

Bowhead whale contaminants: A review of current state of knowledge and possible future research directions.

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ABSTRACT

In this paper, we review contaminants in bowhead whale tissues. Mean concentrations of metals (As, Cd, Co, Cu, Pb, Mg, Mn, Hg, Mo, Se, Ag, and Zn) studied in bowhead whale liver, blubber, epidermis, muscle, and kidney are low or normal compared to most mysticete species. From a consumption or subsistence perspective the kidney represents a source of cadmium (Cd) requiring further scrutiny, while other elements and contaminants are not at levels of concern (see O'Hara et al., SC/56/E2). Mercury (Hg) is at very low concentrations and is of no concern. The mean cesium-137 (Cs-137) levels (Bq/kg w.w.) indicate that the increasing rank order for tissues is blubber < kidney/liver < "skin" (epidermis)/muscle; and concentrations (activity) are considered very low. Strontium-90 (Sr-90), and plutonium (Pu-239/240) are mostly below detection concentrations and thus very low. Polonium-210 (Po-210) was above detection level at approximately 5 Bq/kg and considered low. As expected, some organochlorines (OCs) occurred at higher concentrations in longer (older) male whales than younger males (approximately 1,000 ng/g lipid wt in blubber for longer whales). Spatial trends and bioaccumulation (trophic transfer) of organochlorine pollutants in bowhead prey have been described allowing for a quantification of the biomagnification in bowhead whales. Understanding the trophic ecology of bowhead whales using C and N stable isotope signatures and published stomach contents data has assisted in understanding regional and seasonal feeding habits, and the associated differences in exposure to contaminants. To better understand "bioprocessing" of OCs by the bowhead whale enantiomer-specific accumulation of PCB atropisomers has been documented, and for enantiomer-specific biomagnification of α -hexachlorocyclohexane and selected chiral chlordane-related compounds in an arctic marine food web. The role of metabolism or biotransformation in OC "bioprocessing" for bowhead whales is now better understood as hydroxylated and methylsulfone-containing metabolites of PCBs were described in the plasma and blubber of bowhead whales. These OCs data clearly indicate the bowhead whale is highly selective in the chemicals that accumulate, the metabolites that form, and that sexual maturation likely plays a role in this "processing" of OCs. Some halogenated organics are considered natural and have been found in bowhead whales including the halogenated dimethyl bipyroles. Preliminary data indicates that petroleum hydrocarbons occur at very low

concentrations, and for many samples were below the level of detection (approximately 0.1 to 1.0 ppm). Establishment of baseline levels of biomarkers related to hydrocarbons exposure and effects are underway. In conclusion, tissues of the bowhead whale are low in most natural and anthropogenic contaminants of the inorganic, organochlorine, petroleum hydrocarbon, and radionuclide classes. We expect no adverse effects in the whales related to these contaminants at the concentrations documented to date.

INTRODUCTION

For a review of the basic biology of the bowhead whale we refer the reader to other sources of information (i.e., George et al., 1999, Hoekstra et al., 2002A) and other reports prepared for this meeting of the IWC. Our intent for this paper is to briefly review the contaminants data related to the bowhead whale.

Inupiat and Yupik Eskimos of Alaska have for millennia hunted and consumed arctic wildlife and marine mammals, from small pinnipeds and cetaceans to large baleen whales (Stoker and Krupnik, 1993). The species hunted and tissues consumed are very different in composition and nutrient value from tissues of domesticated food animals, and these wild animals are not easily substituted with available food (i.e. store) alternatives (Kinloch et al., 1992; O'Hara et al., SC/56/E2). The transport of contaminants in the arctic food chain is unique compared to more temperate regions (Barrie et al., 1992; Elinder, 1992). Studying the health and contamination of the bowhead whale is important because of human culture and welfare, climate change, intrigue of mysticetes, assessing industrial contamination and impacts, mandates and recommendations of the International Whaling Commission (IWC), determining nutritional and reproductive status of the whale, food safety, and population health and management (Willette et al., 2002). The bowhead whale and other marine organisms have been promoted as potential indicator species for studying and monitoring marine ecosystem health (Aguirre et al. 2001). The issues in Aguirre et al. (2001) relate to the importance of studying and monitoring chemical contamination of bowhead whales for the Arctic. Natural processes (fires, erosion, volcanism, etc.) and anthropogenic activities (pesticide application, coal and oil combustion, metal smelting) result in releases of contaminants to soil, water, and air; resulting in contamination of the human and wildlife food chain (Nriagu and Pacyna, 1988). Contaminants in bowhead whales and other marine mammal species were recently reviewed in O'Hara and Becker (2003), O'Hara et al. (2003B), and O'Hara and O'Shea (2001). This report will focus on the bowhead whale and multiple contaminant classes (essential and non-essential elements, organochlorines, radionuclides, and petroleum hydrocarbons).

We briefly review the major studies below by chemical class and a more detailed review of these and other studies is provided in the "Discussion of Historic and Current Findings". Suggestions for future studies and monitoring are outlined in the section "Future Directions". Much of the data concerning contaminants has been acquired from animals taken in the subsistence hunt in Northern Alaska by the Inuit and their assistance has been very important. The Inuit are concerned about the welfare of the whale and their exposure to these contaminants.

Organochlorines (OCs)

Organochlorines in bowhead whale tissues were initially studied by McFall et al. (1986). Their results indicating rather low concentrations as compared to other marine mammals. Marine mammals of the Arctic are long lived and develop large lipid or fat depots, and many occupy high trophic levels in this lipid dependent food web. These biological factors are important to the entry and magnification of these persistent and lipophilic agents. Since bowhead whales feed almost exclusively on copepods, euphausiids, and amphipods (Lowry and Frost, 1984) this likely accounts for the lower concentrations of "bioaccumulating" OCs as these whales occupy a relatively low trophic level. However, bowhead whales are very long lived (approximately 150 years or more, George et al., 1999) and males accumulate OCs with increasing body length (O'Hara et al., 1999). During the 1990's more detailed studies of the environment and the prey of the bowhead whale were conducted. Hoekstra et al. (2002A) described the spatial trends and bioaccumulation of organochlorine pollutants in marine zooplankton from the Alaskan and Canadian Arctic. These studies set the stage for evaluation of the biomagnification of organochlorine contaminants in bowhead whales (Hoekstra et al., 2002B) and the trophic transfer through the arctic marine food web (Hoekstra et al., 2003B). These reports showed that seasonal, sex, body length (age), and reproductive status factors affect the resulting concentrations and the profiles of the OCs. In particular, a better understanding of the trophic ecology of bowhead whales compared to other arctic marine biota as interpreted from carbon, nitrogen and sulfur stable isotope signatures assisted in determining the major factors for the observed OCs differences (Hoekstra et al., 2002C). With respect to toxicodistribution and metabolism Hoekstra et al. (2002D and 2003A) demonstrated the enantiomer-

specific accumulation of PCB atropisomers in the bowhead whale and the enantiomer-specific biomagnification of α -hexachlorocyclohexane and selected chiral chlordane-related compounds in an arctic marine food web. These data clearly showed that “bioprocessing” was much more complicated than originally described. These processes very likely involve complicated interactions with enzymes, receptors, binding proteins and other components. The determination of hydroxylated and methylsulfone-containing metabolites of PCBs in the plasma and blubber of bowhead whales demonstrated that cytochrome P450 activity is present and is very similar to CYP2B (a cytochrome P450 enzyme).

Essential and non-essential elements (heavy metals)

A few reports address heavy metals in many individual bowhead whales (>100 individuals) (Bratton et al., 1997; Bratton et al., 1993; Byrne et al., 1985; Krone et al., 1998; Woshner et al., 2001A), the most extensive published work being Woshner et al. (2001A). However, additional data will soon be available on the trophic transfer and health implications of these elements for the bowhead whale (Rosa and Dehn unpublished data). Woshner et al. (2001A) evaluated concentrations of twelve essential and non-essential elements in tissues of bowhead whales. The essential elements are reported to develop reference ranges for health status determination, and to help assess known or suspected interactions affecting toxicoses of cadmium (Cd) and mercury (Hg). Tissue levels of all elements were within ranges that have been reported previously in marine mammals. Mercury concentrations are very low and of no concern. Significant metal-metal or metal-bowhead morphometric associations included: Cd with length (age), Zn, or Cu; Cu with length (age), Zn or Ag; and Hg with length (age), Se, or Zn (Woshner et al., 2001A). Possible explanations for observed elemental correlations (i.e., interactions) and ancillary mechanisms of Cd and Hg detoxification are discussed in “Historic and Current Findings”.

Radionuclides

Certain activities have been proposed as major sources of “potential” significance to arctic contamination by radionuclides and include the explosion of the nuclear reactor at Chernobyl, western Siberia radioactive materials caches, nuclear tests conducted in the Arctic of the Former Soviet Union (FSU), nuclear facilities in NW Europe (especially Sellafield, United Kingdom and La Hague, Netherlands), nuclear testing on Amchitka Island (Alaska), and of course global nuclear testing (511 detonations) as conducted by the United States, FSU, United Kingdom, France and China (Efurd et al., 1997). The radionuclide levels in bowhead whales indicates a lack of accumulation “up” the marine food chain, including the bowhead whale (Efurd et al., 1997, Cooper et al., 2000). Very little anthropogenic radioactivity was detected in bowhead whale samples of northwestern Alaska (Efurd et al., 1997; Cooper et al., 2000) and the concentrations were very low in the marine fish, birds and other mammals sampled (Efurd et al., 1997; Cooper et al., 2000).

Petroleum Hydrocarbons

Oil exploration and development activities along the migration route of the bowhead whale (e.g. Prudhoe Bay, Alaska USA) have raised concerns about exposure of this endangered whale to hydrocarbons as well as possible impacts to this species in the event of an oil spill. McFall et al. (1986) reported hydrocarbon concentrations in bowhead whales using a limited number of animals. However, very little research has been done to address hydrocarbons in various bowhead whale tissues (e.g. blood, liver, epidermis, etc.) or compartments (oral, stomach, lung, etc.), and the biochemical or histologic indicators of exposure or toxicoses. Fortunately, studies are underway to address this deficiency.

Organotins

There is growing concern of this organometallic compound in marine mammals and no data is available for bowhead whales.

CURSORY REVIEW OF METHODOLOGIES

The purpose of this manuscript does not include provision of details of sampling, chemical and statistical analyses, and associated methodologies. Citations are provided to guide readers to the most relevant published literature in the sections below.

Metal (element) analysis

Landed bowhead whales have been sampled for heavy metals analyses since 1984 to the present along the northern coast of Alaska, mostly in Barrow. An increasing number of animals are represented in the 1990's as compared to earlier sampling efforts. Descriptions of sampling and analyses are detailed in Bratton et al. (1997), Byrne et al. (1985), Krone et al. (1998), and Woshner et al. (2001A). For techniques used to microscopically visualize inorganic Hg using thin sections of tissue (autometallography) refer to Woshner et al. (2002).

Radio-isotope analyses

Bowhead whale skin (epidermis), blubber, muscle, liver and kidney were homogenized for direct gamma spectroscopy (see Cooper et al. 2000 for details). Following gamma counting, selected samples were further analyzed for alpha and beta emitters, specifically Sr-90, Pu-239,240 and Po-210 (see Cooper et al. 2000 for details).

Organochlorine contaminants analyses

Samples were analyzed for OCs and percent lipid following standard methods and quality assurance protocols at the Northwest Fisheries Science Center, Seattle Washington (Krahn, 1988; O'Hara et al., 1999) and Environment Canada, Burlington, Ontario (Hoekstra et al. 2002A, 2002B, 2002D, 2003A, 2003B, and 2003C). Halogenated dimethyl bipyrroles analytic measures are described in Tittlemier et al. (2002).

Petroleum hydrocarbons analyses

McFall et al. (1986) reported hydrocarbon concentrations in bowhead whales. More recent methods are based on Wetzel and Van Vleet (2003).

DISCUSSION OF HISTORIC AND CURRENT FINDINGS

Summary

We present information concerning contaminants in bowhead whales landed in northern Alaska as part of a subsistence hunt. The most remarkable observation is that these whales are much less contaminated than many other cetaceans with respect to metals (i.e. Hg), radionuclides, and organic contaminants (i.e. PCBs). As compared to terrestrial arctic wildlife, like caribou, the levels of Cs-137 are 100 to a 1,000 times lower in bowhead whale tissues. A similar trend was seen in studies conducted in Greenland with the terrestrial food chain showing higher concentrations of Cs-137 than marine animals (Dietz et al. 2000). Essential and non-essential elements analyzed in bowhead tissues were generally low from a toxicological perspective and many essential elements are present at adequate levels based on gross and histologic assessments of landed whales (important for animal health and human nutrition). The element of possible concern (minor) from the 12 elements studied to date in the bowhead whale appears to be Cd in the kidney and this is mostly from a human exposure perspective (subsistence use). Cadmium concentrations are elevated in tissues of many arctic Alaska wildlife species as compared to other wildlife species and domestic livestock (O'Hara and Fairbrother, 1996; Bratton et al., 1997; O'Hara et al., 2001; O'Hara et al. 2003A; Woshner et al. 2001A and 2001B; Krone et al., 1998). Thus, this renal cadmium issue is not unique to bowhead whales. Other metals and tissues (lung, ovaries and testes) are now being investigated. The OCs and human exposure via consumption of bowhead whale tissues is addressed in SC/56/E3. Woshner et al. (2002) compared tissular and cellular localization of Hg for bowhead whales and white whales. This technique visualized the Hg in beluga tissue sections but concentrations were low enough in bowheads to not be observed using this microscopic method. Histologic changes in the bowhead whale kidney that may be due to Cd is currently being investigated, however we need to rule out other causes such as normal aging changes.

Metals

Mercury and lead concentrations in bowhead whales are very low as compared to other marine mammals. Many of the essential elements are at expected concentrations and these ranges of values will be useful for future assessments of nutritional status. Bowhead whale liver and kidney Cd concentrations were higher as compared to some mammals (i.e., some domestic livestock). It is difficult to define a concentration of Cd in tissues that would be considered "elevated" since the "natural" (i.e., pre-industrial) background concentrations are unknown. The lack of pristine areas on the globe makes comparisons of true background levels to those found in potentially contaminated areas impossible (Muir et al., 1992). Interactions of metals in tissues and changes with age also must be taken into account when any comparisons are made (Muir et al., 1992). For example, Cd increases with age in most animals, as there is a limited rate of excretion from the body (Andersen and Hansen, 1982).

The levels of Cd reported by Krone et al. (1998) and Woshner et al. (2001A) are very similar to other marine mammals displaying no overt adverse health effects (consider the investigations of effects were likely cursory). However, Fujise et al. (1988) indicated that the kidney of the Dall's porpoise may show development of lesions at 20 ppm (w.w.). Bratton et al. (1997) and Woshner et al. (2001A) concluded that Cd is likely to have no, or a very minimal effect, on renal tissue or function of the bowhead whale. However, due to its complicated interaction with other elements (Zn, Cu, Fe, Se and so on) and the possibility of increased exposure we should develop a better understanding of the subcellular distribution and the systems (metallothionein or MTH) that help protect the organ and cell. MTH's are cysteine rich proteins that are involved in the homeostasis of Cu and Zn in the organism and are induced by the presence Cd and other metals. Concentrations of MTH's in marine mammals are higher than in terrestrial animals, thus they can possibly avoid nephrotoxic effects of elevated Cd concentrations through MTH induction and MTH binding (Das et al., 2000). Some of this work to quantify MTHs in the bowhead whale is underway using *in vitro* systems. Bowhead whale MTH has been sequenced and is similar to the mammalian form (SC/51/AS13) and further characterization addressing concentrations and distribution are needed. Selenium (Se) increased in parallel with Cd in bowhead whales (Bratton et al., 1997) and in some laboratory experiments Se has been determined to be protective of Cd toxicity (Caurant et al., 1994; Ridlington and Whanger, 1981). A histologic assessment is ongoing and renal fibrosis has been noted but may be a normal finding in the bowhead whale and may be an age-related change.

Many marine mammal species have been reported to have Cd residue levels at or above the proposed critical threshold (between 10 and 200.0 mg/kg, w.w.) including narwhal, white whales, minke whales, pilot whale and walrus (Wagemann et al., 1983, 1990; Honda et al., 1987; Caurant et al., 1993; Taylor et al., 1989; and Warburton and Seagers, 1993). These levels reported in the literature are comparable to levels reported here in bowhead whales.

Cadmium is more effective at accumulating in the baleen whales (via invertebrates; Honda et al., 1990) as compared to Hg and Se (via fish and some invertebrates; Friberg et al., 1986) in the toothed cetacean species. Arctic anthropogenic contamination can be by long range transport, and/or with major contributions from local sources as for the Kola Peninsula Cu-Ni smelters (Jaffe et al., 1995). Some of this pollution is quite visible in the form of Arctic haze for long range transport (Shaw, 1995; Ayotte et al., 1995; Kinloch et al., 1992). However, for inorganics some studies have indicated that local or marine sources contribute a high percentage of the body burden, or of that deposited, as compared to long-range transport (Muir et al. 1992). Natural sources of inorganics include erosion, fires, sediment disruption (biotic and abiotic), and other events thus releasing these elements into soil, water and air. Human sources can also contribute to this loading of inorganics and includes agricultural practices, mining, industrial activities (smelting, drilling, combustion, and so on), waste disposal, and others. Many contaminants are transported on particles and in aerosols and deposited during precipitation events (Bidleman et al., 1989) and are trapped and incorporated into the Arctic.

O'Shea and Brownell (1994) reviewed the literature for metals and baleen whales and concluded that the levels were low and of little concern, but they did not have access to health data (i.e., histology, clinical assessments) and the recent literature emphasizing Hg and Cd as elements of concern in some baleen whales (i.e., minke whales). Variations in levels of metals in cetaceans is dependent on the species, tissue sampled, portion of the tissue sampled (i.e. kidney medulla or cortex), age, location (geographic), predominant forage or prey; and other factors. These factors must be considered when making comparisons or interpreting potential health effects. Bratton et al. (1997) reported that a comparison of the available data showed that in general baleen whales have lower levels of metal residues than odontocetes, except for Cd. The order of highest to lowest levels in tissues of the bowhead was kidney > liver > muscle > blubber/visceral fat for Cd and is very similar to other cetaceans (Bratton et al., 1997).

Zinc, iron, selenium, and copper are essential elements and are required by mammals for numerous physiological processes and deficiency of an element can be debilitating, and on rare occasions lethal. Bowheads serve as a source of these nutrients for human residents of Alaska and Chukotka and this is reviewed in SC/56/E2. Copepods and euphausiids have Hg levels that are not considered elevated (Honda et al., 1983) and this may explain the low Hg concentrations in bowhead whales (mean in liver = 0.059 and kidney = 0.052 ppm (w.w.) and other mysticetes (Bratton et al., 1997; Woshner et al., 2001A). Toothed whales clearly have higher levels and for white whales the levels are much higher. The mean concentration of Se in bowhead whale was low compared to the other arctic

marine mammal species like the white whale and ringed seal (Bratton et al., 1997; Woshner et al., 2001A). Lead is not essential for any known biological process and deposition of Pb in the Arctic from increased anthropogenic activity has been documented (Ng and Patterson, 1981) but current levels do not appear to be at levels of concern. The levels of Pb were very low in all tissues of bowhead whales examined and are typically low for most cetaceans (Bratton et al., 1997; Woshner et al., 2001A).

Radionuclides

Concern about nuclear waste and propulsion system disposal by the FSU, and nuclear reprocessing plants at Sellafield (England) have heightened the awareness of radionuclide sources for the Arctic. Levels of radionuclides in tissues of bowhead whales were very low as compared to terrestrial species, like caribou (MacDonald et al., 1996; O'Hara et al., 2003A). Cs-137 was detected in many tissue types and was greatest in muscle and skin; intermediate levels in kidney and liver; and lowest in the blubber (Cooper et al., 2000). This is expected, as Cs-137 is well known to mimic potassium (K) and concentrates in tissues known to contain K (i.e. muscle) and to not concentrate in tissues typically low in K (i.e. bone). Data indicate that Sr-90, Pu-239/240, and Po-210 are at very low levels (in nearly all cases below detection levels) in bowhead whale tissues.

Biological processes can transfer radionuclides through the food web, and Pu has been shown to accumulate 100 times greater in benthic marine invertebrates as compared to free-swimming organisms, however, the concentrations appear to decrease significantly up the food chain (Baskaran et al., 1997). Thus, exposure via a single trophic transfer for Pu results in the highest exposure. The concentration factor derived for Cs-137 and Pu-239,240 was 3.2×10^2 and 2.7×10^4 , respectively for isopods and 1.4×10^4 and 6.0×10^4 , respectively for bivalves (Baskaran et al., 1997). The levels of radionuclides documented in bowhead whales confirm the lack of accumulation "up" the food chain (Efurd et al., 1997, Cooper et al., 2000). The anthropogenic radionuclide content of sediments collected in 1993 in the Beaufort Sea was predominately the result of the deposition of global fallout (Efurd et al., 1997) and would be a pathway of exposure to marine mammals of Alaska, western Canada and eastern Russia. Very little anthropogenic radioactivity was detected in bowhead whale samples of northwestern Alaska (Efurd et al., 1997; Cooper et al., 2000) and the concentrations were very low in the fish, birds and other mammals sampled from this region (Efurd et al., 1997; Cooper et al., 2000) and Greenland (Dietz et al., 2000).

Organochlorines (OCs)

Many OCs are transported on particles and in aerosols and deposited during precipitation events (e.g. Bidleman et al., 1989), and are trapped by the colder temperatures associated with the Arctic. These organic contaminants can be delivered in snow to the Arctic (Gregor and Gummer, 1989). The bowhead whale is well recognized for large stores of lipids, these depots are apparently not accumulating lipophilic agents at a significant rate or extent as compared to odontocetes of the same region (Krahn et al., 1999). This difference is most likely due to the trophic level each species occupies (Hoekstra et al., 2002C) where it was shown these bowhead whales biomagnify many OCs but to comparably lower resulting tissue residue concentrations. These OCs are well known for their lipophilicity and ability to biomagnify. Variability in pollutant levels is a result of diet, body size, body composition, nutritive (body) condition, disease, age, reproductive stage (mature, immature, gestation, lactation) and other factors (IWC 1995). We also include spatial and temporal distribution and changes in technology (new analytical techniques, better sample collection, etc.) as important. These many factors must be taken into account when designing monitoring programs, study designs or experiments, interpreting data, comparing populations or species, and other types of studies addressing the OCs. Many of these factors have been recently investigated for the bowhead whale of the Bering, Chukchi and Beaufort seas. Most OCs are anthropogenic but some halogenated organics are considered natural and have been found in bowhead whales including the halogenated dimethyl bipyrroles (Tittlemier et al., 2002).

Not surprisingly, many OCs concentrations were greater with increasing size (age) for bowhead males while females showed no change or decreases in OCs concentrations with increasing body size (O'Hara et al., 1999). Across the North American Arctic, Hoekstra et al. (2002A) described spatial trends and bioaccumulation of OCs in marine zooplankton. The water and zooplankton were significantly higher in OCs for the eastern regions of North America. This indicates concentrations of OCs in bowhead prey vary by region. From these data, Hoekstra et al. (2002B) described the biomagnification of these OCs in bowheads sampled in northern Alaska which indicated a range of biomagnification factors (BMFs) from 0.1 – 57.7 for the OCs studied. Clearly, some OCs are not magnified (<1.0), and others are magnified or produced (bowhead whale generates and accumulates some metabolites of OCs) as

indicated by BMFs >1.0. Assessment of the PCB congener profiles and OCs metabolites can provide some information on the metabolic or biontransformation potential of the bowhead whale but is a very indirect measure of these systems (i.e., cytochrome P450 isozymes). These data provide a very general description of the “bioprocessing” of OCs by the bowhead whales.

More detailed studies were conducted to further the understanding of bioprocessing of OCs and these utilized techniques measuring enantiomers of chiral OCs, and the OCs metabolites formed. Hoekstra et al. (2002D) reported enantiomer-specific accumulation of PCB atropisomers in the bowhead whale that indicates the biological processing is more complicated and highly selective. Even more revealing was the fact that reproductive status (i.e., sexual maturation) may affect these enantiomer selective processes, as PCB91 was racemic in male whales <12 meters while it was non-racemic in male whales > 12 meters. This phenomenon was not unique to the PCBs and bowhead whales as Hoekstra et al. (2003A) demonstrated enantiomer-specific biomagnification of α -hexachlorocyclohexane (α -HCH) and selected chiral chlordane-related compounds in an arctic marine food web that includes the bowhead whale. These “isomer” based studies indicate that biomolecules (receptors, enzymes, binding proteins, etc.) are interacting to affect the actual concentration and profile (relative proportions of congeners, isomers, etc.) of some OCs and that this is not simply a chemical and physical partitioning based on lipid content. Further evidence of cytochrome P450 activity and other biotransformation functions affecting the OCs in bowhead whales is supported by the presence of hydroxylated and methylsulfone-containing metabolites of PCBs in the plasma and blubber of bowhead whales (Hoekstra et al., 2003C). It is clear that complicated molecular interactions are occurring in the bowhead whale to alter the distribution and structure of many OCs in a very specific manner. Thus, these chemicals are not inert and the whales are responding to them. At these concentrations we do not suspect any adverse effects; however we must conclude that the bowhead whale is responding to these xenobiotics. We discuss the implications of these findings in the “Future Directions” section.

These molecular changes described above significantly alter the toxicokinetics and toxicodynamics of these “metabolized” or biotransformed OCs. Some of these altered OCs may have high affinities (protein binding) for tissues that are not typically thought to be contaminated with OCs, including lung, kidney, intestine, uterine fluids (uteroglobin), and adrenal cortex (which may lead to disruption of glucocorticoid synthesis and a resultant adrenocortical hyperplasia). These systems may be affected due to their cytochrome P450 and/or steroidal binding proteins (including enzymes) that act as high affinity receptors for the OC metabolite ligands. This also implicates these sites as target organs and effects in these tissues or systems have been documented (Bakke et al., 1995), but not in bowhead whales. As endocrine disruptors some members of this OCs class have been implicated in affecting sexual or gonadal development, as early as *in utero*. This is why the observed change in the racemic nature of PCB91 in older male whales is such an important observation. Therefore, we should mention the documentation of true hermaphroditism in the white whale (De Guise et al., 1994) and pseudohermaphroditism in the bowhead whale (Tarpley et al., 1995; O’Hara et al., 2002). However, there is no cause-effect implicated. To our knowledge no published scientifically designed experiment or research has been conducted to assess this potential reproductive or endocrine dysfunction in cetaceans under controlled conditions.

Petroleum hydrocarbons

McFall et al. (1986) reported hydrocarbon concentrations in bowhead whales using a limited number of animals. Very little has been done to address these hydrocarbons in bowhead whale tissues, including measures of hydrocarbons in various tissues (blood, liver, epidermis, etc.) or compartments (oral, stomach, lung, etc.), and the biochemical or histologic indicators of exposure or toxicoses. Fortunately, studies are currently underway to address this information deficiency.

Preliminary data of a more recent study indicates that petroleum hydrocarbons occur at very low concentrations in bowhead tissues, and for many samples were below the level of detection.

Conclusion for historic and current findings

In conclusion, bowhead whales generally have low concentrations of metals, persistent organochlorines, radionuclides, and petroleum hydrocarbons. Radionuclide levels are very low and the major source appears to be global fallout from nuclear weapons testing. It is obvious that anthropogenic activities are influencing tissue composition of this large baleen whale of the Arctic as evidenced by the presence of “man-made” chemicals in the form of pesticides, industrial organochlorines, and certain radioactivity. It is also obvious that bioprocessing of the

OCs is more complicated than originally indicated and a better understanding of the molecular interactions (receptors, enzymes, binding proteins) is needed. The lack of data concerning petroleum hydrocarbons is a concern and recent efforts should begin to fill this data void. From a management perspective efforts should be made to limit the transport of these environmental contaminants (i.e., PCBs, Hg, Cd) to the Arctic and subsequent contamination of the biota. Residents and representatives of the Arctic region have used the above data and been active in policy making to ban or significantly limit some OCs (i.e., the “dirty dozen”) use around the globe. These types of efforts will need to continue so as to limit the inputs of other OCs, mercury and other elements to the arctic food web.

DISCUSSION OF FUTURE DIRECTIONS

In general, the utility of the bowhead whale for monitoring the arctic marine environment has been reviewed here and efforts to continue these studies should be encouraged at the international and national levels. The chemical composition of the tissues of these whales is very informative with respect to feeding ecology, distribution, marine contamination, and health measures (animal and human). Physiologically, much concern has been expressed about endocrine and reproductive disruption in marine mammals (polar bears, North Atlantic right whales) and data presented here indicates that bowhead whales are selectively accumulating some OCs and that sexual maturation may alter the accumulation pattern. It is unlikely these contaminants are adversely affecting the bowhead whale, but it is clear the whale is very specifically responding to the presence of these OCs and that this may depend on the reproductive status of the animal. This is very important information for other more highly contaminated marine mammals (cetaceans in particular) and understanding potential impacts. Data presented here are very useful for managing global industries so as to lessen the inputs of certain contaminants that travel great distances. Many anthropogenic contaminants have been identified in bowhead whale tissues indicating distant sources are reaching the Arctic. Many more chemicals require assessment, especially the many halogenated organics (fluorinated, brominated), so as to limit the contamination of polar marine environments. Biomarker research is underway in the bowhead whale and should prove quite useful in the general health assessment of this whale and specifically address some affects of contaminants in particular an oil release. Access to fresh samples of a large mysticete is rare and this opportunity could assist in development of assays to evaluate highly endangered species such as the North Atlantic right whale. Below we provide some specific examples for the classes of chemicals discussed in this paper and where research may head.

Organochlorines

Research addressing the OCs will likely continue in the form of temporal (trend) monitoring and will possibly be conducted via the Alaska Marine Mammal Tissue Archival Project (AMMTAP). With the development of cell cultures and other *in vitro* techniques the physiological responses to OCs may be better understood. For example, what biomolecules are responsible for the enantioselective accumulation and metabolite formation of OCs in bowheads and other marine mammals?

Elements

Some investigators have initiated studies challenging bowhead whale cell cultures with various elements (Wise et al., 2003A and 2003B). These studies compare the responses of the cells from the whale to more traditionally studied cellular models. These designs will help us better assess the relative sensitivity of the whale to metals and address the systems that are targets for toxicoses and those responsible for detoxification (e.g., MTH, glutathione). Preliminary data indicates that the cellular models used to date show that the bowhead whale is more sensitive than the Steller sea lion to select metals. The exact cell types and the responses being measured require more investigation to ascertain the exact meaning of this observation. We will continue to assess the role of Cd in whale health (i.e., observations of renal fibrosis) and as a source of a contaminant for human consumers of kidney.

Radionuclides

Considering the very low concentrations of radionuclides in bowhead whale tissues no further research has been conducted. Examination of bowhead whales may be warranted in a few years to assess trends over time and space or if a particular event (radionuclide release) increases concern in this region of the Arctic.

Hydrocarbons

This chemical class has become more of a concern with expanded offshore development within the bowhead whale habitat. It is critical to assess the current concentrations in whales and their prey, and establish baseline histological and biochemical biomarkers at the current exposure and for potential effects. In the event of a release of oil, the

impact on subsistence users should be estimated based on known avoidance due to off flavor, fear of contamination, and other reasons and what impact this would have on the whale hunting communities.

Physiologically-based toxicokinetics (PBTK)

This manuscript attempts to tie the various contaminants studies together that have been recently conducted on the bowhead whale. In no way is this a sophisticated synthesis of these findings. Recently, we proposed to undertake a physiologically based exploration of the toxicokinetics (movement of chemical in and out, and within, an organism) of the OCs. This will result in a model of the bowhead whale and the associated behavior of the OCs and the potential for adverse health effects. This model will force us to better understand biological and chemical interactions, and assist in identifying critical research needs (i.e., data gaps). If this effort proves successful then other chemicals could be addressed in this manner (i.e., cadmium).

Cell culture

The science of metals in the bowhead whale is evolving and has required a multidisciplinary approach to answer some of these basic questions. Metals occur in inorganic and organic forms and this can significantly alter the behavior and toxicity of these elements. It is necessary to determine the physico-chemical form (i.e. speciation) of potential toxic levels of trace elements and the varying mechanisms of detoxification (IWC 1995). Simply measuring element concentrations in tissues certainly is not a rigorous assessment of the bowhead whale and metal biology. However, investigators are continuing this work and have included additional elements for analysis (Co, Cr, Ag, Mn, Mg), a histologic assessment (light microscopy, special staining, and electron microscopy), characterization of metallothionein RNA (Kaysen and Hammond, pers. comm.) and attempts at cell culture (T. Goodwin pers. comm., J. Wise). The combination of these efforts appears very promising. Cell culture is being used to study toxicant-induced DNA damage and repair as well (Wise et al., 2003A and 2003B).

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