A TWENTY YEAR (1987-2007) TREND OF PBDEs IN BELUGA FROM THE ST. LAWRENCE ESTUARY, CANADA

Lebeuf M[1], Trottier S[1], Noël M[1], Raâch M[2], Measures L[1]

[1] Maurice Lamontagne Institute, Fisheries and Oceans Canada, 850 route de la mer, Mont-Joli, QC, G5H 3Z4, Canada; [2] Institut des Sciences de la Mer, Université du Québec à Rimouski, 310 Allée des Ursulines, Rimouski, QC, G5L 3A1 Canada

Abstract

Beluga (white whale) from the St. Lawrence Estuary (SLE) was the first wildlife species in eastern Canada to be examined for polybrominated diphenyl ethers (PBDEs). Beluga carcasses showed rapidly increasing PBDEs blubber concentrations between 1988 and 1999, doubling at every 2.2 and 3.0 years in adult females and males, respectively. The current study aims to provide an update on the temporal trends of PBDEs in the SLE beluga. PBDEs were measured in blubber samples from 142 beluga carcasses found stranded on the shores of the SLE between 1987 and 2007. Results showed that concentrations of ΣPBDEs in blubber of female and male beluga are no longer increasing. In females, PBDE concentrations reached a plateau around 1999 followed by a significant decrease starting in 2003. In males, PBDE concentrations have ceased to exponentially increase after 2002 but there is no evidence of a recent decrease. These changes in temporal trends of PBDE concentrations in beluga are likely a result of a slowdown in industrial use and production of PBDEs and/or importation of goods containing these chemicals.

Introduction

The St. Lawrence Estuary (SLE) beluga (*Delphinapterus leucas*) population has declined by about 80-90% of its estimated size of 7 800 – 10 000 animals in 1885, in part due to hunting pressure which continued until 1979. Recent aerial surveys suggest that the decline has ceased, but do not provide evidence of a significant increase in numbers[1]. The presence of elevated concentrations of persistent organic pollutants (POPs) in beluga could be playing a role in limiting the growth rate of the population. Beluga inhabiting the SLE is identified as a species known to bioaccumulate POPs[2]. The prominent POP contamination reported in SLE beluga has been attributed to their high trophic position, their relatively long life span, and their habitat, which is located downstream of the St. Lawrence River and Lake Ontario, a highly populated and industrialized area[3]. Despite the fact that levels of PCBs and other POPs have been stable or even slightly decreasing since the late 1980s[2], no evidence of a recovery of the SLE beluga population has been reported. This may be the result of the emergence of new chemicals such as polybromanited diphenyl ethers (PBDEs) in the environment in the 1980's. PBDEs have been used as flame retardants to reduce the risk of fire in a wide range of manufactured products such as polyurethane foams, computers, furniture, and automobiles. PBDEs are emitted into the environment through several sources such as during production, use, and recycling of products containing PBDEs as well as disposal in domestic waste, landfills, and incineration. In eastern Canada, the SLE beluga has been the first species to show the presence of PBDEs in wildlife and to show rising concentrations in its tissues. Based on the analysis of 54 beluga carcasses collected between 1988 and 1999, concentrations of ΣPBDEs in their blubber were rapidly increasing, doubling at every 2.2 and 3.0 years in adult females and males, respectively[4]. The rising presence of PBDEs in the environment and their risk of toxic effects on human and wildlife populations have led legislators to ban or restrict the use of these chemicals[5]. Of the three main commercial PBDE mixtures (pentaBDE, octaBDE and decaBDE), penta- and octaBDE are no longer manufactured or imported into the United States and Canada since 2004. DecaBDE, however, still finds use in a variety of products in North America, but recently Canada has extended its regulation to include all PBDE mixtures. The current study aims to provide an update on the temporal trends of PBDEs in the SLE beluga. To reach this goal, PBDEs were measured in blubber samples from 142 adult belugas collected over a 20 year time period, between 1987 and 2007.

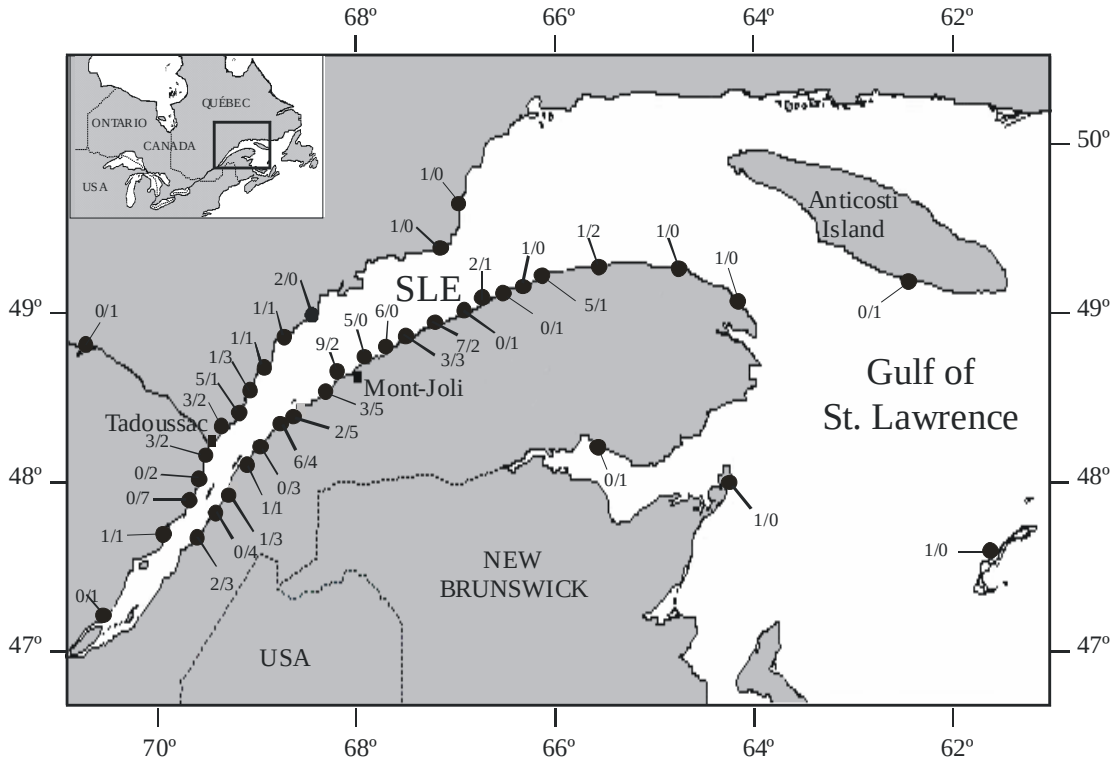

Figure 1. Locations of beluga stranded on the shores of the St. Lawrence Estuary, Canada. Male to female ratio (M/F) is presented at each stranding site.

Materials and Methods

Sampling. Blubber samples were obtained from stranded adult male (*n*=77) and female (*n*=65) beluga found on the shores of the SLE between 1987 and 2007 (Figure 1). The study focused on adult beluga which represent the majority, about 80%, of stranded carcasses examined and aged[6]. Whenever possible, blubber samples were taken at 60-70% of body length from the nose, approximately midway between the spinal column and the mid-lateral region of the beluga. The state of preservation of each carcass was coded according to Geraci and Lounsbury[7]. Sex was recorded, and for most carcasses, length and dorsal blubber thickness were measured. Age of beluga was determined by counting the number of growth layer groups (GLG) in sectioned teeth. According to a recent study by Stewart et al.[8], beluga deposit one growth layer group every year.

Chemical analysis. Blubber samples (0.5-1 g wet weight) were chemically dried with sodium sulfate before being transferred to a glass column. A single $^{13}C_{12}$ PCB (PCB-170) was added to the column before the extraction procedure. Lipids and lipophilic compounds were extracted from the sample with dichloromethane (DCM)-hexane (50:50 v/v). The extraction solution received a mixture of five $^{13}C_{12}$ PBDEs (PBDE-47, -99, -100, -126, and -153) before being reduced in volume for purification. Lipids were removed from the extract by gel permeation chromatography. The lipid-free extracts were further cleaned up by elution through a two-layer column packed with 10 g of hydrated neutral silica (5% water) and 5 g of hydrated alumina (5% water). The first 15 mL hexane fraction was discarded, and the second 70 mL of 50% DCM in hexane fraction containing the PBDE congeners was collected. The final extracts were reduced in volume and spiked with an instrument performance solution containing two additional $^{13}C_{12}$ PCBs (PCB-111 and -189) for a final volume of 100 µL. Forty individual PBDEs for which authentic standards were available were looked for in all blubber samples.

Table 1. Biological characteristics (mean[a] ± standard deviation and [range]) of the examined beluga collected during the 1987-2007 period.

Sex	Age (GLG)[b]	Length (m)	Carcass code[c]	Blubber	
				Lipid content (%)	Thickness (cm)
Male	40.3 ± 11.9 [18-74] (n=73)	4.1 ± 0.2 [3.0-4.6]	3.3 ± 0.6 [2.0-4.0]	89.9 ± 6.1 [63.9-97.4]	7.2 ± 1.9 [3.0-13.0] (n=65)
Female	40.4 ± 12.3 [20-63] (n=64)	3.6 ± 0.2 [3.1-4.0]	3.0 ± 0.7 [2.0-4.0]	90.9 ± 6.5 [64.2-97.9]	6.4 ± 1.9 [1.0-10.5] (n=47)

[a] Unless indicated, calculations are based on 77 males and 65 females; [b] GLG= growth layer group; [c] Based on Geraci and Lounsbury [7]

Details on the quantification of PBDEs have been reported previously in Lebeuf et al.[4]. PBDE congener concentrations were corrected on the basis of the recovery of the $^{13}C_{12}$ labelled surrogate compounds, which ranges from 83 to 101 %. The precision of the PBDE analytical method was assessed by repeated analysis (*n*= 11) of a pilot whale (*Globicephala* sp.) blubber sample available as the standard reference material SRM 1945. The coefficients of variation of replicate analysis varied between 9 and 29% and were inversely proportional to the concentration of individual PBDE congeners. The analytical accuracy of the method was validated for the specific congeners reported in SRM1945 by Wise et al.[9]. Only eleven congeners were systematically detected in beluga's blubber. Two tri (PBDE-17, 28), three tetra (PBDE-47, -49, and -66), two penta (PBDE-99 and -100), three hexa (PBDE- 153, -154, and -155), and one hepta (PBDE-183) bromo-substituted congeners were quantified and reported as the sum of these congeners (ΣPBDEs).

Statistical analysis. Statistical analyses were performed using Systat 10[10]. In all tests, statistical significance was set at $\alpha<0.05$. PBDE concentration data were used for statistical analyses after natural logarithmic transformation whereas biological parameter data were not transformed. Differences in age, lipid content, length, blubber thickness, and contaminant level between female and male belugas were assessed by Student t test. Time trends in contaminant levels were assessed by simple least-squared regression using linear model followed by ANOVA to confirm the linearity of the regression. Values of studentized residuals for linear regressions exceeding a threshold value of 3 were considered as outliers and removed from statistical analysis[11].

Results and Discussion

Age, length, carcass code, lipid content and thickness of blubber. Biological characteristics of beluga collected in the SLE during the 1987-2007 time period are reported in Table 1. All beluga examined were at least 18 years old and sexually mature. The mean age and blubber lipid content were not significantly different between males and females. As expected, males were significantly longer than females. Males had also higher mean blubber thickness than females but it is not clear if this is a normal feature for the species or a sign of the body condition. The mean carcass code indicates that carcasses of males and females were generally in a fair state of preservation or condition, although slightly better in females. It is important to note that the carcass condition does not represent the body condition of the animal at the time of its death but its state of preservation which depends on how long the carcass drifted and remained on shore before it was found.

No linear relationship was detected between length, blubber thickness or carcass code and year of collection for both sexes. In females, however, blubber lipid content slightly decreased over the examined time period as did the age of males. It is difficult to assess the consequences of such trends in biological parameters on the temporal trends of PBDEs in these animals. The examined animals have been exposed to PBDEs only recently and not throughout their life. Consequently, slight age trends in animals examined have likely a very limited effect on

PBDE trends. Although significant, blubber lipid content in females has decreased by less than 4% over the 20 year time period examined.

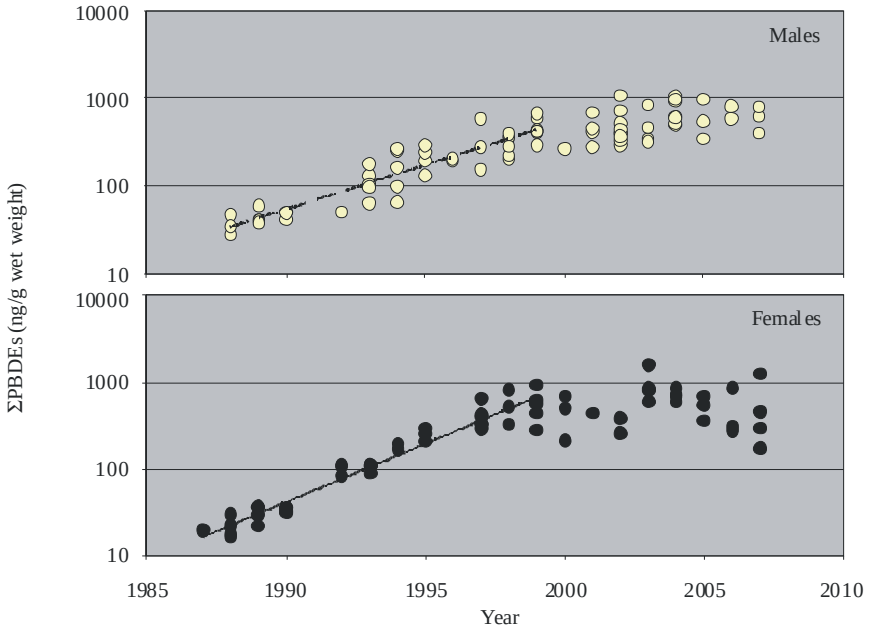

Figure 2. Time trends of ΣPBDE concentrations (ng/g wet weight) in blubber of male and female beluga from the SLE collected between 1987 and 2007. Exponential PBDE concentrations increases (lines) are shown between 1987 and 1999.

Time trends of PBDE concentrations. Blubber PBDE concentrations measured in 142 carcasses of belugas are reported as a function of year of collection in Figure 2. Both males and females exhibit an exponential increase, represented by the straight lines, of blubber PBDE concentrations between 1987 and 1999. Compared to trends previously reported by Lebeuf et al.[4], these trends include 17 and 14 additional data points for males and females respectively. These data confirm that concentrations of ΣPBDEs in blubber of beluga carcasses collected between 1987 and 1999 have doubled every 2.2 and 3.0 years in adult females and males, respectively. Between 2000 and 2007, PBDE concentrations in males have continued to significantly increase but at lower rate, characterized by a doubling time of 7.3 years. Since 2002, however, there is no significant exponential trend. These results indicate that males are levelling off their uptake, metabolism and excretion of PBDEs. In females, PBDE concentrations are not increasing since 2000. During the 2003-2007 time period, PBDE concentrations in females have significantly decreased at a rate of 18% per year. This recent trend in females indicates that elimination processes, which include gestation and lactation in addition to metabolism and excretion, are currently more important than uptake of PBDEs.

Trends in other species. There are a least a few studies that have reported similar changes in temporal trends of PBDEs in biota in North America. For instance, lake trout (*Salvelinus namaycush*) and rainbow smelt (*Osmerus mordax*) in Lake Ontario showed large increases in PBDE concentrations that started in the early 1980s. In mid 1990s, however, PBDE accumulation rates had drastically slowed down (12). Similarly, Gauthier et al. (13) have reported no increasing trend post 2000 in herring gull (*Larus argentatus*) eggs from seven colonies spanning the Laurentian Great Lakes. These observations are likely the results of changes in PBDE uses in recent years in North America, especially for the pentaBDE and octaBDE mixtures.

Acknowledgements
The authors would like to acknowledge the collaboration of the St. Lawrence National Institute of Ecotoxicology, University of Montréal, Faculty of Veterinary Medicine and the Group for Research and Education on Marine Mammals (GREMM).

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