized by near-racemic enantiomeric ratios (ER = 1.0) for many chiral PCB congeners. Nonracemic enantiomeric ratios (ER > or < 1.0) for PCBs 91, 95 and 149 were found in larger (>13 m) male whales. Hoekstra et al. (2000a) suggest that PCB biotransformation or uptake from the marine environment is enantioselective and may be age- and/or sex-dependent for the bowhead whale.

For consumers of bowhead whale blubber there is little, if any, significant exposure to POCs that warrants any dietary restriction, based on our current understanding (O’Hara et al., 1999). However, concentrations of contaminants in tissues are not a sole determining factor for evaluating animal toxicosis. Other histologic, biochemical, immune and physiologic assessments (i.e. health assessment) would better evaluate whether or not there is an effect. Some of these ‘effects endpoints’ are currently being evaluated as part of an ongoing study in northern Alaska, but only in the short term (1998–2001).

**Belugas and narwhal whales**

Belugas are generally circumpolar in distribution, but some populations occur outside of the Arctic. The latter include populations in the St. Lawrence estuary (between Canada and USA in the Great Lakes region; see Chapters 13–15 in this volume) and in Cook Inlet (near Anchorage, Alaska, USA). The narwhal has a more limited range, encompassing the eastern Arctic of Canada and Greenland. Both species are important animals for people of the north, both culturally and nutritionally.

The PCB and DDT concentrations in blubber of Arctic beluga whales from Alaska are similar to those reported from the Canadian Arctic and Greenland belugas, narwhals and polar bears, but at least an order of magnitude lower than in beluga whales of the St. Lawrence estuary (Becker et al., 1997; Krahn et al., 1999). The mean concentrations of ∑DDTs and ∑PCBs in blubber of narwhal (NWT, Canada) were 3.51 and 10.09 µg/g, respectively (Wagemann and Muir, 1984). However, total chlordane
(Σchlorodanes) and toxaphene concentrations in blubber of beluga whales from Alaska are similar to those in belugas, narwhal and polar bears from Arctic Canada, and belugas of western Greenland, and are within the same order of magnitude as in blubber of beluga whales of the St. Lawrence estuary (Becker et al., 1997). There appears to be enrichment or biological accumulation of specific PCCs as compared to a toxaphene standard. Based on an evaluation of narwhal blubber and burbot (Lota lota) liver, octachloro- and nonachlorobornanes are increased (enriched) in the narwhal (Bidleman et al., 1993). The concentrations of total chlordanes, HCHs and chlorobenzenes in Arctic beluga are not significantly different from those in beluga whales of the St. Lawrence estuary, suggesting that the similar concentrations are a result of the relatively higher volatility of these compounds and atmospheric transport to regions more distant from the sources (Muir et al., 1990, 1992).

For the less volatile (and more chlorinated) PCBs and DDT, the concentrations were 25- and 30-fold lower, respectively, for Arctic belugas as compared to beluga whales of the St. Lawrence estuary, which may be related to their higher chlorination (Muir et al., 1990; Letcher, 1996). The beluga whales of the St. Lawrence estuary had about 100 times higher concentrations of mirex than beluga of the Canadian Arctic; however, the BMFs for mirex and PCB are similar in both locations (Muir et al., 1990, 1996a). The BMF for mirex and ΣPCBs from fish to beluga ranged from 11 to 16 (Muir et al., 1996a). The TEQs (2,3,7,8-TCDD toxic equivalents) averaged 330 ng/kg in females and 1400 ng/kg in males, and were dominated by PCB 126, 105 and 118 for the St. Lawrence estuary beluga whales. It would appear that local sources of DDT, PCBs and mirex from the Great Lakes area outweigh atmospheric inputs, and the St. Lawrence estuary beluga whales have higher loading values for DDT, PCBs and mirex when analyzed using principal components analysis (Muir et al., 1996a). Total concentrations of non-ortho PCBs 77, 126 and 169 in blubber of St. Lawrence estuary beluga whales (8000 ng/g in males) were 10–20 times higher than in Arctic belugas (Muir et al., 1996a). In the case of the Greenland beluga whales, Muir et al. (1996a), found no correlation with age for POC concentrations in blubber, which may be explained by a shift in diets of older males.

Becker et al. (1995, 1997) reported concentrations of POCs in beluga whales from Alaska as part of the AMMTAP. The ratio of 4,4'-DDE to ΣDDTs concentrations in blubber from the Alaska whales was similar to that of Canadian and Greenlandic beluga whales. For blubber from beluga whales of Alaska, the descending order of PCB congener concentrations was 153, 138, 149, 118, 101, 180, 187, 52 and 66/95. Becker et al. (1995 and 1997) concluded that toxaphene and total chlordanes represent a more significant proportion of the total chlorinated hydrocarbons in these Arctic animals. Becker et al. (1997) reported lower concentrations of POCs (most notably the chlordanes) in beluga whales of the Cook Inlet stock (Alaska), which may be exposed to different anthropogenic sources of POCs than
beluga stocks in Chukchi and Beaufort Seas, Alaska. However, toxaphene concentrations were in the same range for all Alaska stocks studied (Becker et al., 1997), and ranged from 500 to 6620 ng/g. Wade et al. (1995) reported toxaphene concentrations ranging from 1.35 to 8.21 µg/g (1350–8210 ng/g) and 3.20 to 15.9 µg/g lipid weight (3200–15 940 ng/g) in blubber of beluga whales from Point Lay, Alaska. Krahm et al. (1999) indicated that concentrations and patterns of POC vary by stock in Alaska.

It is evident that POC contamination differences by region vary by specific class (PCBs, DDT, toxaphene, etc.). There was a surprising lack of PCDDs in beluga blubber (detection limit 2 ng/kg). In narwhal blubber the chlorobornanes were the predominant OCs, ranging from 2990 to 13 200 ng/g in males and from 1910 to 8390 ng/g in females. These were mostly octachlorobornane and nonachlorobornane, which are two- to fourfold lower than in St. Lawrence estuary beluga whales (Muir et al., 1992b).

Toxaphene in Alaska beluga whales ranged from 1.49 to 8.94 µg/g dw (Wade et al., 1995), which indicates significant transport to the Arctic as well. ΣPCBs ranged from 2250 to 7290 ng/g in males and 894–5710 ng/g in female Canadian Arctic belugas; concentrations were about 15-fold lower than in beluga whales of the St. Lawrence estuary (Muir et al., 1992a). However, ΣHCHs, dieldrin and Σchlorobenzenes differed by less than twofold between these two groups (Muir et al., 1992a).

Comparative studies of PCB metabolic capacity in mammals indicate that the capacity is greatest in terrestrial species, moderate in some pinnipeds, and lowest in whales (Tanabe et al., 1988, 1994; Boon et al., 1992). There is evidence for a lack of bioaccumulation of 2,3,7,8-TCDD in Arctic beluga, even though ringed seals from the same area with lower concentrations of ΣPCBs have detectable 2,3,7,8-TCDD. These findings may indicate that belugas have the ability to metabolize PCDDs but not PCDFs (Muir et al., 1996a, b). However, they may also be explained by varying dietary sources. Eels represented a likely source of the contaminants detected in the St. Lawrence estuary beluga whales (Muir et al., 1996a, b). The presence of PCDF congeners not fully chlorinated at positions 2, 3, 7 and 8 may imply a diet dominated by invertebrates, as opposed to fish (Muir et al., 1996a).

The relative abundance of certain PCDD/F and non-ortho-substituted PCB congeners can be easily explained by metabolic elimination, because the POC profiles (TCDF greater than TCDD) and non-ortho PCBs (126>77>169) are similar in St. Lawrence estuary beluga whales and the Arctic belugas (Muir et al., 1996a). The non-ortho and mono-ortho PCBs (PCBs 105, 114, 118 and 156) contributed 98 per cent to total TCDD equivalents in narwhal and beluga (Ford et al., 1993). PCB 126/153 ratios indicated that belugas were depleted in PCB 126, as compared to fish (Norstrom et al., 1992). This is additional evidence that CYP1A isozyme activity is present and likely high in beluga whales (Muir et al., 1996a). Muir et al. (1996a) concluded that the differences of PCB52/153 and PCB126/153 ratios between beluga whales of the Arctic and the St. Lawrence estuary might be due to local sources versus
long-range transport, as well as due to a greater (i.e. induced) metabolic capability in the animals with the higher exposure. This was shown by Muir et al. (1996a), using the congener classification developed by Boon et al. (1994), where the relative ratios ($R_{eq}$) for St. Lawrence estuary beluga whales had values that averaged 0.14 and 0.11 for groups III and IV, respectively (indicating metabolism); and values of 1.16, 3.61 and 1.90 for groups I, II and V (indicating a lack of metabolism) of meta, para-substituted congeners or congeners with more than three ortho-chlorines. The results indicate that the St. Lawrence estuary beluga whales have a much greater ability to metabolize congeners with vicinal unsubstituted meta, para-positions, as well as ortho, meta-positions, than the Arctic whales. This implies greater CYP2B and CYP1A activity, which may be a physiologic response to elevated PCB burdens (Muir et al., 1996a). Correlations of CYP1A content and ethoxyresorufin-O-deethylase (EROD) activity in the liver, and non-ortho/mono-ortho PCB content in the blubber of beluga whale supports this hypothesis (White et al., 1994). However, there is the possibility of effects due to multiple confounding variables when interpreting metabolic potential using residue data alone.

This allows us to speculate as to why St. Lawrence estuary beluga whales have elevated concentrations of PCBs and DDT, and to a lesser extent chlorinated benzenes/hexanes and Σchlorodanes, as compared to other beluga whale populations (Muir et al., 1996a). Local sources are likely playing a significant role. The BMFs for mirex and ΣPCBs from fish to beluga were similar to those for Arctic beluga whales, and the lack of age correlations with ΣPCBs and ΣDDTs is also similar (Muir et al., 1996a). This apparent enhanced metabolic capability of the St. Lawrence estuary beluga whales may lead to detoxification. However, it should be recognized that in some cases more potent compounds might be produced, resulting in injury to different target organs than by the parent POCs. The toxicity of these POC metabolites has been poorly characterized.

Temporal changes in POC concentrations have been noted in beluga whales of the St. Lawrence estuary. Based on lipid-normalized and age-adjusted contaminant data, a decline over time was noted for ΣDDTs, Aroclor PCBs, hexachlorobenzene and Σchlorobenzenes in males from 1982–5 to 1993–4 (Muir et al., 1996b). Mean concentrations rose for toxaphene, whereas concentrations of dieldrin, Σchlorodanes and mirex showed no trend (Muir et al., 1996b). Declines in POCs were not detected in females. This type of temporal assessment is required for beluga and narwhal populations of the Arctic to determine whether increases or decreases are occurring for these persistent contaminants. If atmospheric and other sources have been reduced, we may see this reflected as lower concentrations in biota over time. However, if we have not yet reached a steady state and/or loading of the Arctic continues, concentrations in tissues will likely continue to increase.

Beluga whales span the range of exposure and possible effects and should be recognized as a critical species for study within and outside the Arctic.
Persistent organic contaminants in Arctic pinnipeds

The suborder Pinnipedia consists of a diverse group of marine mammals classified into three families: Phocidae, the ‘true’ or ‘hair’ seals, Otariidae, the ‘eared’ pinnipeds (sea lions and fur seals), and Odobenidae, the walruses. One view is that all pinnipeds are descended from a common ancestor, while others suggest that the otariids and odobenids are descended from the dog–bear stock and the phocids from otter–like carnivores (Mitchell, 1975; Repenning, 1976). The following species of phocids are considered to be Arctic species and will be discussed in this section: ringed seal, spotted or largha seal (Phoca largha), ribbon seal (Histriophoca fasciata), harp seal (Pagophilus groenlandicus), bearded seal (Erignathus barbatus), and hooded seal (Cystophora cristata). Two species of otariids, the northern fur seal (Callorhinus ursinus) and Steller’s sea lion (Eumetopias jubatus), occur seasonally (spring and summer) in the southern portion of the Arctic (central and southern Bering Sea), but are considered to be North Pacific rather than Arctic species and are not discussed in this chapter. The single species of odobenid, the walrus (Odobenus rosmarus), is considered to be a true Arctic species.

Almost all species of arctic pinnipeds are considered to be important subsistence food resources for coastal indigenous human populations. The concentrations of POCs in the tissues of these animals have important implications regarding human health and risk to humans from consumption of meat (muscle) and organs (liver and kidney), and oil derived from the rendering of blubber. As a group, pinnipeds feed at various trophic levels and overlap both baleen whales (including gray whales, Eschrichtius robustus) and odontocetes in their principal food resources. Generally speaking, for those pinnipeds that feed near the top of the food web, the potential for accumulation of POCs is probably not as great as that for the Arctic odontocetes (beluga whale and narwhal) and polar bear. The Arctic pinnipeds generally are not as long-lived as cetaceans; therefore, the potential for accumulation may be somewhat less. Most pinnipeds are characteristic of near-shore waters, where they have the potential for being exposed to coastally derived contaminants. However, this is probably not as important in the Arctic as it is in temperate regions because the principal source of POCs in the Arctic is apparently derived from atmospheric transport from lower latitudes (Wania and Mackay, 1993). Evidence also suggests that metabolism and excretion of DDT and PCBs may be less efficient in odontocetes than in pinnipeds, leading to greater magnification in the former (Tanabe et al., 1988, 1994).

Ringed seals

Ringed seals are the most abundant and most widely distributed of all the Arctic phocids, and most of the POC data for Arctic pinnipeds has been
generated on this species. Through use of their long front claws, ringed seals are able to maintain breathing holes in the Arctic land-fast ice throughout the winter. They are the only pinnipeds to remain in the high Arctic during the entire winter, feeding on Arctic cod and invertebrates. They are the principal winter food for polar bears. As such, they are an important component of the Arctic marine food web leading to the top predators, the polar bear and humans. Although the data are not geographically uniform throughout the range of this species, the ringed seal has the largest POC database of any of the Arctic pinnipeds. In addition, reference data on physiological effects of POCs, such as PCBs and DDT, has been generated on this species in some areas of its range, particularly the Baltic Sea (Helle et al., 1976a, b; Helle et al., 1983; Olsson et al., 1992, 1994).

The geographical data on POCs in ringed seals are most abundant for the North American Arctic, particularly for the Canadian Arctic, although some data are also available from Spitsbergen (Svalbard) and the South Kara Sea in the Russian Arctic (Muir et al., 2000). Surveys in the mid-1980s (Muir et al., 1988; Weis and Muir, 1997) showed similar concentrations in ringed seals throughout the Canadian Arctic, although differences were found in patterns of the individual PCBs. For example, there were higher proportions of penta- and hexachlorobiphenyls in seals from Hudson Bay compared to seals from other more northerly and westerly regions. Additional data from the late 1980s and early 1990s showed higher concentrations of POCs in ringed seals from Hudson Bay. Muir et al. (1997) suggested this might be due to these populations being nearer contaminant sources in southern Canada and the eastern United States. Concentrations of ΣPCBs and ΣDDTs were higher in the blubber of ringed seals from Spitsbergen than in those animals from the North American Arctic (Muir et al., 1992a).

Additional data on ringed seals from Alaska (Kranh et al., 1997; Kucklick et al., 2001) suggest similar concentrations of PCBs and DDTs in ringed seals across the western North American Arctic. However, Kucklick et al. (2001) found the concentrations of PCBs to be higher in ringed seals from the Chukchi Sea near Barrow, Alaska than concentrations reported by Kranh et al. (1997) in ringed seals from Norton Sound in the Bering Sea (e.g. 710 ± 182 versus 249 ± 75 ng/g wet weight in blubber of males when summing the same 17 dominant PCB congeners). ΣDDTs and Σchlordane were also higher in the Chukchi Sea animals (e.g. 685 ± 205 versus 188 ± 63 ng/g and 885 ± 612 versus 157 ± 67 ng/g wet weight in blubber of males, respectively). In the Canadian Arctic the non-ortho and mono-ortho PCBs (PCBs 105, 114, 118, and 156) were important contributors (about 50 per cent) to total TCDD equivalents in ringed seals (Ford et al., 1993). These PCB congeners have also been found in the tissues of ringed seals from Alaska (Becker et al., 1997; Kranh et al., 1997; Kucklick et al., 2001).

At least for one geographical location, the ringed seal has the longest temporal database on persistent organic contaminants for any Arctic marine mammal (Addison et al., 1986). Recently, Addison and Smith (1998)
claws, ringed seals fast ice throughout high Arctic during
ates. They are the
or top predators, the
as the largest POC
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the Baltic Sea (Helle
ost abundant for
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ant sources in
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als from Spitzbergen
(Muir et al., 1992a).
Kucklick et al., 1997; Kucklick
and DDTs in ringed
ver, Kucklick et al.
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ons reported by Krahn
Bering Sea (e.g.
r of males when sum-
etale North Orkney
versus 188 ± 63 ng/g
ber of males, respec-
o-ortho PCBs (PCBs
ers (about 50 per cent)
ak, 1993). These PCB
ring seals from Alaska
ald, 2001).

Spotted seals

Spotted seals range in distribution in the western Arctic from the eastern
Beaufort Sea to the western Chukchi Sea, south to the Aleutian Islands and
along the western Pacific coast down through the Sea of Japan. In the winter
and spring this species occurs along the ice front, and during the summer
months it is very common in small groups in the Chukchi Sea. For areas
where they occur in abundance, these animals are an important subsistence
published the results from a 20-year study of organochlorine residues in
ringed seals from Holman, Northwest Territories, Canada. This study
included the re-analysis of blubber samples collected in the early 1970s from
the same study area to assess methodological errors in POC analyses, which
has improved over time. They found that the concentrations of ΣDDT in
blubber were about the same between 1972 and 1981, but after that period
these compounds began to decrease. In 1991 4,4'-DDE was about one-third
and 4,4'-DDT was about 20 per cent of the 1972 values (mean 1972 concentra-
tions for 4,4'-DDE were 0.3 mg/g for females and 0.8 mg/g for males,
whereas 4,4'-DDT concentrations were 0.3 mg/g for females and 0.5 mg/g
for males). Concentrations of PCBs appeared to decrease early (between
1972 and 1981) and remained relatively constant between 1981 and 1991
(one-third of the 1972 concentrations, which were 1.8 mg/g for females and
3.8 mg/g for males). Although during the 1981–1991 period the concentra-
tions of total PCBs remained relatively constant, the relative proportions
of individual congeners changed. This suggests possible metabolic effects
on these compounds or other mechanisms of redistribution of congeners.
Between 1981 and 1991, the concentrations of HCHs did not change, but
HCB decreased by 50 per cent in both males and females.

Historically, the most success in linking contaminants to health effects
and population declines in pinnipeds occurred in studies of ringed seals,
grey seals (Halichoerus grypus) and harbor seals (Phoca vitulina) in the
Baltic Sea during the 1980s (Olsson et al., 1992, 1994; see Bergman et al.,
Chapter 19 in this volume). A decline in pinniped populations in the Baltic
was first observed in the 1950s and the suspicion that it was linked to
organochlorine pollution was formulated during the 1960s (Olsson et al.,
1992). Key to these studies was the indication of reproductive impairment
and symptoms suggesting immune dysfunction in these animals, bone deter-
ioration (particularly in the area around the teeth), gastrointestinal lesions
and proliferation of gastrointestinal parasites. Reproductive impairment was
first noticed by the decreases in fecundity, followed by the documentation of
abnormalities in the reproductive organs of the females (i.e. uterine stenosis
or occlusions) (Olsson, 1972, 1978; Helle et al., 1976a, 1983; Olsson et al.,
1994). A 60 per cent decrease in the number of females becoming pregnant
occurred in ringed seals from PCB-contaminated Bothnian Bay (Helle et al.,
1976a).
food resource. The only data on concentrations of POCs in this species is from Tanabe et al. (1988), who reported $\Sigma$PCBs concentrations in blubber of spotted seals from waters off Hokkaido, Japan, as ranging between 0.67 and 1.5 $\mu$g/g (mean = 0.98 $\mu$g/g; $n = 4$). This is within the range of concentrations reported for harbor seals from the Gulf of Alaska and ringed seals in the Arctic (Krahn et al., 1997). Because of its similarity to ringed seals and harbor seals in trophic position, one would expect concentrations of these compounds in spotted seal tissues to be similar to the other two species, particularly where the ranges of these three species overlap (Alaska).

**Ribbon seals**

Ribbon seals are somewhat solitary. They range in distribution in the western Arctic from the eastern Beaufort Sea to central Chukchi Sea and south to the Aleutian Islands, and along the western Pacific coast down through the Sea of Okhotsk. Not much is known about this species. It is associated with the sea ice and maintains itself away from coastal areas. Although occasionally taken by indigenous subsistence hunters in the Arctic, it is a very minor component of the marine subsistence resources, as compared to ringed seals, bearded seals, spotted seals and walrus. Tanabe et al. (1988) reported $\Sigma$PCBs in the blubber of ribbon seals from waters off Hokkaido, Japan, ranging from 1.0 to 1.5 $\mu$g/g (mean = 1.3 $\mu$g/g; $n = 5$).

**Harp seals**

Harp seals occur in the open sea of the eastern Arctic from the Kara Sea to Greenland, and from the high Arctic of eastern Canada south to Newfoundland and the Gulf of St. Lawrence. In some regions, harp seals are used for food. This species occurs in gregarious migratory groups associated with sea ice. The most recent data on POCs in harp seals come from papers by Addison et al. (1984), Ronald et al. (1984), Beck et al. (1994), Oehme et al. (1995, 1988) and Zitko et al. (1998). These are based on harp seals from the Gulf of St. Lawrence, Hudson Strait and Greenland Sea.

Concentrations of PCBs in the blubber of harp seals from the Gulf of St. Lawrence declined by about 50 per cent between 1972 and 1981, as did PCBs in the blubber of Arctic ringed seals (Addison et al., 1984). Zitko et al. (1998) also reported declines in PCBs and DDTs for harp seals over a 20-year period. PCDD and PCDF concentrations in blubber of harp seals from the Greenland Sea were slightly lower than those of ringed seals from the Arctic, but concentrations of PCBs were comparable (Oehme et al., 1995). Concentrations of PCDD, PCDF, non-ortho substituted (or coplanar) PCBs (77, 126 and 169), and di-ortho substituted PCBs in brain and blubber of harp seals were also compared, and concentrations in brains were one to two orders of magnitude lower. A highly significant positive correlation existed between age and the concentrations of 4,4$'$.DDE and di-ortho PCBs
Cs in this species is concentrations in blubber ranging between 0.67 and 1.04 ng/g, and ringed seals in contrast, 1.68 ng/g. Concentrations of these two species, however, concentrations in muscle, liver and kidney were 2-3 times higher in males.

Bearded seals

Bearded seals are circumpolar in distribution, but do not remain in the high Arctic during winter. They tend to follow the ice edge, moving to lower latitudes during the fall and winter, and into the high Arctic during the spring and summer. Due to its large size, use of hide for constructing skin boats (umiak), and palatability, it is one of the most popular subsistence pinnipeds in the Arctic, especially Alaska. The bearded seal feeds on bottom invertebrates (e.g., crabs, shrimp, clams, octopus) and near-bottom fish in relatively shallow water. It is also an important component of the polar bear diet during periods when it is available.

The bearded seal occupies a very different position in the food web as compared to the ringed seal and, therefore, one would expect concentrations in tissues and patterns of POCs to be different. Concentrations of PCBs, DDTs, ΣHCHs and chlordane in blubber have been reported for bearded seals sampled at Baffin Island in the mid-1980s (Thomas and Hamilton, 1988). Concentrations of each of these groups of compounds were similar to what was reported for the same period for Arctic ringed seals. A comparison between individuals of these two species sampled in the same region, season and year would be more informative. Krahn et al. (1997) compared concentrations of PCBs, DDTs, chlordane, HCB and dieldrin in the blubber of bearded seals and ringed seals sampled in Norton Sound (Alaska) in 1993-5. For both species, concentrations in adult males ranged from 0.05 to 0.36 mg/kg for PCBs, 0.01-0.36 mg/kg for DDTs, and 0.01-0.45 mg/kg for chlordane. PCBs and DDTs were slightly lower in the bearded seals, but this difference was not significant; differences in concentrations of chlordane were not apparent, but concentrations of HCB and dieldrin in the bearded seals were an order of magnitude lower than in the ringed seals. Considering the subsistence value of bearded seals for indigenous people of the Arctic, additional information on the POC concentrations in this animal is warranted. The proposed difference in trophic level as compared to ringed seals must be questioned, based on the similarity of contaminant concentrations in bearded to ringed seals. Studies currently under way in northern Alaska will test this comparison using concentrations of POC, carbon and nitrogen stable isotopes, and heavy metals.
Hooded seals

Hooded seals occur in the open sea of the eastern Arctic from Spitsbergen to Greenland and from the high Arctic of eastern Canada south to Newfoundland and the Gulf of St. Lawrence. This species prefers deep water and thick, drifting ice flows. Somewhat solitary, it forms small family groups during the spring breeding season. Although Clausen et al. (1974) and Johansen et al. (1980) reported PCB and DDT concentration data for this species in Greenland, the hooded seal is an Arctic pinniped for which we have no recent POC information.

Walruses

Walruses are circumpolar, shallow-water pinnipeds that feed on benthic organisms such as clams and gastropods, but some specialize in feeding on seals. Two subspecies are recognized, Odobenus rosmarus rosmarus occurs in the eastern Arctic and O. rosmarus divergens occurs in the western Arctic (King, 1983). This species prefers areas of moving pack ice. This allows individuals to feed and rest over large geographical areas, and provides a means of transport during the spring and fall, while minimizing energy expenditure. The walrus is an extremely important subsistence food resource to the indigenous population of the Arctic coast.

Earlier studies reported very low concentrations of POCs in the blubber of walruses over all geographical areas (Born et al., 1981; Thomas and Hamilton, 1988; Taylor et al., 1989). However, Muir et al. (1995) reported concentrations of PCBs and chlorinated pesticides orders of magnitude higher in walrus blubber from some Hudson Bay groups, and attributed this to the possible consumption of seals, a habit reported by Lowry and Fay (1984) for some of the older male Alaska walrus. The Hudson Bay males had median concentrations of ΣPCBs and ΣDDTs (11.5 and 2.2 ng/kg, respectively) that were two orders of magnitude higher, and chlordane concentrations (6.3 ng/kg) one order of magnitude higher, than reported for other Arctic areas (Muir et al., 1995; de March et al., 1998). Elevated concentrations similar to those in Hudson Bay walrus were found by Skaare et al. (1994) in skin/blubber biopsies of walrus from Svalbard. The hypothesis of seal-eating to explain these relatively high POC concentrations was supported by carbon and nitrogen isotope analysis of the walrus muscle tissue in comparison with that of ringed seals and other walrus prey (Muir et al., 1995).

These elevated concentrations have not been found in any of the Alaska walrus so far. Seagars and Garlich-Miller (2001) report levels of POCs measured in 27 walrus sampled in the Bering Sea in 1991 to be similar to the low levels previously reported by Taylor et al. (1989). Efforts are also under way at the National Institute of Standards and Technology (NIST) Charleston to selectively analyze blubber tissues from older male walruses that have been archived.

Polar bears

POC continues to be a concern for polar bears because they are considered sentinel species that are good indicators that contaminants are entering the environment (Samuelson and Macdonald, 1998). High levels of PCBs, DDE, and DDT have been found in polar bears, including a group of healthy pregnant females in the North Slope (food-web) of Alaska (Hines et al., 1998). The northern study group is a primary marine food source for indigenous peoples, and contaminant levels in their food can therefore be transmitted to other members of their community, including their blood.

Kuckuck et al. (1996) review the results of monitoring the Arctic maritime zones (ABAF) of the International Arctic Buoy Network (IABN) program for polar bears. The lower levels of PCBs and DDTs in polar bears from the North Arctic (Canada, Norway, Russia, and Alaska) were probably due to wider variation in their diet, as is the case in the Arctic, where marine mammals are the primary food source for the bears, and much less terrestrial vegetation is available. The diet of polar bears is more varied in the North Atlantic, where the diet is more carnivorous; thus, contaminant levels were higher in the North Atlantic than in the North Arctic.
archived at the National Biomonitoring Specimen Bank, to see if a pattern of elevated POCs can be identified in any of these samples from the western Arctic walrus population. Preliminary results indicate very low POC concentrations in these samples, similar to those reported by Seagars and Garlich-Miller (2001) and J. Kucklick (NIST-Charleston, personal communication).

**Polar bear**

**POC concentrations in tissues and associated biological factors**

Polar bears are considered a critical species for biomonitoring programs because they occur throughout the Arctic and Subarctic and are top predators that accumulate and integrate many contaminants (Norstrom et al., 1998). However, many factors can affect POC concentrations in polar bears, including diet, fasting (i.e. pregnant sows), region or stock, season, sex, age, presence or absence of cubs, available prey, forage preferences of prey (food-web structure) and others (Polischuk et al., 1995; Norstrom et al., 1998). The difficulty in collecting adequate samples is also restrictive. The primary prey species, ringed seal, is also Holarctic and will integrate contaminants over a limited range (Norstrom et al., 1998). Differences in POC accumulation and possible physiologic and metabolic roles as compared to other marine mammals are emphasized here.

Kucklick et al. (2001) determined the ‘apparent bioaccumulative factor (ABAF)’ for polar bears and ringed seals from Barrow, Alaska, based on the ratio of the lipid-based organochlorine concentrations in fat of polar bear divided by that in ringed seal, and compared these with ABAFs for polar bears and ringed seals from several Canadian Arctic locations. The lower ABAFs for Barrow, Alaska, for compounds that substantially biomagnify in polar bear, suggest that the polar bears from the western North American Arctic (and Alaska in particular) may prey on a much wider variety of prey than polar bears from the eastern North American Arctic, which may be more restricted to preying on ringed seals.

**Chlordane**

The largest contributor to total chlordane in polar bear fat and liver is the metabolite oxychlordane (56 per cent and 61 per cent, respectively) (Letcher, 1996). Total chlordane was dominated by oxychlordane (62 per cent) in polar bear fat, with approximately equal concentrations of nonachlor-Ill (13 per cent), trans-nonachlor (11 per cent), and heptachlor epoxide (11 per cent) (Zhu et al., 1995). In studies by Zhu et al. (1995) of POCs in ringed seals, polar bears, and the blood plasma from humans from northern Quebec, it was found that polar bear fat contained 5–6 times more total chlordane (4287 ng/g lipid) than did human plasma (840 ng/g lipid) or seal blubber (706 ng/g lipid). Photoheptachlor in polar bear was 3.4 per cent of total
chlorodanes and had a similar BMF as oxychlorodane. The oxychlorodane contribution was approximately 40 per cent for ringed seal blubber and 10 per cent for whole Arctic cod, indicating the metabolic capacity (formation of oxychlorodane) may be cod < seal < bear (Letcher, 1996), or variability in absorption and biomagnification. Nonachlor-III is an original component of chlorodane that is not easily biotransformed, and is biomagnified nearly ten-fold from seal blubber (59 ng/g lipid) to polar bear fat (545 ng/g lipid) (Zhu et al., 1995). The median concentration of total chlorodane was 2.3 µg/g lipid, 72 per cent of which was represented by the metabolite oxychlorodane.

Young and subadult bears had significantly higher chlorodane concentrations than adult and old male bears (Bernhoft et al., 1997), and concentrations in matched sows and cubs were twice as high in cubs (Polischuk et al., 1995; Norstrom et al., 1998). The sum chlorodanes (CHL) in fat of polar bears from Hudson Bay was higher for cubs and subadults (<5 years old) than adults, and decreased from young of the year (Y0Y) to 5 years of age (Norstrom et al., 1998). Norstrom et al. (1998) indicated that sum chlorodanes (geometric mean) was 30 per cent lower in males than females (with and without cubs). The decrease in CHL over approximately 4 years for subadults would fit with a half-life of 1 year (nearly achieving a steady state in 4 years), suggesting a very slow clearance rate (Norstrom et al., 1998) if one makes many toxicokinetic assumptions. For chlorodane, the decrease with age in male bears and the lower concentration in male than in female adults may be due to sex differences in metabolism. However, Norstrom et al. (1998) also considered the higher concentrations of ΣPCBs as inducers of hepatic CYP2B, which may increase clearance of CHL. Whatever the mechanism, polar bears do appear to metabolize chlorodane when concentrations in prey are compared to concentrations in the bear (Letcher et al., 1996; Wiberg et al., 2000; Kucklick et al., 2001). These results are in contrast to the findings of higher chlorodane concentrations in males than females of other marine mammals, which do not have this metabolic capacity (Bernhoft et al., 1997).

PCBs and DDTs

In general, the ratio of higher to lower chlorinated PCBs decreased from west to east in polar bears from the Bering Sea to Greenland, indicating there may be a higher input of higher chlorinated PCBs to the eastern Arctic (Norstrom et al., 1998). Declines in pinnipeds, critical prey species for polar bears, have been causally linked with PCBs elsewhere, based upon known reproductive and immunologic effects of this class of POCs (Borrell, 1993; Kuiken et al., 1994), and ringed seal blubber makes up the majority of the polar bear diet (Best, 1985). Therefore any decreases in seal productivity could affect the polar bear. ΣPCBs concentrations in bear fat (6819 ng/g lipid) were more than ten times that of seal blubber and human plasma, and
congener patterns were similar (Zhu et al., 1995). In previous studies of polar bears in arctic Canada, Norstrom et al. (1988) found that the $\Sigma$PCBs and total chlordane accounted for more than 80 per cent of the total organochlorines in polar bear adipose tissue.

The PCB concentrations present in the polar bears of Svalbard are extremely high. The POC patterns in yearlings reflect the low transfer of the highest chlorinated PCB congeners into maternal milk, and the other PCB congeners were at higher concentrations in the yearlings compared to their mothers (Bernhoft et al., 1997). The median concentration of $\Sigma$PCBs in subcutaneous fat for 85 polar bears was found by Bernhoft et al. (1997) to be 15.5 $\mu$g/g lipid, 62 per cent of which was contributed by PCB 153 and 180. The highest concentration of the PCBs was found in adult male bears, and was significantly higher than in young and adult female bears. Nine of 14 congeners showed significantly higher concentrations in adult males than in one or more of the other age or sex groups studied. Concentration of the PCBs seems to increase with age until about 7 years in females and 14 years in males, and thereafter declines (Bernhoft et al., 1997). However, the $\Sigma$PCB was higher for cubs and subadults (5 years) than adults; and concentrations were 46 per cent higher in male than female adults (Norstrom et al., 1998). In lactating bears, similar concentrations of chlordane, HCB and $\Sigma$HCHs were found in lipids of milk, subcutaneous tissue and plasma. The concentrations of DDE, and penta- and hexa-chlorinated PCBs in milk lipid were similar to the corresponding concentrations in plasma lipids. The POC concentrations in subcutaneous fat of yearlings were generally higher than in their mothers. However, the concentrations of the hepta- to decachlorinated biphenyls (PCB 187, 194, 206, 209) in yearlings compared to their mothers decreased gradually with increased chlorination and were below maternal concentrations. PCB 105 and 118, and DDE were found in similar concentrations in mothers and yearlings. Mothers that had been lactating for 1.25 years contained significantly less chlordane, HCB, $\Sigma$HCHs, and $\Sigma$PCBs than females that had been lactating for 2.25 years or had no young.

Denning status is regarded as a measure of polar bear reproduction success. The POC concentrations in denning bears were not significantly different from those not denning (Bernhoft et al., 1997). Concentrations of $\Sigma$PCBs in adult males from Svalbard were about six and three times higher than the averages in polar bears in Alaska and Canada (Bernhoft et al., 1997). $\Sigma$PCBs were significantly higher (11-16 mg/kg) in eastern Greenland, Svalbard and M’Clure Strait, above 14 other study areas which averaged 3.7 ± 1.6 mg/kg. Bernhoft et al. (1997) associated this with geographical differences in POC distribution, but we should consider differences in feeding behavior of bears and seals in these regions as well. In ringed seals, higher concentrations of PCBs are found in the Svalbard area as compared to the Canadian Arctic (Muir et al., 1992a). Biomagnification of oxychlordane, HCB, HCHs and PCBs from ringed seals to polar bears is evident, with a BMF of about 10 for PCBs. Metabolism of lower chlorinated PCBs and biomagnification of
the more highly chlorinated forms can explain the species differences observed (Bernhoft et al., 1997).

Tri- and tetrachlorinated biphenyls, in addition to penta- and hexa-chlororinated biphenyls with meta-para adjacent hydrogen atoms, are not found in polar bears (Bernhoft et al., 1997). These are typically present in other marine mammals. The age- and sex-based differences for most of the PCBs and the HCHs (disproportional accumulation with age in males) is opposite that of chlordane. The deviation in females from the PCB concentrations seen in males at 7–11 years of age coincides with sexual maturation and breeding, with the first offspring occurring at 6–7 years of age. This represents the initiation of reduction in female body burdens of POCs through transfer to the offspring during pregnancy and lactation (Bernhoft et al., 1997). Milk has a high fat content and lactation may occur for as long as 2.5 years. The incomplete transfer of lipid from the circulatory system may reduce the efficiency of the POC transfer, particularly for the most lipophilic compounds. This is supported by the correlations between plasma and milk lipids for most POCs, particularly for the higher chlorinated PCBs and DDE (Bernhoft et al., 1997).

Concentrations of POCs in subcutaneous fat of yearling polar bears reflect a similar pattern to that of the mother’s milk. Most of the POCs are present at higher concentrations in the yearling offspring than in the mother (Bernhoft et al., 1997). Seal blubber gradually becomes a more available food source for young polar bears and is less contaminated than maternal milk (Bernhoft et al., 1997). Higher concentrations have been found in cubs in other studies (Polishuck et al., 1995). A difference in POC content between pregnant versus non-pregnant females was not detected, but the sample size was limited. There is concern, because high cub mortality has been observed in polar bears at Svalbard (Bernhoft et al., 1997). PCBs have been suggested as potential causative agents in seven cases of vestigial male reproductive organs (both male and female genital structures) in ‘genetically’ female polar bears of Svalbard, some of which have cubs (Wiig et al., 1998). The capability to metabolize several toxic POCs may protect the polar bear. However, the generation of toxic metabolites, as well as age-based accumulation and rather high exposure of offspring via lactation, are of concern. Mean PCB concentrations in fat are difficult to interpret because they are 4–10 times lower than concentrations associated with reproductive effects based on laboratory studies (Norstrom et al., 1998), but if the polar bear is sensitive to these compounds, some individuals may be approaching levels of concern. The unique metabolism of polar bears may enhance excretion and elimination of these compounds, but may also produce active metabolites with affinity for critical tissues (e.g. liver, adrenal gland). Occupying the highest trophic level and the potential for high metabolic activity related to OCs makes the polar bear a critical animal for improving understanding of the impact(s) of PCBs in arctic marine mammals.
POCs in Arctic marine mammals

Polychlorinated dibenz-p-dioxins and dibenzofurans

Polychlorinated dibenz-p-dioxins and dibenzofurans were determined in ringed seals and polar bears. No apparent biomagnification (BMF < 1.0) of TCDD, OCDD or TCDF occurred from seal to bear fat; in contrast, the BMFs for PCBs and HCB were 5–17 and 14–21, respectively (Norstrom et al., 1990). All polar bears studied had detectable concentrations of TCDD and OCDD, but no TCDF or HxCDD. The polar bear must have a mechanism for efficient elimination of TCDD and TCDF. OCDD may accumulate in bears, but the limitation of the detection level hampered this assessment (Norstrom et al., 1990). PCDD and PCDF have been detected in blubber of ringed seals from the eastern northern Atlantic (Oehme et al., 1988; Biggert et al., 1989). Norstrom et al. (1990) indicated that the highest concentrations were in bears from Barrow Strait and Larsen Sound, and lowest from Hudson Bay, similar to patterns in ringed seals. This distribution is the opposite of that reported for ΣPCBs, Σchlorodanes, ΣDDTs, ΣHCHs, and dieldrin (Norstrom et al., 1988, 1990; Norstrom and Muir, 1994).

Toxaphene and HCH

Fifteen congeners of toxaphene were analyzed in polar bear fat (total 1.0 mg/kg) and ringed seal blubber (total 0.25 mg/kg) (Zhu and Norstrom, 1993). Proportions of toxaphene compounds were quite different for polar bears and ringed seals compared to other marine organisms. Only 8–11 per cent of total toxaphene was octachloroborane (T2) and nonachloroborane (T12) in ringed seal and polar bear (Zhu and Norstrom, 1993), whereas these typically dominate in Arctic amphipods, burbot, narwhal and beluga (Stern et al., 1992; Bidleman et al., 1993). A better understanding of toxaphene pathways in Arctic biota is needed.

The median concentrations of DDE, HCB and ΣHCH in blubber were 272, 146 and 240 ng/g lipid, respectively. Males had higher concentrations of ΣHCH and ΣPCBs than females. The lower HCH concentration in females corresponds with the finding of relatively high concentrations of HCHs in milk (Bernhoft et al., 1997). In males, ΣHCH increased with age until about 12 years, whereas in females no change with age was evident. The HCH accumulation was not expected, because ΣHCH has been noted to decrease up the food chain. However, β-HCH, which is the most persistent isomer of HCH, constituted 81 per cent of the ΣHCH (Bernhoft et al., 1997). Tanabe et al. (1996) proposes that higher β-HCH/ΣHCH indicates higher metabolic capacity of a species to metabolize α-HCH and γ-HCH. Furthermore, both HCH and PCB patterns differ between polar bear and ringed seal: β-HCH dominating in the polar bear, whereas α-HCH was the dominant form in ringed seal, and γ-HCH (lindane) was found in the seal but not the polar bear.
POC metabolism

POC metabolism and mixed function oxidases (MFO)

Polar bears were shown to metabolize congeners of PCBs and 4,4'-DDE that are normally recalcitrant or not biotransformed (Letcher, 1996; Letcher et al., 1996) in other mammals addressed here. This is presumably based upon differences in hepatic CYP metabolic capacity and differential transfer of some PCB congeners from one trophic level to the next (cod \(\rightarrow\) ringed seal \(\rightarrow\) polar bear) (Figure 8.1). PCB 153 represented 44 per cent, 14 per cent and 4 per cent of the \(\Sigma\)PCBs of the polar bear, ringed seal and cod, respectively, indicating a proportional magnification of PCB 153 and/or loss of non-PCB 153 congeners. This PCB congener is known to be resistant to metabolism and can be used to determine metabolic indices (Letcher, 1996). Many congeners present in cod are not present in polar bears (Figure 8.1) and this indicates likely metabolic degradation and/or excretion by the polar bear.

The presence in ringed seals of PCBs with meta-para vicinal hydrogen atoms indicate low CYP2B-type metabolism for seals as compared to polar bears. CYP1A-type metabolism of PCBs occurs in ringed seals, but at a lower activity in ringed seals than in polar bears (Letcher, 1996; Letcher et al., 1996). This high CYP1A activity seems to be unique in the polar bear as compared to other marine mammals in the Arctic regions of the western hemisphere. CYP2B-type activity was also high, as evidenced by the lack of PCBs with meta-para vicinal hydrogen atoms and high concentrations of methylsulfone polychlorinated biphenyls (MeSO\(_2\)-PCBs) (Letcher, 1996; Letcher et al., 1996). There is clear evidence of mobilization of MeSO\(_2\)-PCBs from adipose tissue, and lactational transfer from mother to cub, which may be more rapid during fasting (Letcher, 1996). The accumulation of methylsulfone metabolites of PCBs has been shown to be enantioselective for ringed seals and polar bears (Wiberg et al., 1998). This can involve selective formation, uptake, transport, storage and/or clearance. The presence of MeSO\(_2\)-CBs in polar bears results from both formation by the bear (e.g. 3- and 4-MeSO\(_2\)-PCB 91 and 4-MeSO\(_2\)-PCB 149) and accumulation from

Figure 8.1 (opposite) Ratios of various PCB congeners to PCB 153 in blubber or fat of Arctic cod (Boreogadus saida), ringed seals (Pusa hispida) and polar bears (Ursus maritimus). Polar bears metabolize congeners of PCBs that are normally recalcitrant or not biotransformed in other mammals. This is presumably based upon differences in hepatic CYP metabolic capacity and differential transfer of some PCB congeners from one trophic level to the next (cod \(\rightarrow\) ringed seal \(\rightarrow\) polar bear). PCB 153 represented 44, 14 and 4 per cent of the \(\Sigma\)PCBs of the polar bear, ringed seal and cod, respectively, indicating a proportional magnification of PCB 153 and/or loss of non-PCB 153 congeners. Many congeners present in cod are not present in polar bears and this indicates likely metabolic degradation and/or excretion in the polar bear. (After Letcher, 1996; Letcher et al., 1996.)
PCBs and 4,4'-DDE (Letcher, 1996; Letcher et al., 1996) is presumably based on the higher accumulation and differential transfer of the congeners. PCB 153 is known to be resistant to oxidative metabolism indices (Letcher, 1996), which may explain the higher concentrations in polar bears (Figure 8.1) and Arctic cod (Figure 8.12). It is common in the polar bear to observe elevated levels of PCB 153 in blubber, but at a lower ratio than in Arctic cod (Letcher, 1996; Letcher et al., 1996). It is possible that high concentrations of 4,4'-DDE are responsible for the variation observed in the Arctic cod (Letcher, 1996; Letcher et al., 1996). The accumulation of PCB 153 has been shown to be enantioselective in the blubber of Arctic cod. This can involve selective metabolism or clearance. The presence of enantiomers in the Arctic cod by the bear (e.g., Figure 8.12) and accumulation from lower levels of PCB 153 in blubber or fat in polar bears (Pusa hispida) and polar bears (P. b. alcaica) and fat in other mammals. This indicates the presence of higher hepatic CYP metabolic capacities in Arctic cod (Letcher, 1996; Letcher et al., 1996). PCB 153 represented 44, 75 and 86% of PCBs in polar bear, ringed seal and cod, respectively. The indication of PCB 153 and/or PCB 138 as the most important congeners present in cod are not surprising given the low solubility of PCB 153. It is important to note that the metabolic degradation of the bearing PCB congeners is not complete.
the seal (3- and 4-MeSO₂-PCB 132). However, the Arctic cod does not produce these metabolites (Wiberg et al., 1998).

Bandiara et al. (1995) immunohistochemically evaluated rat subfamily cytochrome P450s and detected homologues for 1A, 2B, 2C and 3A, and rat epoxide hydroxylase in polar bear liver. The bears had 'high' concentrations of 1A and 2B compared to other marine mammals, and this could be a consequence of induction by environmental contaminants (Bandiera et al., 1995). Letcher et al. (1996) showed CYP1A (P450 expression) was correlated with concentrations of PCBs, PCDDs and PCDFs, and that CYP2B (P450 expression) was correlated with ortho-Cl substituted PCBs and chlordanes. A better understanding of polar bear metabolism is needed. This will be key to recognizing their unique detoxification/excretion mechanisms, and to better recognize the potential target organs (e.g. adrenal glands) for these metabolites.

**DDT and PCB methylsulfones**

The considerably lower DDE concentrations in polar bears than in ringed seals possibly reflects the capacity of the polar bear to metabolize the most persistent of the DDT compounds. Similar DDE concentrations were found in polar bears from Svalbard, Canadian bears (Bernhoff et al., 1997) and Alaskan bears (Kucklick et al., 2001). The tendency of decreasing DDE concentrations from young to subadults may suggest a lower capacity for metabolism of DDE in younger bears (Bernhoff et al., 1997). The findings in polar bears are in contrast to the age-related accumulation of DDTs seen in other male marine mammals. The lack of significant age-class or sex differences in DDE concentrations in polar bears may be due to a higher metabolic capacity of DDT-based compounds in polar bears than in other mammals (Kucklick et al., 2001). Females with cubs have 32 per cent higher sum DDTs than males, and Norstrom et al. (1998) reports 22 per cent higher DDE concentrations in females with cubs as compared to solitary females and males. Polar bear fat contained more than 98 per cent of the total body burden of POCs, except for 38.5 per cent of the methylsulfone-DDE (S-MeSO₂-4,4'-DDE) which was in the liver (liver mass makes up only 2.6 per cent of the total body mass of polar bears) (Letcher, 1996).

Polar bears are exposed to high concentrations and different MeSO₂-PCB and -4,4'-DDE patterns, indicating that the potential toxicological risks from chronic exposure may be different in polar bears relative to ringed seals. Methylsulfone-DDE formation in bears was high; however, another unknown metabolic path must be substantial for 4,4'-DDE. The retention of MeSO₂-PCBs and -4,4'-DDE may be a consequence of stellate cells specialized in the retention of polar retinols and retinol esters or binding to specific proteins. This clearly favors pentachloro-3- and MeSO₂-PCB 87 (Norstrom et al., 1998). Letcher et al. (1998) showed that Arctic cod had no detectable MeSO₂-PCBs or 4,4'-DDE (detection level of <0.01 ng/g lipid). In
contrast, ringed seals contained 0.4 ng/g 3-MeSO₂-4,4'-DDE and 13 ng/g 3- and 4-MeSO₂-PCB isomers, and polar bear fat contained 432 ng/g of MeSO₂-PCB isomers and 2.0 ng/g 3-MeSO₂-4,4'-DDE. Fifteen MeSO₂-PCB congeners are likely bioaccumulated, whereas seven are completely or partially formed in the bear (Letcher et al., 1998). However, this may also result in the production of toxic metabolites, and may be related to the presence and amount of CYP.

High activity of CYP1A (loss of PCB 105 and 118, small change in PCB 99), and high CYP2B activity (loss of PCB congeners with meta-para vicinal hydrogen atoms in bear versus seal) were evident in polar bears (Letcher, 1996). Induction may enhance this enzymatic process, and the presence of POCs may be critical for the maintenance of the CYP system at this 'high' activity level. All PCBs with significant bioaccumulation potential in polar bears have 2,2',4,4'- Cl substitutions (Letcher, 1996; Letcher et al., 1996). According to Letcher (1996), the residual anthropogenic compound patterns demonstrate that, relative to ringed seals and cod, the polar bear has a high capacity to sequester, with or without metabolism, all persistent OCs measured.

Methylsulphonies of six PCB congeners (99, 153, 158, 180, 170, 194) made up about 93 per cent of the PCB metabolites in polar bears and beluga whales (Bergman et al., 1994). Based on PCB and MeSO₂-PCB patterns, ringed seals have low cytochrome P450 (CYP) 1A and CYP2B-type enzyme activities, whereas polar bears apparently have higher levels of both types (Letcher, 1996; Letcher et al., 1996). In polar bears these enzyme levels correlated with the presence of some chlorinated hydrocarbons. All precursor PCBs had 2,5- or 2,5,6-chlorination on the MeSO₂-substituted ring. The polar bear is capable of metabolizing some PCBs because the BMF is less than 1.0 for 4,4'-DDT and some PCB congeners are altered (Muir et al., 1988; Norstrom et al., 1988). Muir et al. (1988) showed that ringed seals did not accumulate (concentrations were less in seals than in cod) PCB 177, 183, 187, 194 and 201, and these would not reach the polar bear. Polar bears can biotransform additional congeners, reducing further the number of congeners (those in seals plus PCB 99, 128, 138 and 177) that it accumulates (Muir et al., 1988). The congeners PCB 153, 180 and 194 are persistent (Muir et al., 1988).

Reproduction implications and associations

Risk from exposure to POCs in polar bears may be greatest at two phases in the reproduction cycle: lactation and delayed implantation. Polar bear mating occurs in spring and the fertilized eggs do not implant until September–October. This implantation is usually concurrent with denning. Only pregnant females tend to den. Species with delayed implantation may be more susceptible to POCs (Sandell, 1990). The cubs are born in late December or early January and the mother and cubs emerge from the den in March or April. At this point the mother has fasted for approximately 6 months, but
continues to lactate. Polar bears can enter a hyperphagic phase in the late spring and early summer, and as a result more than 50 per cent of their body weight can be lipid. During phases of fasting and lactation these lipid stores are mobilized (Polischuck et al., 1995). As fasting takes place, a higher concentration of some persistent OCs (e.g. PCBs) is found in milk and fat of sows, whereas others (such as 4,4’-DDT) do not change and may be affected by metabolism (Polischuck et al., 1995). The cubs of the year had the highest OCs of any life stage, and this indicates a significant transfer of contaminants to young. This could be a significant phase to examine for adverse health effects or exposure leading to delayed effects of parent compounds or metabolites of POCs. In utero and/or neonatal exposure to persistent OCs has been implicated as a possible cause of female pseudohermaphrodites at Svalbard (north of Scandinavia) at a rate of 1.5 per cent (4 of 269 examined animals) (Wiig et al., 1998). However, investigations of other polar bear stocks (i.e. less contaminated) are needed to determine the ‘baseline’ occurrence of pseudohermaphroditism in relation to POC exposure.

**Special significance of POCs in polar bears**

In summary, the polar bear may be quite unique in its exposure, metabolism and expression of possible adverse effects, compared to other marine mammals in the Arctic. This species merits special consideration for effects assessment, not simply residue analysis, because it represents the top of the food chain and integrates these accumulative compounds of the Arctic. Evidence indicates that the most contaminated of the polar bears (i.e. Svalbard animals) are suffering suspicious effects that may be related to POC exposure.

**Conclusions**

This chapter reviewed the occurrence and possible effects of POCs in Arctic marine mammals. Recent work has clearly indicated that many differences in ecologic, regional and physiologic factors are related to exposure and potential adverse effects of POCs for these species. Unfortunately, we do not understand how these differences relate to individual and population health and responses. Current efforts will only detect gross, dramatic changes, and at that point we are unlikely to be able to reverse unwanted trends. A better understanding of POC effects and toxicoses is needed for these marine mammals from the Arctic, especially if we are concerned about cetacean (i.e. beluga whale), pinniped (i.e. ringed seal) and polar bear populations and health.

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