

Temporal and Spatial Trends of Emerging and Legacy Contaminants from Samples Archived in the National Biomonitoring Specimen Bank

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Abstract

The National Biomonitoring Specimen Bank (NBSB) operated by the National Institute of Standards and Technology (NIST) contains several collections of marine mammal tissues and seabird eggs. Samples included in these collections have in many cases been taken from multiple locations and times allowing for temporal and spatial trends to be discerned. This paper provides an overview of several studies that have used marine mammal tissues or seabird eggs contained in the NBSB to examine for trends in either legacy pollutants such as DDT and PCBs or pollutants of emerging interest such as brominated flame retardants.

Introduction

The contamination of marine biota by persistent organic pollutants (POPs) was first documented at least 40 years ago [1]. Since these first reports, there has been an explosion of literature describing the concentrations of POPs in abiotic and biotic environmental samples. In many cases the documentation of POPs in biota, or the temporal trends of these compounds in biota, has led to that particular compound being phased out of production or banned through legislation. Many of the first studies examining temporal or spatial trends of contamination by POPs were done using abiotic samples such as peat cores or sediment cores. The extrapolation of these abiotic temporal trends to living organisms is somewhat tenuous due to process affecting the concentration of POPs in abiotic samples versus biological ones.

The systematic archival of environmental samples using an established protocol and controlled storage conditions provides a much better opportunity for the detection of environmental trends in biological samples. This was realized by a number of institutions and has led to the establishment of specimen banks by many countries (see Becker et al. this issue). In the United States, the NIST NBSB was established in 1979 with a major aim of collecting samples for the detection of environmental trends of contaminants [2]. This specimen bank is currently maintained at two locations; Gaithersburg, Maryland, and Charleston, South Carolina. The NBSB houses a number of collections including those from the Seabird Tissue Archival and Monitoring Project [3], The Alaska Marine Mammal Tissue Archival Project [4], and collections of marine mammal tissues obtained through the National Marine Mammal Stranding Network [5]. These samples provide a wealth of opportunity for the detection of environmental trends. This paper gives examples of how

results from the analyses of these collections have provided useful information on the temporal and spatial trends of both legacy POPs and POPs that have received more recent attention such as brominated flame retardants and perfluorinated substances.

Materials and Methods

The samples for this work originated from a variety of sources. Eggs of seabirds (common and thick-billed murres) were collected from sites in the Alaska Maritime Refuge by the a number of groups including subsistence collectors and the U.S. Fish and Wildlife Service and processed using an established protocol (e.g. [3]). Kidney and blubber samples were collected beluga whales and ringed seals through native subsistence hunts (e.g., [6]). Samples of California sea lion blubber, kidney and liver were collected with the aid of the Marine Mammal Center in Sausalito, California [7] and white-sided dolphin kidney, liver, and blubber samples were obtained with the assistance of the Cape Cod Stranding Network[8]. All samples were maintained at the NBSB in liquid nitrogen vapor freezers in a clean room environment [2].

Organochlorine and organobromine POPs were measured using several techniques. Ringed seal samples were extracted for the analysis of organochlorine compounds using either pressurized fluid extraction or by Soxhlet extraction, cleaned up by liquid chromatographic techniques and analyzed by gas chromatography electron-capture or mass spectrometry detection [9]. White-sided dolphin blubber samples were analyzed for organochlorine compounds and polybrominated diphenyl ether compounds by gas chromatography mass spectrometry as described previously [8]. Blubber and liver samples were further analyzed for hexabromocyclododecane (HBCD) stereo isomers by liquid chromatography tandem mass spectrometry (LC-MS/MS) [10]. Organotin compounds were analyzed in ringed seals and beluga whale liver and blubber samples by gas chromatography inductively coupled plasma mass spectrometry using a method described previously [11]. Methods for brominated flame retardant determination in sea lions are similar to those described above and are detailed in [7]. Perfluorinated compounds will be analyzed in the liver of beluga whales using a method under development that utilizes isotopically labeled internal standards, processed through Oasis WAX (Waters, Milford, Massachusetts) solid phase cartridges and then analyzed by LC-MS/MS.

Results and Discussion

The sets of samples and analytes examined are given in Table 1 along with accompanying references. For the PBDEs, temporal trends were not observed in the white-sided dolphin or the California sea lion contrary to other studies on PBDEs in marine mammals (e.g., [12]). HBCDs increased exponentially in California sea lion samples with time, while there was no trend observed as a function of time in white-sided dolphins. This suggests differences in exposure to HBCDs at different locations. Butyl tin concentrations increased with time in both beluga whales and ringed seals from 1988 to 1998. The reason for the increase in butyl tins with time is not clear. For seabird eggs collected from Alaska, differences in organochlorine compounds were observed between murre species inhabiting the same colony, suggesting differences in feeding ecology. For most organochlorines, concentrations were generally lower in eggs collected from colonies in the Bering/Chukchi Sea relative to those collected from the Gulf of Alaska. Current work is examining eggs collected more recently for POPs to examine for temporal trends. For ringed seals,

organohalogen compounds were generally higher in seals collected in Barrow, Alaska, than those collected from more southerly Nome, Alaska [9]. Work is currently underway to examine temporal trends of perfluorinated compounds in beluga whales archived in the NBSB.

Table 1. Species used for the evaluation of temporal or spatial trends of contaminants.

Species	Sampling Location	Analytes	References
Thick-billed murre	Bering/Chukchi Seas, Gulf of Alaska	Legacy organochlorines, butyl tins, brominated flame retardants	[3] [11]
Common murre	Bering/Chukchi Seas, Gulf of Alaska	Legacy organochlorines, butyl tins, brominated flame retardants	[3] [11]
California sea lion	Northern California	Brominated flame retardants	[13]
Ringed seal	Bering Sea/Chukchi Seas	Legacy organochlorines, butyl tins	[9] [11]
Beluga whale	Bering Sea/Chukchi Seas	Legacy organochlorines, butyl tins, perfluoro compounds	
White-sided dolphin	North East U.S.	Legacy organochlorines, brominated flame retardants	[8, 14]

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