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CONCENTRATIONS OF CHLORINATED HYDROCARBONS AND TRACE ELEMENTS IN MARINE MAMMAL TISSUES ARCHIVED IN THE U.S. NATIONAL BIOMONITORING SPECIMEN BANK

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Abstract. The U.S. National Biomonitoring Specimen Bank (NBSB) provides for the long term storage of well documented and preserved specimens representing several types of environmental matrices. A major part of this inventory consists of marine mammal tissues (e.g., blubber, liver, kidney, and muscle). Within the NBSB selected specimens are periodically analyzed for chlorinated hydrocarbons and trace elements. Although only 20% of the 560 marine mammal specimens in the NBSB have been analyzed, the database is of value in evaluating the stability of analytes and sample degradation during storage, for comparing with results from samples collected in the future for long-term monitoring, and for comparing with analytical results from other laboratories on samples collected at the same time for monitoring purposes. The NBSB analytical database contains results for 37 elements, many of which are not analyzed routinely by conventional analytical techniques used in monitoring programs, and the following organic compounds: selected PCB congeners, DDT compounds, α- and γ-HCH, HCB, heptachlor epoxide, oxychlordane, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, and dieldrin in 9 marine mammal species: northern fur seal (*Callorhinus ursinus*), ringed seal (*Phoca hispida*), spotted seal (*P. largha*), bearded seal (*Erignathus barbatus*), pilot whale (*Globicephala melas*), harbor porpoise (*Phocoena phocoena*), white-sided dolphin (*Lagenorhynchus acutus*), beluga whale (*Delphinapterus leucas*), and bowhead whale (*Balaena mysticetus*). Analyses of beluga whale blubber for toxaphene and additional chlorinated hydrocarbons are obtained through collaboration with the Department of Fisheries and Oceans Canada.

INTRODUCTION

Over the last two decades, environmental specimen banking has gained recognition internationally as an important component of long-term environmental monitoring. Specimen banking will enable future investigators to extend their research into the past, thereby increasing their time-line of study. Specimen banking also provides specimens that may be used for future verification of analytical results, thus, contributing to the quality assurance of environmental monitoring data. The U.S. National Biomonitoring Specimen Bank (NBSB) was developed by and is maintained at the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland. This banking system is the direct result of a pilot Environmental Specimen Bank Program initiated in 1979 by the NIST in cooperation with the U.S. Environmental Protection Agency (U.S. EPA) to determine the feasibility of long-term storage of environmental samples [1]. The specimen type selected for this pilot program was human liver tissue. The NBSB provides for the long-term storage of well documented and preserved specimens that represent several different types of environmental matrices [2].

The largest portion of the NBSB inventory comes from the marine ecosystem and a very important part of this inventory consists of tissue samples collected from marine mammals [3]. Tissues from marine mammals have been collected and banked in the NBSB since 1987 as a result of collaboration with several organizations, including the National Oceanic and Atmospheric Administration (NOAA), the U.S. Fish and Wildlife Service (USFWS), the New England Aquarium (Boston, Massachusetts), the Marine Mammal Center (Sausalito, California), the North Slope Borough Department of Wildlife Management (Barrow, Alaska), and the Natural Resources Department of Kawerak, Inc. (Nome, Alaska). Major financial support for the archival of marine mammal specimens at the NBSB has been provided by two programs, the Alaska Marine Mammal Tissue Archival Project (AMMTAP) and the Marine Mammal Health and Stranding Response Program (MMHSRP).

The AMMTAP began in 1987 as a collaboration between NIST and NOAA's National Ocean Service (NOS) with funding from the U.S. Department of the Interior, Minerals Management Service (MMS). The purpose of the AMMTAP is to collect and store for long time periods (decades) tissue samples collected from marine mammals in Alaska. Of principle interest are specimens from regions under consideration for offshore oil and gas development or coastal mining. The principle source of these specimens is from Alaska Native subsistence hunts, which allows for the collection of fresh specimens immediately following death of the animal. A detailed description of the AMMTAP has been published [4].

Primarily as a result of the 1987-88 mass mortality of bottlenose dolphins (*Tursiops truncatus*) on the east coast of the U.S. and the lack of baseline data on the levels of anthropogenic contaminants in marine mammals of the

U.S., the National Marine Mammal Tissue Bank (NMMTB) was established in 1989 at the NBSB in conjunction with NOAA's National Marine Fisheries Service, Office of Protected Resources. A protocol for the collection, preparation and storage of tissue samples for the NMMTB was based on protocols previously used for the AMMTAP; however, in the case of the former, sample sources were stranded animals and incidental catches of marine mammals during commercial fishing operations. To evaluate the practical aspects of employing the collection protocol for both incidental catches and strandings, a demonstration phase (Pilot Program) was initiated by NIST in 1990 through a collaboration with the New England Aquarium. Based on the results of this pilot program, the NMMTB Program was continued and expanded into other regions of the U.S. [5,6].

In 1992, principle management of the AMMTAP was transferred from NOS to NMFS, Office of Protected Resources, to be conducted as part of the NMMTB Program. Funding for the AMMTAP is now provided by the U.S. Geological Survey, Biological Resources Division. Based on legislation enacted in 1992, the NMMTB Program was expanded and directed toward facilitating the collection and dissemination of data on marine mammal health and health trends in marine mammal populations in the wild, correlating these trends with available data on physical, chemical, and biological environmental parameters, and coordinating effective responses to unusual marine mammal mortalities [6]. This program, now known as the Marine Mammal Health and Stranding Response Program (MMHSRP), is coordinated by the NMFS in cooperation with the USFWS. Specimen banking is one component of this larger program. The MMHSRP is focused on animal health assessment, real-time contaminant monitoring, tissue archival in the NBSB, response to marine mammal strandings and mass mortalities, quality assurance/quality control of analytical results, and establishment and management of a nationwide database on the health of marine mammal populations in the U.S. [7].

Real-time monitoring of environmental contaminants is usually a component of the research programs supporting specimen banking in the NBSB. The chemical analyses conducted by these programs (including the MMHSRP) are performed by other laboratories; however, NIST analyzes selected specimens from the NBSB in order to: (1) provide organic and inorganic data for evaluating the stability of analytes and sample degradation during storage; (2) compare with results from samples collected in the future for long-term monitoring; and (3) compare with analytical results from other laboratories on samples collected at the same time for monitoring purposes. The results of these analyses have been published in several agency reports and scientific journals. In this paper, we present an overview and summarize the results to date.

METHODS

Sample Collection and Archival

Samples of blubber, liver, kidney and muscle were collected using standard AMMTAP and NMMTB protocols designed to preserve sample integrity and minimize sample contamination from handling. Both the NMMTB and AMMTAP protocols have been published [6,8,9]. The sex of each animal was recorded and standard body measurements made. Standard body measurements included: standard length, axillary girth, weight (where practical) and blubber thickness. For cetaceans, fluke widths were also measured. For the polar bears, pinnipeds and odontocetes, teeth were collected for determining the ages of the animals and additional samples of liver and kidney were collected from all animals and provided to the Armed Forces Institute of Pathology for histology analysis and archival.

The collection of specimens for the NBSB is usually associated with other ongoing operations or research. All data and information collected by other researchers from animals sampled for the NBSB are included in the NBSB database. For example, the collection of tissues from stranded animals usually occurs as part of other activities associated with the stranding response, e.g., collection of tissues and fluids for viral screening, genetic research, and real-time contaminant analysis. In many cases complete necropsies are performed and the results included as part of the database for each specimen archived in the NBSB.

Sample Preparation

Each tissue sample to be analyzed was homogenized using a cryogenic procedure designed to reduce the likelihood of changes in sample composition due to thawing and re-freezing [10]. Subsamples of the tissue homogenate, a frozen (non-freeze dried) powder, were aliquoted into Teflon jars (10 mL) for storage until analyses are performed.

Organic Analysis

The organic contaminant data summarized in this paper were generated at NIST Analytical Chemistry Division and the Department of Fisheries and Oceans (DFO) Canada. The NIST methodology has been described in detail elsewhere [11-13]. Briefly, the blubber samples (2-3 g) were mixed with sodium sulfate and Soxhlet extracted using methylene chloride. The majority of lipids were removed by size exclusion chromatography (SEC) and then polychlorinated biphenyl (PCB) and pesticides fractions were isolated by normal-phase liquid chromatography (LC) on a semi-preparative-scale aminopropylsilane column. The fractions were analyzed by gas chromatography with electron capture detection (GC-ECD) using a 60 m x 0.25 mm i.d. 5% phenyl methylpolysiloxane capillary column with helium as the carrier gas. The samples that have concentrations reported for both PCB 66 and PCB 95 were also analyzed by GC-ECD using 50 m x 0.25 mm i.d. 5% phenyl methylpolysiloxane with 10% methyl-C-18 (C-18) column. The DFO procedures have been described in several publications [14-17]. Blubber samples (2-5 g) were mixed with sodium sulfate and extracted by ball-milling with hexane. Lipids were removed using SEC and three fractions were obtained using Florisil. The fractions were then analyzed by GC-ECD using the same type of column as employed by NIST. Toxaphene was quantified by DFO with a modification of previously published procedures [15,17]. Response factors for individual toxaphene peaks were calculated from weight percent of each peak in the total ion chromatogram of a toxaphene standard as determined by electron impact mass spectrometry on a GC-mass selective detector. Total toxaphene (s-Toxaphene) was the sum of the concentrations of 19 peaks [16].

Inorganic Analysis

Although trace element concentrations have been determined for liver, kidney and muscle, liver is the tissue that is routinely analyzed because it is the organ that reflects best the trace element status of the animal for a large number of elements. The NBSB employs several analytical procedures for the determination of trace elements involving collaboration between several investigators and organizations.

The principle approach uses instrumental neutron activation analysis (INAA), a multi-element analytical technique that provides data for a large number of trace elements using only a limited amount of a sample. INAA is routinely used to measure 37 elements in the NBSB specimens (Na, Mg, Al, Cl, K, Ca, Sc, V, Mn, Fe, Co, Cu, Zn, As Se, Br, Rb, Sr, Mo, Ag, Cd, Sn, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, Au, Hg, Th, and U). The INAA method has been previously described in detail [18-20].

In addition to INAA, other analytical techniques have been used to provide data on elements that are not routinely measured by INAA (e.g., Pb and Ni) and to provide quality control data for selected elements (Co, Cu, Zn, Cd, and Hg) by comparing data from two different analytical techniques. Analyses of Ni and Pb were performed at the Institute of Applied Physical Chemistry, Research Centre of Jülich, Germany, by differential pulse and square wave voltammetry using previously published procedures [21] after high pressure ashing digestion with nitric acid [22]. Mercury concentrations were also determined at the Research Centre of Jülich using cold vapor atomic absorption spectrometry (CVAAS) as described elsewhere [23,24].

RESULTS AND DISCUSSION

Species, number of individual animals, and collection locations for marine mammal specimens archived in the NBSB are presented in Table 1. Tissue specimens from 102 individual animals representing six species of cetaceans and 98 individuals representing nine species of pinnipeds are archived. Cetaceans include: bowhead whale (*Balaena mysticetus*), pilot whale (*Globicephela melas*), harbor porpoise (*Phocoena phocoena*), common dolphin (*Delphinus delphis*), white-sided dolphin (*Lagenorhynchus acutus*), and beluga whale (*Delphinapterus leucas*). Pinnipeds include: harbor seal (*Phoca vitulina*), ringed seal (*P. hispida*), spotted seal (*P. largha*), bearded seal (*Erignathus barbatus*), northern elephant seal (*Mirounga angustirostris*), Steller sea lion (*Eumetopias jubatus*), northern fur seal (*Callorhinus ursinus*), California sea lion (*Zalophus californianus*), and Pacific walrus (*Odobenus rosmarus rosmarus*). Specimens from four polar bears (*Ursus maritimus*) are also included in the collection.

An inventory of tissues collected from these 204 individual animals is presented in Table 2. Only a small part of this collection has been analyzed. Analyses of beluga whale tissues, which are of interest to both DFO Canada and this program, have been emphasized. Although the database on the banked specimens is still limited, some results have been previously published [11,12,18-20,24-27]. The following discussion summaries these results.

Comparison of Tissue Types

Schantz et al. (1993) compared concentration levels of 15 PCB congeners, DDT compounds (2,4'-DDE, 2,4'-DDD, 2,4'-DDT, 4,4'-DDE, 4,4'-DDD, and 4,4'-DDT), gamma-hexachlorocyclohexane (γ-HCH or lindane), heptachlor epoxide, cis-chlordane, trans-nonachlor, and dieldrin in several tissue types (blubber, liver, kidney, and muscle) banked from two pinniped species: northern fur seals and ringed seals. For both species, the highest concentrations of these compounds based on wet weight were found in the subcutaneous fat layer (blubber). Concentrations in blubber were at least an order of magnitude higher than those for the other three tissue types. For example, 4,4'-DDE concentrations in the fur seal blubber were 1050 - 1330 ng/g wet weight. For the liver, kidney, and muscle, the 4,4'-DDE concentrations were 37 - 85 ng/g, 34 - 187 ng/g, and 36 - 72 ng/g wet weight, respectively (Fig. 1). For the ringed seal blubber, 4,4'-DDE concentrations were 27 - 350 ng/g, while values for liver and kidney were 3.8 - 10 ng/g and 2.9 - 6.8 ng/g wet weight, respectively. When the concentration values are compared on an extractable fat basis, the concentrations in blubber were not necessarily the highest values for a particular animal. For example, 4,4'-DDE concentrations in blubber, liver, kidney, and muscle of the northern fur seals were 1204 - 1530 ng/g, 1194 - 2428 ng/g, 630 - 3895 ng/g, and 1440 - 2322 ng/g extractable fat, respectively (Fig. 1).

Table 1. Species, number of individual animals sampled, and sampling locations for marine mammal specimens archived in the NBSB.

Group	Species	Region	Geographic Location	Number of Individuals
Cetacea:	Bowhead whale (*Balaena mysticetus*)	Arctic	Barrow, Alaska	31
	Pilot whale (*Globicephala melas*)	North Atlantic	Massachusetts	9
		North Atlantic	Georges Bank Canyon	2
	Harbor porpoise (*Phocoena phocoena*)	North Atlantic	New England	9
		North Pacific	Washington	1
	White-sided dolphin (*Lagenorhynchus acutus*)	North Atlantic	Massachusetts	6
	Common dolphin (*Delphinus delphis*)	North Atlantic	Georges Bank Canyon	3
	Beluga whale (*Delphinapterus leucas*)	Arctic	Point Lay, Alaska	20
		Arctic	Point Hope, Alaska	4
		North Pacific	Cook Inlet, Alaska	17
Pinnipedia:	Harbor seal (*Phoca vitulina*)	North Pacific	Prince William Sound, Alaska	3
		North Pacific	Cook Inlet, Alaska	1
	Ringed seal (*P. hispida*)	Arctic	Barrow, Alaska	32
		Bering Sea	Nome, Alaska	16
	Bearded seal (*Erignathus barbatus*)	Arctic	Barrow, Alaska	2
		Bering Sea	Nome, Alaska	7
	Spotted seal (*P. largha*)	Bering Sea	Nome, Alaska	2
	Northern elephant seal (*Mirounga angustirostris*)	North Pacific	Cold Bay, Alaska	1
	Steller sea lion (*Eumetopias jubatus*)	North Pacific	Cook Inlet, Alaska	1
	Northern fur seal (*Callorhinus ursinus*)	North Pacific	St. Paul Island, Alaska	15
	California sea lion (*Zalophus californianus*)	North Pacific	Central California	4
	Pacific walrus (*Odobenus rosmarus rosmarus*)	Bering Sea	St. Lawrence Island, Alaska	8
		Bering Sea	Nome, Alaska	6
Fissipedia:	Polar bear (*Ursus maritimus*)	Arctic	Barrow, Alaska	4
TOTAL NUMBER OF ANIMALS				204

Table 2. Inventory of archived marine mammal tissue specimens that have been analyzed at NIST.

Species/Tissue Type	Specimens Archived	Samples Analyzed Organics	Inorganics
Pinnipedia:			
Harbor Seal (*Phoca vitulina*)			
Liver	4	-	-
Kidney	4	-	-
Blubber	4	-	-
Ringed Seal (*P. hispida*)			
Liver	45	4	13
Kidney	45	2	2
Blubber	48	4	-
Spotted Seal (*P. largha*)			
Liver	2	-	1
Kidney	2	-	-
Blubber	2	-	-
Bearded Seal (*Erignathus barbatus*)			
Liver	9	-	3
Kidney	8	-	-
Blubber	9	-	-
Elephant Seal (*Mirounga angustirostris*)			
Liver	1	-	-
Kidney	1	-	-
Blubber	1	-	-
Steller Sea Lion (*Eumatopias jubatus*)			
Liver	1	-	-
Kidney	1	-	-
Blubber	1	-	-
Northern Fur Seal (*Callorhinus ursinus*)			
Liver	15	2	2
Kidney	15	2	2
Blubber	15	2	-
Muscle	5	2	2
California Sea Lion (*Zalophus californianus*)			
Liver	4	-	-
Kidney	4	-	-
Blubber	4	-	-
Muscle	1	-	-
Pacific Walrus (*Odobenus rosmarus rosmarus*)			
Liver	14	-	-
Kidney	14	-	-
Blubber	14	-	-
Total	293	18	25

Table 2. (Continued) Inventory of archived marine mammal tissue specimens that have been analyzed at NIST.

Species/Tissue Type	Specimens Archived	Samples Analyzed Organics	Samples Analyzed Inorganics
Cetacea:			
Bowhead Whale (*Balaena mysticetus*)			
Liver	27	-	3
Kidney	2	-	-
Blubber	31	1	-
Pilot Whale (*Globicephala melas*)			
Liver	11	-	9
Kidney	2	-	-
Blubber	11	7	-
Harbor Porpoise (*Phocoena phocoena*)			
Liver	10	-	6
Blubber	10	6	-
White Sided Dolphin (*Lagenorhynchus acutus*)			
Liver	6	-	4
Kidney	6	-	-
Blubber	6	1	-
Common Dolphin (*Delphinus delphis*)			
Liver	3	-	-
Kidney	3	-	-
Blubber	3	-	-
Beluga Whale (*Delphinapterus leucas*)			
Liver	38	-	15
Kidney	36	-	-
Blubber	39	17	-
Muscle	13	-	-
Total	257	32	37
Fissipedia:			
Polar Bear (*Ursus maritimus*)			
Liver	4	-	-
Kidney	4	-	-
Abdominal Adipose Tissue	2	-	-
Total	10	0	0
Grand Total	560	50	62

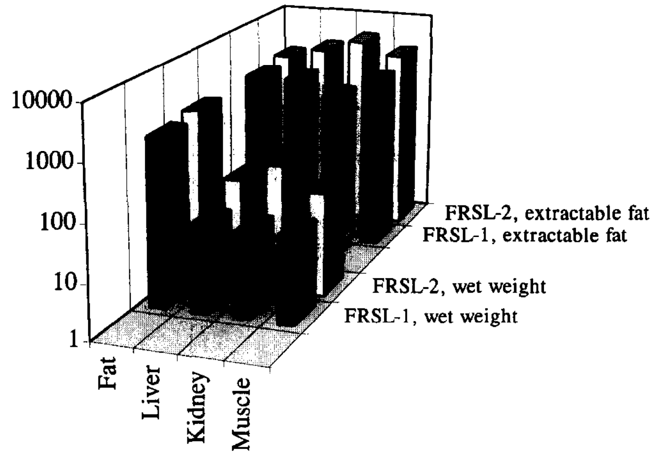

Fig. 1. Comparison of 4,4'-DDE concentrations in four tissue types of northern fur seal, *Callorhinus ursinus*, expressed as ng/g wet weights and ng/g extractable fat. The data are from Schantz et al. [12].

The northern fur seals had higher concentrations of organochlorines in their tissues than were found in the ringed seals, and the relative concentrations of each of the organochlorine compounds were consistent between tissue types: total DDT>total PCBs>trans-nonachlor>heptachlor epoxide>γ-HCH>dieldrin>cis-chlordane. However, this was not the case for the ringed seals; the relative concentrations of these compounds in the liver and kidney were not reflected in the blubber. These differences could be due to species-specific differences in the metabolism of these compounds, seasonal changes in stored fat, or more recent exposure of the ringed seals to organochlorine contaminants.

The concentration levels of 23 trace elements were determined for northern fur seal liver, kidney, and muscle tissue [25]. The concentrations of Mg, Al, Ca, Sc, Zn, Rb, Sb, and Cs were similar for all three tissue types, while other elements were present at substantially higher levels in one or two of the three tissue types. For example Hg, Se, V, I, Ag, Cu, Mn, and Fe levels were consistently higher in the liver and Cd was highest in kidney.

Establishing Baseline Concentration Levels of Contaminants in Banked Marine Mammal Specimens

Chlorinated Hydrocarbons. A summary of chlorinated hydrocarbon data generated on blubber specimens archived in the NBSB is presented in Tables 3 and 4. Both cetaceans from the North Atlantic Ocean, pilot whale and harbor porpoise, had higher concentrations of PCBs, DDT compounds, and cis-chlordane in their blubber than the animals sampled in Alaska (beluga whales, northern fur seals, and ringed seals). Of the six species listed in Table 3, the harbor porpoise had the highest levels of chlorinated hydrocarbons. Of the 33 congeners composing the "total PCB" (s-PCB), as identified in Table 3, the following (in descending order) had consistently the highest concentration values: 153, 138/163/164, 66, 95, 101/90, 187, 149, 180, 170/190, 118, 52, 44, and 105. Table 4 gives the range of values for each of these congeners found in the various species.

DDE is a metabolite of the parent compound DDT and the 4,4'-DDE isomer usually dominates the total DDE levels. Since DDE is relatively stable and tends to persist, it accumulates readily in vertebrate tissues. A large DDE/s-DDT value suggests that the DDT has been in the system for a relatively long time, while a small ratio suggest relatively recent exposure to the parent compound (discussed in more detail in Becker et al. [26]). In Table 5, the ratio of the concentrations of 4,4'-DDE to s-DDT in blubber specimens from the NBSB are compared to results reported for beluga whales from Canada [28] and western Greenland [17]. The ratios for male and female beluga whales from the same locations are similar and there appears to be little difference among locations. Ratios for the St. Lawrence belugas (considered to be highly contaminated with chlorinated hydrocarbons) are basically the same as those for the Arctic belugas in Greenland, Canada, and Alaska, and the ratio for the Cook Inlet belugas (a subarctic, isolated population in Alaska) is also similar. The two open-ocean northern fur seals analyzed by NIST have ratios approaching 1, as do the two ringed seals from Barrow, Alaska, while the ratios for the ringed seals from Nome, Alaska, (Bering Sea) varied more widely. Additional analyses of ringed seal specimens are necessary to determine if the regional differences suggested by the preliminary data for these animals are significant and consistent.

As part of an effort to determine the circumpolar baseline concentration levels of chlorinated hydrocarbons in the beluga whales, samples of blubber are routinely provided to the DFO Canada for analysis. Within the NBSB specimens, the beluga whale is the marine mammal species for which the largest database on PCBs and chlorinated pesticides exists. Blubber samples from three beluga whale populations sampled in Alaska at Point Lay (1989), Point Hope (1990), and in Cook Inlet (1992-95) were analyzed by both NIST and DFO. The results of analyses for 85 PCB congeners and 35 pesticide compounds, including 4 chlorobenzenes, 3 HCH isomers, 15 chlordane compounds, 6 DDT compounds, mirex, dieldrin, and toxaphene have been reported for the Point

Table 3. Concentration ranges and mean ± standard deviation values (ng/g wet weight) of chlorinated hydrocarbons in fat tissue (blubber) of marine mammals from the NBSB.

	Pilot Whale (North Atlantic) n = 7	Harbor Porpoise (North Atlantic) n = 5	Beluga Whale (Arctic) n = 12	Beluga Whale (Cook Inlet) n = 12	Northern Fur Seal (North Pacific) n = 2	Ringed Seal (Arctic) n = 4
s-PCB[a]	2030 - 17200 7900 ± 5330	7420 - 22600 14800 ± 6200	648 - 5230 3670 ± 1380	267 - 1920 977 ± 484	275 - 590 432	371 - 686 540 ± 170
s-DDT[b]	1708 - 13035 7748 ± 4701	4690 - 11200 7280 ± 2870	332 - 3820 2492 ± 1120	133 - 2350 1050 ± 658	1090 - 1480 1280	35 - 1430 543 ± 608
4,4'-DDE	942 - 7118 3847 ± 2128	1880 - 4900 3260 ± 1250	142 - 2230 1415 ± 679	65.9 - 1630 624 ± 484	1050 - 1330 1190	27 - 350 198 ± 135
HCB	43 - 465 223 ± 179	223 - 1070 515 ± 353	81.9 - 952 700 ± 264	138 - 741 368 ± 212	na	125 - 156[c] 140
α-HCH	20 - 62.2 32.6 ± 14.0	232 - 708 406 ± 199	43.9 - 196 121 ± 47.7	26 - 246 91.2 ± 71.8	na	na
γ-HCH	3.42 - 20 7.86 ± 5.74	42.2 - 152 81.2 ± 41.8	11.5 - 95.9 49.7 ± 18.3	na	2.8 - 26 14.4	2.4 - 633 223 ± 293
cis-chlordane	68.3 - 366 223 ± 137	397 - 1640 822 ± 539	19 - 74.8 37.2 ± 15.8	5 - 77 22.5 ± 19.6	<1 - 4.3	0.7 - 103 34.5 ± 47.7
cis-nonachlor	39.3 - 125 82.2 ± 60.6	325 - 697 511 ± 263	37.2 - 232 149 ± 53.7	5 - 96 26.8 ± 30.9	na	na

Table 3. (continued) Concentration ranges and mean ± standard deviation values (ng/g wet weight) of chlorinated hydrocarbons in fat tissue (blubber) ofmarine mammals from the NBSB.

	Pilot Whale (North Atlantic) n = 7	Harbor Porpoise (North Atlantic) n = 5	Beluga Whale (Arctic) n = 12	Beluga Whale (Cook Inlet) n = 12	Northern Fur Seal (North Pacific) n = 2	Ringed Seal (Arctic) n = 4
trans-nonachlor	280 - 2420 1340 ± 901	1920 - 3420 2660 ± 558	176 - 1260 880 ± 310	32 - 326 190 ± 90.7	65 - 302 184	44 - 1220 412 ± 544
oxychlordane	26.7 - 270 143 ± 106	183 - 801 424 ± 228	32.3 - 536 385 ± 146	na	na	na
heptachlor epoxide	14.6 - 138 81.1 ± 48.8	196 - 564 304 ± 158	19.4 - 215 145 ± 51.3	1 - 68 20.8 ± 22.5	15 - 34 24.5	34 - 603 187 ± 278
dieldrin	56.8 - 604 262 ± 240	658 - 1450 963 ± 294	45.9 - 420 290 ± 106	11 - 181 105 ± 66.2	1.2 - 26 13.6	0.6 - 122 43.2 ± 53.8

[a]Sum of 33 congeners: 18, 28, 31, 44, 49, 52, 66, 87, 95, 99, 101/90, 105, 110/77, 118, 128, 138/163/164, 149, 151, 153, 156, 170/190, 180, 183, 187, 194, 195, 206, 209

[b]Sum of 2,4'-DDE; 4,4'-DDE; 2,4'-DDD; 4,4'-DDD; 2,4'-DDT; 4,4'-DDT

[c]n = 2

Table 4. Concentration ranges and mean ± standard deviation values (ng/g wet weight) of major PCB congeners in fat tissue (blubber) of marine mammals from the NBSB.

	Pilot Whale (North Atlantic) n = 7	Harbor Porpoise (North Atlantic) n = 5	Beluga Whale (Arctic) n = 12	Beluga Whale (Cook Inlet) n = 12	Northern Fur Seal (North Pacific) n = 2	Ringed Seal (Arctic) n = 4
44	17 - 188 84 ± 70.1	28.6 - 101 46.1 ± 30.9	6.6 - 78.1 45.6 ± 20.2	7.67 - 58.8 30.6 ± 13.6	<2 - 2.8	<3 - 10
52	43 - 982 377 ± 380	336 - 1541 739 ± 479	14.1 - 275 202 ± 77.7	21.5 - 146 76.5 ± 35.6	13 - 22 17.5	4 - 26 16.8 ± 10.2
66	27.5 - 404 174 ± 161	106 - 648 291 ± 212	27.7 - 355[a] 240 ± 94.6	12.8 - 75.9[a] 40.7 ± 17.8	30 - 111[a] 70.5	<3 - 38[a]
95	45.6 - 621 297 ± 239	291 - 1430 786 ± 429	[a]	[a]	[a]	[a]
99	38 - 1260 470 ± 488	180 - 1920 861 ± 698	29.1 - 313 196 ± 79.6	1.83 - 107 51.3 ± 31.5	na	na
101/90	43.9 - 1320 611 ± 519	217 - 907 591 ± 277	36.3 - 391 270 ± 105	20.1 - 222 109 ± 58.3	7.8 - 8.5 8.2	61 - 205 124 ± 71.4
105	22.6 - 397 150 ± 51	20.9 - 168 93 ± 59	11.3 - 88.7 46.4 ± 22	3.79 - 37.7 18.5 ± 9.56	15 - 19 17	11 - 35 19.5 ± 11.1
118	86.4 - 1256 502 ± 414	351 - 1010 710 ± 270	31.3 - 307 183 ± 82.3	6.09 - 104 51.1 ± 29.9	31 - 96 63.5	40 - 87 55.5 ± 21.9

Table 4. (continued) Concentration ranges and mean ± standard deviation values (ng/g wet weight) of major PCB congeners in fat tissue (blubber) of marine mammals from the NBSB.

	Pilot Whale (North Atlantic) n = 7	Harbor Porpoise (North Atlantic) n = 5	Beluga Whale (Arctic) n = 12	Beluga Whale (Cook Inlet) n = 12	Northern Fur Seal (North Pacific) n = 2	Ringed Seal (Arctic) n = 4
138/163/164	172 - 2600 1030 ± 821	1030 - 3770 2360 ± 1120	50.8 - 460[b] 309 ± 125	19.6 - 181 92.0 ± 50.4	18 - 92 55	61 - 133 87.8 ± 33.2
149	124 - 1210 545 ± 381	643 - 1890 1180 ± 533	55.7 - 400 235 ± 107	32.2 - 148 84.3 ±36.7	na	na
153	246 - 2670 1120 ± 820	1747 - 5600 3170 ± 1530	72.6 - 539 367 ± 145	27.7 - 229 118 ± 61.2	120 - 191 156	94 - 179 137 ± 43.7
180	270 - 1200 564 ± 301	450 - 2120 982 ± 663	34.4 - 139 92.2 ± 38.6	11.7 - 84.4 39.4 ± 23.4	1.5 - 38 17.2	14 - 36 21 ± 10.4
170/190	85.6 - 346 197 ± 88	156 - 953 354 ± 337	10.3 - 55.6[c] 33.9 ± 14	3.84 - 19.1[c] 10.8 ± 5.53	12 - 12 12	<4 - 12
187	232 - 1300 582 ± 353	446 - 2440 1174 ± 772	25.2 - 206 121 ± 57.2	12.6 - 70.6[d] 33.9 ± 17.5	<1 - <3[e]	11 - 15[e] 13.8 ± 1.9

[a]66/95
[b]138
[c]170
[d]187/182
[e]187/182/159

Table 5. Ratios of 4,4'-DDE to s-DDT in beluga whale blubber specimens banked in the NBSB as compared to ratios for this species in other areas of the Western Arctic. Values are mean ± one standard deviation.

Species	Location (Date)	Sex	Number of Animals	4,4'DDE/s-DDT	Reference
Beluga Whale	W. Greenland (1989-90)	M F	71 67	0.56 ± 0.05 0.52 ± 0.05	[17]
Beluga Whale	St. Lawrence (1986-87)	M F	4 5	0.66 ± 0.06 0.56 ± 0.09	[28]
Beluga Whale	Hudson Bay (1984-85)	M F	4 4	0.57 ± 0.04 0.57 ± 0.04	[28]
Beluga Whale	Jones Sound (1986)	M F	8 7	0.55 ± 0.04 0.56 ± 0.05	[28]
Beluga Whale	Beaufort Sea (1983, 1987)	M F	10 1	0.47 ± 0.15 0.50	[28]
<u>Specimens in the NBSB:</u>					
Beluga Whale	Beaufort Sea (1989)	F	2	0.53 ± 0.01	[11]
Beluga Whale	E. Chukchi Sea (1990)	M F	7 3	0.58 ± 0.02 0.48 ± 0.18	[11]
Beluga Whale	Cook Inlet (1992-95)	M F	7 5	0.57 ± 0.10 0.53 ± 0.09	NBSB (unpublished)
Ringed Seal	Barrow, Alaska	M	2	0.85 ± 0.10	[12]
Ringed Seal	Nome, Alaska	M	2	0.34 ± 0.25	[12]
N. Fur Seal	St. Paul I., Alaska	M	2	0.93 ± 0.06	[12]
Harbor Porpoise	N. Atlantic	M F	1 4	0.32 0.49 ± 0.06	NBSB (unpublished)
Pilot Whale	N. Atlantic	M F	1 6	0.35 0.58 ± 0.07	NBSB (unpublished)

Lay and Point Hope specimens [11]. Analyses of the majority of the Cook Inlet specimens have been completed recently, but have not yet been published. For comparison with previously published data generated by the use of electron-capture negative ion mass spectrometry, the sum of toxaphene was calculated using a single response factor based on the area of 19 peaks in the standard, and the same peaks in the sample as described by Muir et al. [16].

For the blubber specimens of the Alaska beluga whales, major PCB congeners in descending order of concentrations were 153, 138, 149, 118, 101, 99, 180, 187, 52, and 66/95. The PCB and DDT concentrations in the blubber of Alaska Arctic beluga whales are similar to those reported for beluga whales from the Canadian Arctic and western Greenland (<5 μg/g wet weight), narwhals (*Monodon monoceros*) and polar bears, but an order of magnitude lower than those reported from beluga whales from the St. Lawrence River estuary [11,29]. The levels of total chlordane and toxaphene in the Alaska belugas are similar to those reported for beluga whales and narwhals from the Canadian Arctic, beluga whales from western Greenland [17], and for polar bears from Canada [30], and the levels are the same order of magnitude as belugas from the St. Lawrence Estuary [29].

The relatively large contribution of chlordane and toxaphene has been reported for other Arctic animals and appears to be characteristic of North American Arctic ecosystems [16,29]. The ratios of s-chlordane and s-toxaphene to s-PCB for blubber specimens from beluga whales archived in the NBSB were compared to those reported from beluga whales from Arctic Canada, the St. Lawrence Estuary, and Western Greenland (Figs. 2 and 3). Both ratios for the animals from Point Lay (Eastern Chukchi Sea stock) and Point Hope, Alaska, (Beaufort Sea stock) were basically the same as that derived from data reported by Muir et al. [28] for beluga whales sampled at the mouth of the Mackenzie River in western Canada (also of the Beaufort Sea stock). Although the Arctic animals from Hudson Bay and Jones Sound had much higher s-chlordane:s-PCB ratios, beluga whales from western Greenland had ratios similar to belugas from the Eastern Chukchi Sea and Beaufort Sea stocks. The lowest ratios for both chlordane and toxaphene were observed for animals from the lower latitude of the St. Lawrence Estuary, reflecting the larger contribution of both of these compounds to the chlorinated hydrocarbon burden for the Arctic animals. Oxychlordane and trans-nonachlor contributed the most to the total chlordane concentration.

Chlorinated hydrocarbon levels for the Cook Inlet stock were generally lower than those reported for the Arctic belugas (Tables 3 and 4). This group, which represents an isolated population of this species, ranges in and around Cook Inlet, a major estuary of the Gulf of Alaska (North Pacific). The Cook Inlet animals are considered to be a reproductively isolated subarctic group and may therefore be exposed to different anthropogenic sources of organochlorines than the Eastern Chukchi and Beaufort Sea stocks.

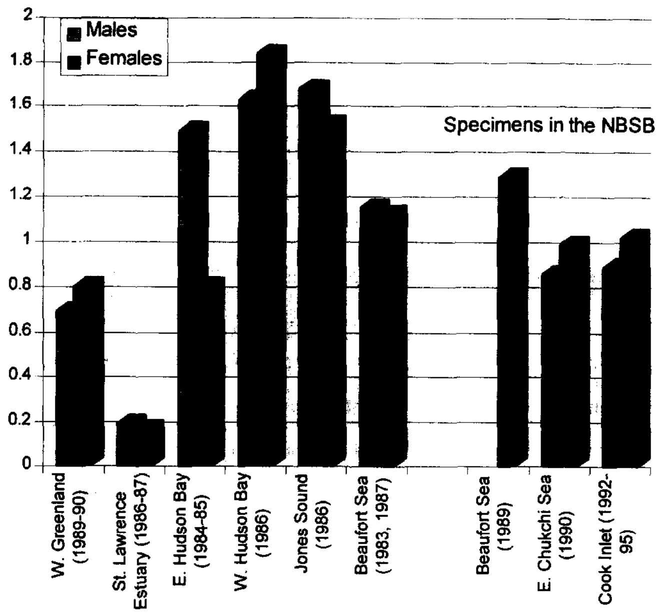

Fig. 2. Ratios of s-toxaphene to s-PCB in beluga whale blubber specimens banked in the NBSB as compared to ratios for this species in other areas of the Western Arctic. Values are derived by dividing the mean s-toxaphene values for each beluga stock by the mean s-PCB. The data are from Becker et al. [11], Muir et al. [28], Stern et al. [17], and NBSB (unpublished).

Toxaphene concentrations in the blubber of the Cook Inlet beluga whales were within the same range as concentrations in the Eastern Chukchi and Beaufort Sea animals. The range of values for the former population was 950 - 3360 ng/g wet weight, while those for the Beaufort Sea and Eastern Chukchi stocks were 1120 - 6620 ng/g and 500 - 5380 ng/g wet weight, respectively. The similarity of the toxaphene contribution to the chlorinated hydrocarbon burden of the Cook Inlet animals with toxaphene contribution to other beluga whale populations in Canada is suggested by the ratios of s-toxaphene:s-PCB shown in Fig. 2.

Unlike toxaphene, the concentrations of chlordane compounds in the Cook Inlet animals were substantially lower than levels found in the Arctic beluga whales sampled by the NBSB, as well as reported for Greenland animals [17] and the Canadian Arctic [28]. This is reflected in the ratios of s-chlordane:s-PCB shown in Fig. 3. The range of s-chlordane levels in the Cook Inlet animals was 160 - 640 ng/g wet weight, while those measured in the Beaufort Sea and Eastern Chukchi stocks were 440 - 2560 ng/g and 330 - 2420 ng/g, respectively.

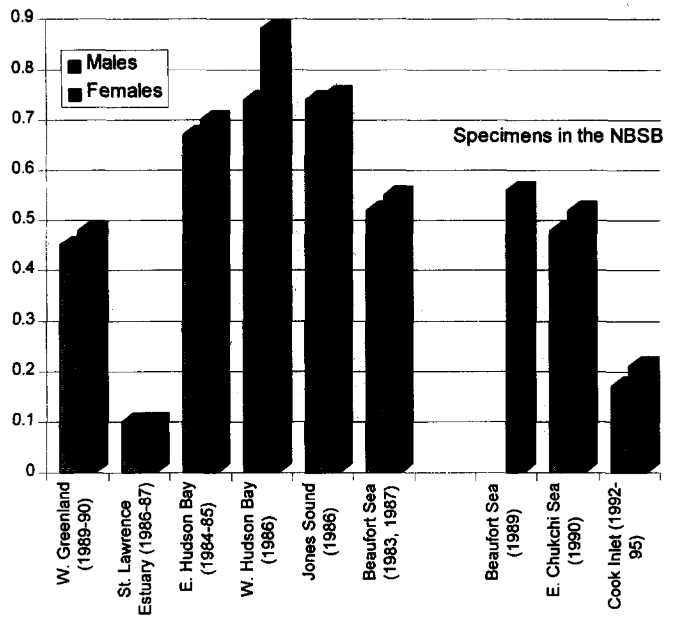

Fig. 3. Ratios of s-chlordane to s-PCB in beluga whale blubber specimens banked in the NBSB as compared to ratios for this species in other areas of the Western Arctic. Values are derived by dividing the mean s-chlordane values for each beluga stock by the mean s-PCB. The data are from Becker et al. [11], Muir et al. [28], Stern et al. [17], and NBSB (unpublished).

Trace Elements. For many of the trace elements in marine mammal tissues, little is known of what concentrations are within the normal ranges for a particular species. Many researchers analyze tissues for a few essential elements, such as Zn, Cu, or Se, and/or for potentially toxic elements, such as Cd, Hg, or Pb. The use of INAA typically provides data for 30 to 40 elements, many of which are not routinely measured by researchers using more conventional analytical methods. Concentrations for 30 - 40 elements were determined using INAA in liver tissues from 9 pilot whales, 6 harbor porpoises, 4 white-sided dolphins [20]; 15 beluga whales, 13 ringed seals, 3 bearded seals, 3 bowhead whales [11]; and 2 northern fur seals [24]. The concentration ranges, mean values, and standard deviations for selected elements in the livers of the eight species are presented in Tables 6 and 7.

Concentrations of K, Cl, Na, Mg, Ca, Br, and Rb in liver tissues are generally consistent from animal to animal and from species to species. The relative standard deviations of the mean values for these elements range from 5 to 25 percent. The biological half-lives for most of these elements are relatively short, so that one would not

Table 6. Concentration ranges and mean ± standard deviation values (μg/g of wet weight) of trace elements in liver tissues of marine mammals from the NBSB.

	Pilot Whale *(Globicephala melas)* *n = 9*	*Harbor Porpoise* *(Phocoena phocoena)* *n = 6*	*White-Sided Dolphin* *(Lagenorhynchus acutus)* *n = 4*	*Beluga whale* *(Delphinapterus leucas)* *n = 15*	*Ringed Seal* *(Phoca hispada)* *n = 13*	*Bowhead Whale* *(Balaena mysticetus)* n = 3
Na	1260 - 1620 1480 ± 152	1200 - 1700 1430 ± 167	1110 - 1260 1190 ± 65	961 - 1580 1320 ± 192	699 - 1030 863 ± 84	1030 - 1660 1420 ± 306
Mg	81 - 150 120 ± 24	128 - 267 204 ± 51	134 - 162 148 ± 14	58 - 219 133 ± 40	163 - 330 235 ± 38	63 - 127 97 ± 30
Cl	1630 - 2230 1810 ± 196	1590 - 2030 1810 ± 1820	1360 - 1530 1470 ± 80	1380 - 1910 1700± 187	733 - 1220 1020 ± 138	1560 - 1960 1810 ± 191
K	1640 - 2640 2190 ± 306	2130 - 3310 2680 ± 458	2770 - 3150 2900 ± 176	2210 - 2700 2430 ± 184	2610 - 3390 3050 ± 238	1910 - 2800 2180 ± 478
Ca	24 - 68 48 ± 12	29.7 - 63.3 48.8 ± 12	41 - 58 50.5 ± 7	19 - 44 31.6 ± 8.6	30 - 60 43 ± 9	20.5 - 44.5 32.5 ± 14
V	≤0.01 (ND)[a] - 0.02 0.02 (n=2)	≤0.01 (ND) - 0.02 n = 1, 0.02	≤0.01 (ND) - 0.06 n = 1, 0.06	0.034 - 0.28 0.128 ± 0.078	0.019 - 0.472 0.221 ± 0.141	0.084 - 1.23 0.696 ± 0.518
Mn	1.78 - 2.98 2.45 ± 0.41	2.68 - 5.15 4.49 ± 0.93	3.1 - 4.1 3.7 ± 0.5	1.62 - 3.36 2.21 ± 0.59	2.94 - 6.07 4.24 ± 0.92	0.88 - 1.14 1.02 ± 0.127
Fe	144 - 806 388 ± 209	226 - 562 388 ± 116	66 - 297 179 ± 100	332 - 781 555 ± 131	208 - 5210 1380 ± 1660	172 - 694 419 ± 234
Co	0.007 - 0.015 0.012 ± 0.003	0.004 - 0.010 0.006 ± 0.002	0.010 - 0.0160 0.013 ± 0.003	0.008 - 0.021 0.013 ± 0.004	0.013 - 0.123 0.041 ± 0.028	0.012 - 0.040 0.028 ± 0.015
Cu	1.13 - 3.8 2.83 ± 0.81	3.84 - 15.3 8.87 ± 3.97	3.18 - 8.06 6.33 ± 2.15	6.89 - 54.1 17.2 ± 13.3	6.47 - 45.17 14.3 ± 10.7	2.3 - 4.1 3.18 ± 1.24

Table 6. (Continued) Concentration ranges and mean ± standard deviation values (μg/g of wet weight) of trace elements in liver tissues of marine mammals from the NBSB.

	Pilot Whale (Globicephala melas) n = 9	*Harbor Porpoise (Phocoena phocoena) n = 6*	*White-Sided Dolphin (Lagenorhynchus acutus) n = 4*	*Beluga whale (Delphinapterus leucas) n = 15*	*Ringed Seal (Phoca hispada) n = 13*	*Bowhead Whale (Balaena mysticetus)* n = 3
Zn	28.3 - 51.1 38.2 ± 7.65	25.3 - 38.2 28.4 ± 4.9	30.9 - 50.7 41.6 ± 9.9	20.9 - 38.5 26.0 ± 4.9	27.7 - 114 50.6 ± 23.4	19 - 33 28 ± 8
As	≤0.4 (ND) - 1.17 0.45 ± 0.33	0.18 - 0.58 0.34 ± 0.13	0.179 - 0.415 0.297 ± 0.105	0.05 - 0.62 0.196 ± 0.155	0.165 - 2.42 1.03 ± 0.722	≤0.04 (ND) - 0.34 0.332 ± 0.011, n=2
Se	1.59 - 28.5 12.8 ± 9.2	1.11 - 4.23 2.04 ± 1.19	2.22 - 9.05 5.31 ± 2.98	3.5 - 75.5 18.5 ± 17.8	1.19 - 5.67 2.95 ± 1.46	0.46 - 1.19 0.91 ± 0.40
Br	NA[b]	11.75 - 16.38; n = 4 14.1 ± 2.1; n = 4	12.4 - 16.6 14.0 ± 1.8	17.2 - 35.6 22.2 ± 4.6	9.2 - 34 16.3 ± 6.7	21.1 - 23.1 22 ± 1
Rb	1.44 - 2.1 1.89 ± 0.2	1.04 - 1.73 1.38 ± 0.28	≤1 (ND) - 2.7 n = 1, 2.7	≤1 (ND) - 1.7 1.36 ± 0.03; n = 7	1.64 - 3.52 2.66 ± 0.52	1.48 - 2.55 2.11 ± 0.56
Ag	0.013 - 0.333 0.16 ± 0.11	0.148 - 0.757 0.398 ± 0.256	0.27 - 1.50 0.75 ± 0.53	10.0 - 107 26.2 ± 24.4	0.0145 - 0.228 0.102 ± 0.066	0.010 - 0.050 0.027 ± 0.020
Cd	2.78 - 14.28 8.48 ± 3.14	≤0.4 (ND) - 0.51 n = 1, 0.51	0.24 - 0.886 0.42 ± 0.29	≤0.7 (ND) - 3.65 2.10 ± 1.01; n = 9	1.16 - 8.79;n=10 3.22 ± 2.46	≤0.3 (ND) - 19.7 19.2 ± 0.7; n=2
Cs	≤0.002(ND)-0.010 0.006 ± 0.002	0.033 - 0.050 0.11 - 0.019	0.027 - 0.042 0.032 ± 0.006	0.021 - 0.046 0.031 ± 0.006	0.0045 - 0.0478 0.0203 ± 0.0142	0.003 - 0.010 0.006 ± 0.004
Hg	1 - 83 43.2 ± 36.4	2.19 - 43.4, n = 3 28.1 ± 22.5; n = 3	1.01 - 22.8 9.06 ± 12.0	1.4 - 73 28.0 ± 27.6	0.446 - 5.181 1.93 ± 2.18	0.295; n=1 0.15

[a]ND indicates that the levels are below the detection limit; quantitative determination was not possible.

[b]NA indicates that analyses were not performed.

Table 7. Concentration ranges and mean ± standard deviation values (μg/g of wet weight) of trace elements in liver tissues of marine mammals from the NBSB.

	Bearded Seal (Erignathus barbatus) n = 3	*Northern Fur Seal (Callorhinus ursinus) n = 2*	*Spotted Seal (Phoca largha) n = 1*
Na	794 - 1370 1060 ± 290	700, 760	973
Mg	166 - 232 209 ± 37	213, 194	240
Cl	733 - 1380 1090 ± 327	891, 1020	1230
K	2200 - 3130 2790 ± 510	3160, 3320	2940
Ca	49.5 - 52 51 ± 2	31, 38	50
V	0.15 - 1.04 0.478 ± 0.487	0.11, 0.08	0.072
Mn	3.1 - 7.2 4.83 ± 2.10	3.2, 4.2	5.55
Fe	228 - 1270 584 ± 594	114, 172	1418
Co	0.05 - 0.11 0.087 ± 0.030	0.015, 0.017	0.0578
Cu	9.64 - 33.3 18 ± 14	15, 55	27
Zn	33 - 102 59 ± 37	56, 58	65.3
As	0.17 - 0.56 0.40 ± 0.20	0.2, ≤0.1	0.35
Se	0.43 - 5.30 2.35 ± 2.60	5.2, 6.3	1.37
Br	14.4 - 18.4 16.4 ± 2.0	Na[b]	14.2
Rb	≤3 - 2 2.00 ± 0.05	1.68, 1.87	3
Ag	0.075 - 0.172 0.114 ± 0.051	0.36, 0.17	0.21

Table 7. (Continued) Concentration ranges and mean ± standard deviation values (μg/g of wet weight) of trace elements in liver tissues of marine mammals from the NBSB.

	Bearded Seal (Erignathus barbatus) n = 3	*Northern Fur Seal (Callorhinus ursinus) n = 2*	*Spotted Seal (Phoca largha) n = 1*
Cd	≤0.1 (ND) - 2.04 1.51 ± 0.75; n=2	7.7, 17.7	≤0.6 (ND)
Cs	0.004 - 0.008 0.006 ± 0.003	0.023, 0.017	0.0023
Hg	0.295; n=1 0.15	1.72; n=1	NA[b]

[a]ND indicates that the levels are below the detection limit; quantitative determination was not possible.
[b]NA indicates that analyses were not performed.

expect to find much animal to animal variability. Concentrations of Cs vary much more from animal to animal than those of the other electrolytes. The variation for Cs may be due to Cs being much less abundant in the marine environment than other electrolytes and probably is not metabolically regulated.

Concentrations of the essential trace elements, such as Cu, Zn, and Se, are generally characterized by a relatively narrow range of values within a species and, for many elements, the ranges are similar from one species to another. The relative standard deviations for the mean values ranged from 15 to 45 percent within a species for all elements except Se, for which the relative standard deviations ranged from 50 to 70 percent. The relatively narrow range of values and similarity from species to species probably indicates that these elements are well regulated and may indicate relatively short biological half-lives. The wider range of values for Se is due to the accumulation of this trace element as the animal ages. Concentrations of Se are generally higher in the beluga whale and pilot whale livers than in the livers of any of the other species studied.

The nonessential, potentially toxic elements, such as As, Cd, and Hg, show the greatest variability with concentration ranges often spanning several orders of magnitude. These elements accumulate in liver tissue with age of the animal, so that the observed levels probably reflect the magnitude and duration of exposure to the element. Both Cd and Hg can occur in relatively high concentrations in the livers of marine mammals, depending upon the species and the type of prey they feed on. Although the livers of beluga whales had Cd concentrations at relatively low levels, their Hg levels were high. As a comparison, the bowhead whales were found to have very low Hg concentrations and relatively high Cd levels [20].

Three other elements show the same pattern of widely varying concentrations within and between species (i.e., V, Se, and Ag). The V levels in livers of the marine mammals from Alaska span three orders of magnitude with concentrations ranging from 0.02 μg/g to 1 μg/g wet weight (Fig. 4). Levels in the livers of mammals from the North Atlantic are generally near or below the detection limit. This appears to be a regional difference and is discussed in detail below. Many researchers have reported a positive correlation between hepatic Se and Hg concentrations for several different species of animals. Hepatic Se exhibits positive linear correlation with hepatic Hg for the NBSB marine mammals as well [19]. Although hepatic Cd has sometimes been reported as being positively correlated with Se in marine mammals, no such relationship has been found so far in the NBSB specimens.

For most of the marine mammal species in this study, Ag concentrations in livers are also correlated with Se and Hg. For example, whether using multiple regression, simple linear regression or Spearman's rank correlation, both Ag and total Hg have been reported to be strongly correlated with Se in the livers of beluga whales and pilot whales banked in the NBSB [18]. Selenium may have a role in the detoxification of Hg in the liver, either by association with the metal binding proteins or by directly binding to Hg. These correlations between hepatic Ag, Se, and Hg concentrations may also be simply an indication of accumulation of all three elements with age for the animal or may indicate that there exists a more direct biochemical relationship. Physiological mechanisms involving the interaction of Ag and Se have been shown for other species of mammals and may also function in these marine mammals. The possible biochemical relationships have been previously discussed in detail [18]. Silver concentrations generally range from 0.01μg/g to 0.1 μg/g wet weight in liver tissues of all of the marine mammals studied, with the exception of beluga whales. Levels in the liver tissues of the beluga whales are generally orders of magnitude greater than those found in other species, with concentrations ranging from 10 μg/g to 107 μg/g wet weight. The source or cause of these comparatively elevated levels of Ag in the beluga whale livers has not been identified.

Marine organisms generally have higher concentrations of As than terrestrial or freshwater organisms and the majority of the As is in organic form [31]. In marine fish, crustaceans, and molluscs this element occurs mainly as the non-toxic pentavalent organic compound, arsenobetaine. Hepatic As concentrations for the 12 ringed seals from the Norton Sound (Nome) were, on average, two to three times greater than the average concentrations found in this and other species from other locations in Alaska and elsewhere (Table 6). While the range of As values in livers of ringed seals from Nome (0.2 - 2.4 μg/g) overlaps the concentration range for the other species (0.1 - 1.2 μg/g), there were more values at the upper end of the range for these ringed seals with half of the values greater than 1 μg/g wet weight. Additional sampling of pinnipeds in Alaska will be required to determine if these apparently higher As levels in the Norton Sound ringed seals are statistically significant when compared to levels in other pinniped species in Norton Sound and in ringed seals from other regions of Alaska. Because total As was measured, it is not known what fraction, if any, occurs in the liver tissue as non-toxic arsenobetaine.

Hepatic Bioaccumulation of Trace Elements

Results of INAA of marine mammal liver tissues will be helpful in determining whether concentrations are increasing over time or whether bioaccumulation is occurring for a given species within a given organ. One measure of bioaccumulation is to determine whether concentrations increase with the age of the animal. Positive correlations with age were observed for Cd, V, Se, Ag, and Hg in livers of beluga whales [20]. These elements accumulate in beluga whale liver tissue with age. Because age information was not available for any of the other species, length was used as an indication of relative age of the animals. For some species, e.g., pilot whales [32] and beluga whales [33], there is a known relationship between the length and the age of the animal.

The elements for which there were positive correlations between hepatic concentrations and animal age or length are listed in Table 8. For several species, the number of animals for which data is available is still too few to determine whether the observed correlations are significant. However, it is clear that hepatic Hg, Se, and Ag increase over time for most of these mammals and that V concentrations increase with age for the Alaska marine mammals [20]. Bioaccumulation of V has also been reported in livers of harbor seals and grey seals (*Halichoerus grypus*) from the Swedish coast [34]. Hepatic levels of Cd were correlated with age or length only for the beluga whales and ringed seals [20].

Although uptake and bioaccumulation of Hg, Se, Ag, V, and Cd are determined by many factors, the diet of the animals probably plays a major role. The possible role of prey in the bioaccumulation of trace elements in these marine mammals has been previously discussed [18-20]; however, additional research is needed to determine whether the concentration levels found in the liver tissues for these marine mammals reflect levels that would be present naturally or whether the levels reflect the influence of anthropogenic inputs into the marine environment.

Table 8. Trace elements that accumulate in livers of marine mammals.

Species	Elements
Alaska:	
Beluga Whale (*Delphinapterus leucas*)	V, Se, Ag, Cd, Hg
Bowhead Whale (*Balaena mysticetus*)	V, Se, Ag, Hg
Ringed Seal (*Phoca hispida*)	V, Se, Cd, Hg
Bearded Seal (*Erignathus barbatus*)	V, Se, Ag
North Atlantic:	
Pilot Whale (*Globicephala melas*)	Se, Ag, Hg
Harbor Porpoise (*Phocoena phocoena*)	Se
White-Sided Dolphin (*Lagenorhynchus acutus*)	Hg

A Geographic Difference in Hepatic Trace Element Concentrations

A major difference between the trace element concentrations of the livers from the Alaskan animals as compared with those from the North Atlantic animals (i.e., pilot whales, harbor porpoises, and white-sided dolphins) is the level of V (Fig. 4). As mentioned previously, V is present at measurable levels in the livers of all of the Alaskan marine mammals, whereas for most of the North Atlantic animals, hepatic V concentrations are near or below the detection limit of 0.01 μg/g.

Vanadium concentrations in the liver of ringed seals, bowhead whales, and beluga whales varied widely with highest values found in livers of two of the bowhead whales (0.77 μg/g and 1.23 μg/g wet weight). For these three species, hepatic V concentrations were linearly correlated with age or size of the animal. However, these levels are similar to those reported for other Arctic species. Concentrations in the livers of pinnipeds from Swedish waters [34] were similar to those found in the beluga whales and ringed seals from the NBSB, while the NBSB bowhead whales and bearded seals had higher levels, from about 0.1 μg/g to 1 μg/g. Levels found in walrus livers [35] were generally higher than those in the NBSB tissues. An average of 0.07 μg/g wet weight of V in pooled polar bear liver samples from Canada [36] is similar to the lower end of the range found in the beluga whale liver tissues.

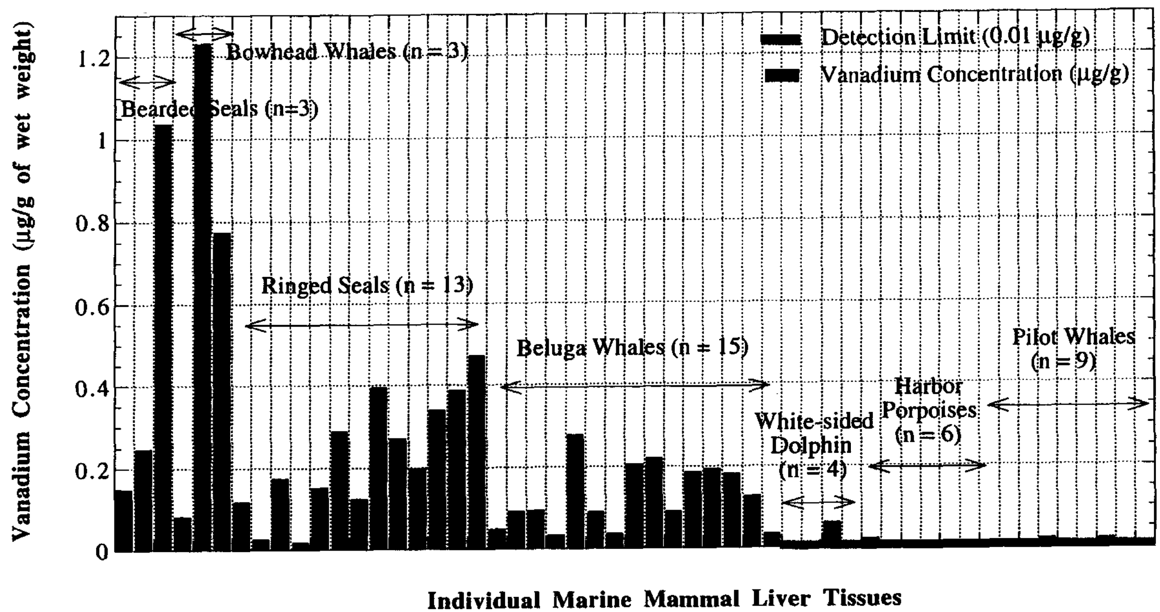

Fig. 4. Concentration of V in liver tissues of marine mammals specimens banked in the NBSB.

Available information suggests that certain lower trophic level taxa accumulate V in relatively high amounts and that this accumulation is reflected directly in concentration levels in the upper trophic levels of the food web [20]. Some species of ascidians contain very high concentrations of V. These organisms are common in the world's oceans, including the Arctic and, although little is presently known, they may be very important components in the Arctic marine food web. Vanadium is also used as an environmental indicator for the presence of crude oil. Crude oil contains V in varying concentrations, depending upon the geological source. Oil from Prudhoe Bay, the largest petroleum producing field in Alaska (located on the North Slope area of the Beaufort Sea) contains from 0.2 μg/g to 141 μg/g of V with a median value of 71 μg/g [37]. Oil production in various parts of Alaska has taken place since the turn of the century and 14 confirmed natural oil seepage sites have been found along the Alaska coast since that time [38]. It is possible that petroleum producing activities as well as natural oil seepages provide sources of additional V for the Alaska marine environment. Further research is needed to determine whether V levels in the Alaska marine environment and the food web are indeed greater than those found in the northeast Atlantic marine environment.

CONCLUSIONS

Of the 560 marine mammal tissue specimens archived in the NBSB over the last few years, only a small part of this collection has been analyzed. Although limited, this database has been used for NBSB program development and for determining baseline concentrations of trace elements and chlorinated hydrocarbons in the banked specimens. The banked marine mammal specimens are proving to be very useful in establishing a database on organic compounds and inorganic substances in animals from widely separate geographical areas. Many of these species feed at the same trophic level and occupy similar habitats, even though they occur in very different climatic regions. As the database continues to grow, it will provide a valuable resource for investigations of input of anthropogenic contaminants to the marine environment as well determining the "normal" levels of many naturally occurring, essential and nonessential (and sometimes toxic) elements.

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