Temporal trends (1987-2002) of regulated POPs in beluga whales from the St. Lawrence Estuary, Canada

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Introduction

The population of beluga (*Delphinapterus leucas)* in the St. Lawrence Estuary (SLE) is considered by the Committee on the Status of Endangered Wildlife in Canada (COSEWIC) as threatened.[1] Historically, the population was estimated at some 5000 animals but now only about 1000 individuals remain in the SLE.[2] The decline of the population has been attributed, in large part, to hunting. Although hunting was prohibited in 1979, the SLE beluga population has not shown any clear sign of recovery.[2] Several causes have been suggested to explain the lack of recovery, including potential toxicological impacts due to the presence of high concentrations of persistent organic pollutants (POPs) in the tissues of the SLE beluga.[3] The habitat of the SLE belugas is downstream from the Great Lakes and the St. Lawrence River, an industrialized and populated area that exports POPs to the SLE mostly by fluvial transport.[4]

No recent studies have reported temporal trends of POPs in beluga except for toxaphene.[5] In 1996, Muir et al.[6] reported time trends of several POPs in belugas by comparing POP levels in animals collected during different time periods, namely 1982-85, 1986-88, 1989-90 and 1993-94 for males, and 1982-85, 1987, 1988, 1989-90 and 1993-94 for females. They found that males had decreasing concentrations of certain POPs such as DDTs and PCBs whereas declines in concentrations of the major POP groups were not observed in females.

The objective of this study was to assess temporal trends of several regulated POPs, including PCBs, DDT and its metabolites, Chlordanes, HCH isomers, HCB and Mirex in SLE belugas between 1987 and 2002. The approach consisted in best fitting the blubber concentrations of individual POP or POP groups in both male and female belugas to simple natural logarithm (ln)-linear regression analyses.

Materials and Methods

Samples. Blubber samples of 42 females and 44 males were obtained from stranded beluga carcasses found on the shores of the SLE between 1987 and 2002. Age of each animal was determined by counting growth layer groups in tooth sections.[7] Only animals older than 10 years were examined in this study. In general, a large piece of skin-blubber-muscle was taken from the dorso-lateral region at 60-70% of body length from the rostrum of each individual. Each sample was wrapped in solvent rinsed aluminium foil and placed in a sealed plastic bag, and then stored at –20°C until analysis.

Analysis of POPs. PCBs and organochlorine pesticides (OCPs) were determined in blubber samples according to the method reported in Hobbs et al.[8] In brief, blubber subsamples spanning the entire depth of the blubber, from the skin to the muscle, were first taken from a larger piece of skin-blubber-muscle samples. Blubber samples were then chemically dried with sodium sulphate before being transferred to a glass column. Lipids and lipophilic compounds were extracted from the sample with dichloromethane. Lipids were removed from the remaining extract by gel permeation chromatography. The extract was further cleaned by elution through a two-layer column packed with neutral 5% hydrated silica and alumina. Quantification of PCBs and OCPs were performed separately using a gas chromatograph equipped with a ion trap detector, a split/splitless programmable injector (5 µl injection volume) operated in splitless mode, and an autosampler. The chromatographic separation was achieved using a 30m DB-5MS column (0.25 mm ID, 0.25 µm film thickness) with helium as the carrier gas. The ion source was operated in electron impact ionisation mode and the ion trap in MS/MS mode. Concentrations of PCB congeners and OCPs were calculated using relative response factors determined from a multiple-point calibration curve. PCB results are reported as the sum of the 42 congeners (ΣPCBs). DDT group pesticides (ΣDDTs) were calculated as the sum of

the concentrations of 2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4, 4'-DDD, 2,4'-DDT and 4,4'-DDT. Chlordane-related compounds (ΣChlor) were calculated as the sum of a-chlordane, g-chlordane, *cis*-nonachlor and *trans*-nonachlor. Concentrations of HCH compounds (ΣHCHs) were calculated as the sum of α-HCH and γ-HCH (Lindane).

Statistical analysis. All statistical analyses were performed using SYSTAT 10 software[9] with statistical significance set at α= 0.05. POP concentrations were expressed on a lipid weight basis. Concentration of POPs as well as age, lipid content and length of animals were natural logarithm-transformed prior to statistical analysis. Temporal trends of biological parameters, individual POP or POPs group concentrations in both females and maleswere assessed using simple ln-linear regression from which half-life time ($t_{½}$) was calculated for each statistically significant time trend.

Results and Discussion

Age, lipid content and length. Temporal trends of biological parameters, such as age, lipid content and length of the animals, were assessed separately for both female and male belugas. No linear relationship was detected between the age (females, *p*=0.478; males, *p*=0.646), the lipid content (females, *p*=0.245; males, *p*= 0.795) or the length of the animals (females, *p*=0.101; males, *p*=0.494) and the year of collection for both sexes.

Table 1. Results of ln-linear regression[a] analyses between POP concentrations in blubber of SLE belugas and collection year of the animals.

POPs	Females				Males			
	Trend	*p*	$t_{½}$ (year)	n	trend	*p*	$t_{½}$ (year)	n
ΣPCBs	↓	0.042	13.1	42	↓	0.003	17.8	42
ΣDDTs	↓	0.002	7.5	40	↓	0.006	18.2	40
ΣChlor	n.s.[b]	0.238	-	42	n.s.	0.563	-	42
ΣHCHs	↓	<0.001	7.0	42	↓	<0.001	8.9	44
HCB	n.s.	0.919	-	40	↓	<0.001	9.6	44
Mirex	n.s.	0.084	-	41	n.s.	0.128	-	43

[a]ln[POPs]= b x year + a; [b] slope not significantly different from zero

PCBs and OCPs. Time trends of POPs in blubber of SLE belugas were mainly assessed on POP groups except for HCB and Mirex. Results of linear regression analyses between POPs in both female and male belugas and the year of collection of the animals are reported in Table 1. About half of the POPs showed significant decreasing levels in female beluga between 1987 and 2002 and in males between 1988 and 2002. None of the POPs showed significant increasing levels in belugas. Temporal trends of ΣPCB, ΣDDT and ΣHCH were significant in both males and females whereas ΣChlor and Mirex were not significant in either sex. HCB was the only examined POP that exhibited a significant time trend in males but not in females.

Muir et al.[6] assessed time trends of POPs in SLE belugas between 1982 and 1994. Their results were somewhat different than our results. For example, they reported that concentrations of PCBs, expressed as Aroclor 1254/60, and DDTs decreased in males during that time period but these POP groups increased in females. When the time period in question was limited to 1986-1994, then temporal trends of PCBs (sum of congeners) in males and DDTs in females were no longer significant. Muir et al.[6] reported a significant decrease of ΣHCH (sum of α, β and γ-isomers) only in males between 1986 and 1994 whereas our results indicate significant decreases of ΣHCHs concentrations in both sexes during 1987-2002 time period. Muir et al.[6] also reported that HCB, the only chlorobenzene isomer found in significant concentrations in blubber of SLE beluga, decreased in males but exhibited no significant trend in females during the 1986-1994 time period, in agreement with our observations. No significant trends of Mirex and ΣChlor concentrations in SLE belugas were found in this study, which contrasts with the significant increase of ΣChlor concentrations in females between 1986-1994 reported by Muir et al.[6] It must be noted, however, that oxychlordane, a predominant Chlordane degradation product, was included in ΣChlor reported by Muir et al.[6] but not analyzed in our samples.

The time trends reported in this paper for ΣPCBs, ΣDDTs and ΣHCHs are in agreement with the expected declines for regulated POPs. The rates of decline of these POPs in belugas, expressed as $t_{½}$, varied between 7.0 and 18.2 years. For HCB in male belugas, $t_{½}$ was 9.6 years. These rates are similar to those reported for toxaphene congeners in SLE belugas.[5] For other regulated POPs such as Mirex and ΣChlor, the lack of significant time trends indicates that depuration of these chemicals by belugas represents an even longer process. Belugas are long lived animals that rapidly accumulate significant amounts of POPs in their blubber but slowly eliminate them. Consequently, time trends of POPs in belugas do not necessarily represent changes of POP concentrations in their diet or their habitat.

This study shows that bioaccumulative persistent organic pollutants must be regulated rapidly, before they reach high levels, because once accumulated these compounds are very slowly eliminated by belugas.

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