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Metals, Trace Elements, Polychlorinated Biphenyls, Organochlorine Pesticides, and Brominated Flame Retardants in Tissues of Barrow's Goldeneyes (*Bucephala islandica*) Wintering in the St. Lawrence Marine Ecosystem, Eastern Canada

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Abstract The eastern North American population of Barrow's goldeneyes winters in the St. Lawrence Estuary and Gulf of St. Lawrence where the sediments and food web are known to be contaminated with inorganic and organic compounds. Therefore, there is a potential for contamination of this population, which is designated of Special Concern by the Committee on the Status of Endangered Wildlife in Canada. Specimens were collected during three consecutive winters (2005–2007) in three regions (Manicouagan, Charlevoix, and Chaleur Bay) and analysed for metals, trace elements, polychlorinated biphenyls (PCBs), organochlorine pesticides, and brominated flame retardants (BFRs). Liver mercury levels were greater in the St. Larence Estuary (4.4 mg/kg in Manicouagan, 3.8 mg/kg in Charlevoix) than in Chaleur (2.4 mg/kg), whereas selenium showed the opposite pattern (7.3 mg/kg in Manicouagan, 7.0 mg/kg in Charlevoix, and 36.9 mg/kg in Chaleur). Liver PCB levels were greater in specimens from Manicouagan (236 ng/g) than in those from the two other regions (72 ng/g in Charlevoix, 35 ng/g in Chaleur). DDT was greater in Chaleur (66 ng/g) versus 10 ng/g in Manicouagan and 16 ng/g in Charlevoix. BFRs were not compared among regions because of smaller sample sizes, but mean total concentration was low (4.02 ng/g). Overall, although significant differences were found across regions, levels of all contaminants measured are generally low and not of toxicological concern for this population.

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The eastern North American population of Barrow's goldeneye (*Bucephala islandica* ([Gmelin 1789]), a sea duck species of the tribe Mergini, is designated of Special Concern by the Committee on the Status of Endangered Wildlife in Canada (Committee on the Status of Endangered Wildlife in Canada 2010). For 6 to 8 months each year, the majority of this population at risk (estimated at 6000 individuals) winters along 300 km of coastline along the northern shore of the St. Lawrence Estuary and Gulf of St. Lawrence in Quebec, Canada (Robert and Savard 2006; Ouellet et al. 2010). This distribution makes the population highly vulnerable to any degradation of its coastal habitat, such as oil spills and pollution (Robert et al. 2000). For instance, large numbers of individuals congregate every winter in Baie des Anglais near the mouth of the Manicouagan River, one of the most severely polychlorinated biphenyl (PCB)-contaminated coastlines in Eastern Canada (Lee et al. 1999; Lacroix et al. 2001). In addition, a smaller but significant portion of the population winters in Chaleur Bay (Robert and Savard 2006; Ouellet et al. 2010), which has for decades received various metals from industrial discharges (Uthe et al. 1986; Parsons and Cranston 2006; Fraser et al. 2011).

The eastern North American population of Barrow's goldeneye nests in the boreal forest near head waters (Robert et al. 2008) free of any direct anthropogenic contamination, except for atmospheric transfers. Soon after the female birds begin incubation, the male birds leave on a moult migration to Arctic coastal waters where they stage for several weeks until they return south to the wintering ground in late fall (Robert et al. 2002). Posthatch movements of female birds and their young, until they join the wintering ground in fall, are poorly understood.

The main objective of this study was to determine the level of contamination in tissues of Barrow's goldeneyes wintering in the St. Lawrence marine ecosystem. A secondary objective was to compare levels between regions and determine whether some contaminants in some regions may pose a threat to conservation of this population.

Methods

Specimen Collection and Tissue Dissection

Specimen collection took place in winter from December to April in 2004 to 2005, 2005 to 2006, and 2006 to 2007 along the northern shore of the St. Lawrence Estuary and in the Gulf of St. Lawrence. Although sea ice is abundant from December to March (Saucier et al. 2003) and complicates the sampling, it is the only time of year when this species can be found in significant numbers. Collection areas included Cap-à-l'Aigle ($n = 1$) and Baie des Rochers ($n = 15$), which are in the Charlevoix region; in Baie des Anglais ($n = 7$), the estuary of the Manicouagan River ($n = 5$), and the mouth of the Godbout River ($n = 4$), which are in the Manicouagan region; and near Dalhousie ($n = 12$) in Chaleur Bay (Fig. 1). A total of 42 Barrow's goldeneyes (32 male birds and 10 female birds) were shot under license with nontoxic ammunition. In addition, two adult male birds were mist-netted in Baie des Rochers on April 16, 2005, and killed by injection of 0.3 ml/kg T-61 by a qualified veterinarian. Every individual collected appeared healthy and exhibited apparently normal behaviour before collection. After recovery, carcasses were labelled, wrapped in plastic bags, and frozen at −15 °C. In the laboratory, carcasses were thawed for dissection of the liver, kidneys, and humerus bone. Tissue samples were kept at −18 °C until shipment to the National Wildlife Research Center (NWRC) in Ottawa, Ontario, where they

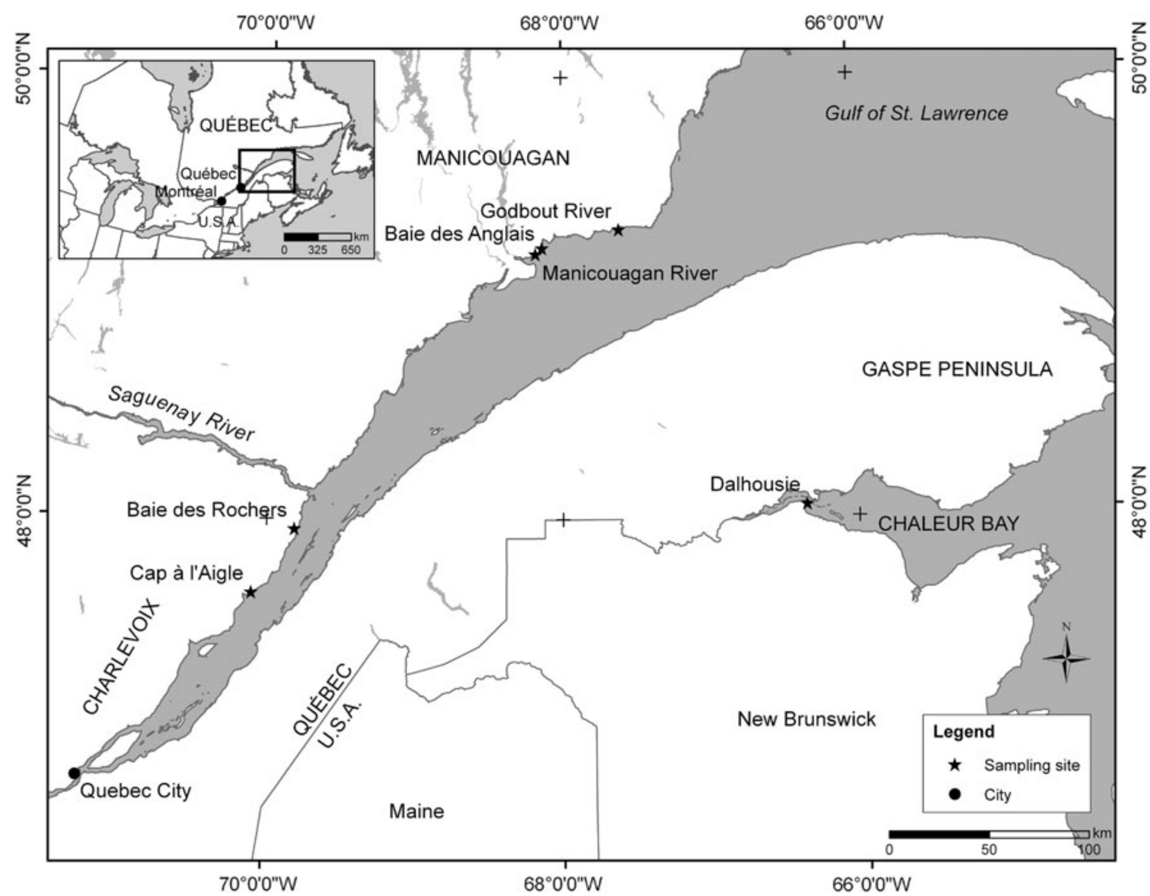

Fig. 1 Map of the goldeneye study area showing the collection sites in the St. Lawrence Estuary and Chaleur Bay

were stored at −40 °C until they were processed. Tissue samples were homogenized later, and resulting aliquots were kept at −20 °C until extraction and chemical analysis.

Chemical Analysis

Total mercury (Hg), selenium (Se), lead (Pb), cadmium (Cd), and arsenic (As) were measured in liver and kidney, and Pb was also measured in humerus bone. Hg determination was performed without acid digestion by atomic absorption spectrometry with an advanced mercury analyser (AMA-254, Leco Corporation, St. Joseph, Mi, USA), which employs direct combustion of the sample in an oxygen-rich atmosphere (method MET-CHEM-AA-03G, NWRC 2007, available on request; EPA Method 7473, 1998). Tissues were freeze-dried and homogenized Prior to Hg determination. Methyl mercury (MeHg) was measured in liver with an AMA-254 after extraction into toluene as methyl mercuric bromine and partitioning the bromine into aqueous phase as a thiosulfate complex (Neugebauer et al. 2000). Se, Pb, and As were determined by graphite furnace atomic absorption spectrophotometry with an AAnalyst 800 (Perkin Elmer, Waltham, MA, USA) equipped with a transversely heated graphite atomizer and Zeeman background correction (Neugebauer et al. 2000). Cd was determined by flame atomic absorption spectrophotometry with a Perkin Elmer AAnalyst 800 equipped with deuterium background correction (Neugebauer et al. 2000). Accuracy of the analysis was determined by analysis of certified reference materials (CRM); recoveries of the CRMs were within acceptable confidence intervals.

Organic contaminants measured in livers included PCBs (72 PCB congeners), organochlorine pesticides (OCPs: hexachlorocyclohexane (alpha-, beta-, gamma-HCH), chlordane (cis-, trans-, oxy-), chlorobenzene (1,2,3,4-tetra-, 1,2,4,5-tetra-, penta- and hexa-), dieldrin, heptachlor epoxide (isomer B), mirex, photomirex, nonachlor (cis-, trans-), octachlorostyrene, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, and tris (4-chlorophenyl) methanol), and brominated flame retardants (BFRs: polybrominated diphenylether, congeners 17, 28, 47, 49, 66, 85, 99, 100, 101, 138, 153, 154/BB153, 183, and 209, and hexabromocyclododecane [HBCDD]). Extraction, purification, and quantification procedures were conducted according to test method MET-CHEM-OC-06B (NWRC 2007 [available on request]). In summary, aliquots were weighed and homogenized with Na_2SO_4 and extracted with DCM and hexane (1:1 ratio). All samples were spiked with ^{13}C-labeled internal standards and brominated diphenyl ether internal standards before removal of lipids and biogenic material by gel permeation chromatography and further cleanup by Florisil column chromatography. Levels of OCPs, PCBs, and BFRs were quantified with a capillary gas chromatograph (Agilent 6890N, Agilent Technologies, Missisauga, ON, Canada) coupled with a mass selective detector (Agilent 5973 N) operated in a selected ion monitoring mode. The BFR results were automatically recovery corrected. Two duplicate extractions, two duplicate injections, and one blank were processed with each batch of samples.

Statistical Analysis

Metals were analysed in individual specimens. Determinations of organic contaminant levels were conducted on 21 composite samples composed of one to four individuals of the same region, year of collection, sex, and age class. Age is a binary variable, adult or juvenile, with “juvenile” referring to hatch-year or second-year birds (i.e., individuals in their first winter) and “adult” referring to post-second year birds. Median concentrations of contaminants were compared between age classes and sexes using Mann–Whitney *U* test and among sampling years and geographic regions using Kruskal–Wallis and Tukey–Kramer (TK) tests. Because 9 of 11 juvenile birds in our sample were collected in the Manicouagan region, we compared contaminant levels between age classes within this region only. No difference in contaminant concentrations was found between sexes ($p > 0.05$) or among year of collection ($p > 0.05$). No difference in levels of organic contaminants was found between adult birds and juvenile birds ($p > 0.05$). Hence, for organics, samples composed of only one individual were pooled mathematically for each region, resulting in a total of 15 groups of 2 to 4 individuals each used in the subsequent analysis to compare regions. Owing to the absence of a relationship between organic contaminant concentrations and lipid content (Pearson correlation [see Results]), concentration values were not lipid-corrected in accordance with Hebert and Keenleyside (1995). Contaminants for which concentrations were lower than the detection limit were assigned a value equal to half the detection limit.

Results

Metals and Trace Elements

Renal and hepatic Cd and hepatic Pb levels were different between adult birds and juvenile birds ($p < 0.05$). Cd concentration was greater in adult birds, whereas Pb concentration was greater in juvenile birds (Table 1). No other difference in levels of metals or trace elements was found between adult birds and juvenile birds.

Hepatic total Hg was significantly greater in specimens from the Estuary than in those from Chaleur ($p < 0.01$), but levels were not different between Charlevoix and Manicouagan ($p > 0.05$; Table 1). Renal total Hg concentration was significantly greater in Manicouagan than in

Table 1 Mean metal concentrations in liver, kidney, and bone of Barrow's goldeneyes collected in winter in three regions of the St. Lawrence marine ecosystem[a]

Tissue	Detection (%)	Manicouagan	Charlevoix	Chaleur
Total Hg				
Liver[1]	100	$4.44^{a} \pm 1.90$	$3.80^{a} \pm 1.82$	$2.38^{b} \pm 1.02$
Kidney[2]	100	$2.76^{a} \pm 0.98$	$2.02^{b} \pm 0.58$	$1.36^{b} \pm 0.46$
MeHg liver	100	$3.25^{a} \pm 1.15$	$2.78^{a} \pm 1.35$	$1.76^{b} \pm 0.67$
Se				
Liver[1]	100	$7.30^{b} \pm 2.38$	$6.99^{b} \pm 2.56$	$36.9^{a} \pm 15.3$
Kidney[1]	100	$9.51^{b} \pm 3.09$	$8.88^{b} \pm 2.38$	$44.0^{a} \pm 20.8$
As				
Liver[1]	100	$0.76^{b} \pm 0.35$	$1.37^{a} \pm 0.45$	$1.32^{a} \pm 0.60$
Kidney[1]	100	$0.72^{c} \pm 0.29$	$1.36^{b} \pm 0.43$	$2.06^{a} \pm 1.37$
Pb				
Liver, adult birds[3]	95	$0.05^{b} \pm 0.01$	$0.07^{b} \pm 0.04$	$0.18^{a} \pm 0.06$
Liver, juvenile birds[4]	100	$0.11^{a} \pm 0.08$	$0.07^{a} \pm 0.03$	ND
Kidney[2]	100	$0.19^{b} \pm 0.17$	$0.36^{a} \pm 0.20$	$0.49^{a} \pm 0.24$
Bone[1]	100	$1.27^{a} \pm 0.71$	$1.42^{a} \pm 0.56$	$1.52^{a} \pm 0.84$
Cd				
Liver—adult birds[5]	100	$3.76^{ab} \pm 1.21$	$5.06^{a} \pm 1.77$	$2.80^{b} \pm 0.89$
Liver, juvenile birds[4]	100	$2.09^{a} \pm 2.37$	$2.64^{a} \pm 1.61$	ND
Kidney, adult birds[5]	100	$33.0^{b} \pm 12.5$	$47.4^{a} \pm 18.7$	$27.2^{b} \pm 8.1$
Kidney, juvenile birds[4]	100	$5.00^{a} \pm 1.46$	$8.34^{a} \pm 4.78$	ND
Liver moisture (%)		$70.8^{a} \pm 2.4$	$69.9^{ab} \pm 1.7$	$69.3^{b} \pm 1.3$
Kidney moisture (%)		$76.4^{a} \pm 1.0$	$76.4^{a} \pm 1.1$	$76.3^{a} \pm 0.8$

[a] Data are presented as mg/kg dry weight ± SD. Sample size (individuals): [1] Manicouagan $n = 16$, Charlevoix $n = 16$, Chaleur $n = 12$; [2] Manicouagan $n = 16$, Charlevoix $n = 10$, Chaleur $n = 6$; [3] Manicouagan $n = 7$, Charlevoix $n = 8$, Chaleur $n = 6$; [4] Manicouagan $n = 9$, Charlevoix $n = 2$; and [5] Manicouagan $n = 7$, Charlevoix $n = 14$, Chaleur $n = 12$. Values on the same line showing the same *superscript letters* are not different (TK, $p > 0.05$)

Charlevoix or Chaleur ($p < 0.01$) but was similar in the latter two regions ($p > 0.05$).

Hepatic and renal Se concentrations were on average five times greater in specimens from Chaleur than in those collected in the Estuary ($p < 0.001$; Table 1) but were not different between Charlevoix and Manicouagan ($p > 0.05$).

Renal and hepatic As levels were significantly lower in Manicouagan ($p < 0.01$); hepatic As did not differ between Chaleur and Charlevoix ($p > 0.05$), but renal As was lower in Charlevoix than in Chaleur ($p < 0.01$).

Renal Pb concentrations were similar between Chaleur and Charlevoix ($p > 0.05$) and lower in Manicouagan than in the other two regions ($p < 0.01$). Hepatic Pb concentrations were different between age classes. In adult birds, hepatic Pb was greater in Chaleur than in the Estuary ($p < 0.01$), but no differences were observed in juvenile birds. Pb levels in bone did not show any spatial segregation ($p > 0.05$).

Cd levels were significantly different between age classes. In adult birds, hepatic Cd concentrations were greater in Charlevoix than in Chaleur, with Manicouagan showing intermediate values ($p < 0.01$); renal Cd concentrations were greater in Charlevoix than in the two other regions ($p < 0.01$). No differences were observed in juvenile birds ($p > 0.05$).

Organics

No significant relationship was found between lipophilic contaminants and lipid content of liver ($p > 0.05$). Adult birds showed greater relative lipid content in liver than juvenile birds, but the difference was small (relative lipid content 4.00 % ± 0.54 % and 3.03 % ± 0.30 % for adult birds and juvenile birds, respectively; $p < 0.01$).

The 12 PCB congeners that contributed individually ≥2 % to total PCBs are listed in decreasing order of relative contribution in Table 2. Apart from a few exceptions, PCB levels were consistently greater in groups of specimens collected in Manicouagan than in the other two regions and were similar between Charlevoix and Chaleur ($p > 0.05$) (Table 2).

The most abundant OCP measured in liver of Barrow's goldeneyes was total DDT, which was mostly constituted

Table 2 Mean concentrations of major PCBs and OCPs in liver of Barrow's goldeneyes collected in three regions in winter in the St. Lawrence marine ecosystem

PCB congener	Detection (%)	Manicouagan ($n = 5$)	Charlevoix ($n = 6$)	Chaleur ($n = 4$)	Contribution (%)
PCB153	100	$38.3^a \pm 11.4$	$16.1^b \pm 9.4$	$8.2^b \pm 2.6$	19.3
PCB138	100	$39.0^a \pm 11.6$	$10.5^b \pm 6.9$	$5.3^b \pm 1.0$	15.1
PCB180	100	$25.8^a \pm 13.1$	$7.2^b \pm 3.8$	$2.4^b \pm 0.9$	9.7
PCB187	100	$21.5^a \pm 6.4$	$5.2^b \pm 3.0$	$2.1^b \pm 0.6$	7.6
PCB118	100	$8.4^a \pm 4.1$	$4.8^a \pm 3.3$	$2.6^a \pm 0.6$	5.3
PCB177	100	$16.5^a \pm 6.8$	$1.8^b \pm 1.1$	$0.7^b \pm 0.1$	4.3
PCB170/190	100	$10.8^a \pm 5.7$	$2.4^b \pm 1.3$	$0.9^b \pm 0.3$	3.7
PCB146	100	$6.1^a \pm 1.7$	$2.9^b \pm 1.6$	$1.3^b \pm 0.3$	3.2
PCB183	100	$8.0^a \pm 2.6$	$1.8^b \pm 0.9$	$0.8^b \pm 0.3$	2.8
PCB99	100	$3.5^a \pm 1.8$	$2.6^a \pm 1.5$	$1.4^a \pm 0.3$	2.8
PCB196/203	100	$5.0^a \pm 2.8$	$1.4^b \pm 0.7$	$0.6^b \pm 0.2$	2.0
PCB105	100	$3.1^a \pm 1.9$	$1.9^a \pm 1.3$	$1.0^a \pm 0.2$	2.0
Total PCBs	100	$236.4^a \pm 63.1$	$72.4^b \pm 42.2$	$34.8^b \pm 8.1$	100
pp'DDE	100	$9.2^b \pm 3.7$	$15.8^b \pm 6.7$	$57.1^a \pm 13.0$	48.2
pp'DDD	90	$0.7^b \pm 0.3$	$0.5^b \pm 0.3$	$7.1^a \pm 3.8$	3.6
pp'DDT	19	0.05 ± 0	0.1 ± 0.1	1.7 ± 2.2	0.6
Total DDT	100	$9.9^b \pm 3.7$	$16.4^b \pm 7.0$	$65.9^a \pm 15.8$	52.4
Oxychlordane	81	2.4 ± 1.0	4.9 ± 3.7	2.9 ± 0.6	9.5
Dieldrin	71	1.7 ± 1.9	5.4 ± 3.3	2.4 ± 0.8	10.7
HCB	100	2.0 ± 0.6	3.7 ± 1.5	3.0 ± 1.4	9.1
Heptachlor epoxide	100	1.8 ± 0.2	3.0 ± 1.5	1.8 ± 0.5	7.7
t-nonachlor	100	0.9 ± 0.2	1.2 ± 0.8	0.4 ± 0.1	3.2
OCPs	76	0.2 ± 0.2	0.6 ± 0.4	0.3 ± 0.1	1.3
C-nonachlor	95	$0.2^{ab} \pm 0.1$	$0.2^a \pm 0.1$	$0.08^b \pm 0.04$	0.8
Mirex	33	$0.05^b \pm 0$	$0.3^a \pm 0.3$	$0.1^{ab} \pm 0.2$	0.7
Total OCPs	100	$29.6^b \pm 9.1$	$44.2^b \pm 15.5$	$108.3^a \pm 37.7$	100
Lipid (%)		3.6 ± 0.6	3.9 ± 0.9	4.0 ± 0.4	

Data are presented as ng/g wet weight ± SD). Sample size (pools) is given in parentheses.Values on the same line showing the same *superscript letters* are not different (TK, $p > 0.05$)

of *p,p'*-DDE (Table 2). On average, total DDT concentration was five times greater in specimens from Chaleur than in those collected in the Estuary. The relative contribution of *p,p'*-DDE to total DDT was lower in Chaleur than in the Estuary (87.3 % ± 7.6 % and 93.7 % ± 4.3 %, respectively). However, total DDT levels were generally low in Barrow's Goldeneyes with values ≤100 ng/g ww. Levels of non-DDT pesticides were generally low and showed no spatial structure (Table 2). Five BDE congeners each contributed ≥2 % and together 62 %, of total BDEs (Table 3). HBCDD was never detected.

Discussion

The winter movements of Barrow's goldeneyes in the St. Lawrence marine ecosystem are largely unknown. Although there are specific areas where Barrow's goldeneyes are steadily found by hundreds or thousands of individuals throughout the winter (Robert and Savard 2006; Ouellet et al. 2010), the amount of time spent by our specimens in the sites where they were collected is unknown. Therefore, the extent to which their toxicological signature reflects that of their collection site is uncertain. However, despite these uncertainties, our results suggest that some site fidelity exists. For instance, it is unlikely that the adult birds from Chaleur, which had one tenth the PCB burden measured in juvenile birds collected in Manicouagan, ever spent a prolonged period of time in the Manicouagan region.

Hg is widespread in the food web of the St. Lawrence ecosystem due to anthropogenic inputs from upstream waters and atmospheric deposition (Cossa and Gobeil 2000; Miller et al. 2005). Hg levels in our specimens were greater than those in Barrow's and Common goldeneyes from Northern Canada (Braune and Malone 2006a). Maximum Hg concentrations in livers of goldeneyes from

Table 3 Hepatic concentrations of major BDE in Barrow's goldeneyes collected in the St. Lawrence marine ecosystem

BDE congener	Mean ± SD	Range	Contribution (%)
Tetra-BDE			
BDE-47	0.53 ± 0.37	0.15–1.33	12.3 ± 6.6
Penta-BDE			
BDE-99	0.73 ± 0.44	0.24–1.89	17.2 ± 6.1
BDE-100	0.69 ± 0.23	0.28–1.18	17.1 ± 3.9
Hexa-BDE			
BDE-153	0.39 ± 0.24	0.12–0.99	9.8 ± 5.7
BDE154/BB153	0.24 ± 0.10	0.13–0.49	6.0 ± 2.0
Total BDE	4.02 ± 1.04	2.78–6.71	100

Data are presented as ng/g wet weight. $n = 15$ groups and 32 individuals; relative detection frequency = 100 %

Manicouagan approached 15 mg/kg ww (as MeHg [equivalent to 4 to 5 mg/kg dw in our samples]), the threshold for toxic effects and death in various tissues of adult birds (Scheuhammer et al. 2007). However, based on an extensive literature review, Shore et al. (2011) recently proposed 20 and 2 mg/kg ww in liver as thresholds for adverse effects on bird survival and reproduction, respectively.

Se, an essential micronutrient, is rapidly accumulated in liver and eliminated at an exponential rate after exposure ceases (Heinz et al. 1990). Se toxicity is associated with mortality and developmental abnormalities (Heinz 1996) and with male reproductive impairment (Pollock and Machin 2008). A hepatic Se concentration of 20 mg/kg dw has recently been proposed as a toxic threshold, whereas concentrations between 20 and 75 mg/kg dw in marine species present a low probability of adverse effects (Ohlendorf and Heinz 2011). Nine (20 %) Barrow's goldeneyes had hepatic Se levels > 20 mg/kg dw, and the maximum level was 61 mg/kg dw. Our range of Se concentration values was wider than the values reported by Braune and Malone (2006a) for hepatic Se in Barrow's goldeneyes from northwestern Canada (3.0 to 9.7 mg/kg ww) but comparable with values reported by Elliott et al. (2007) and Henny et al. (1995), both of whom reported no adverse effects. Se concentrations > 100 mg/kg dw were found in various diving ducks without evidence of adverse effects (Braune and Malone 2006a; DeVink et al. 2008). Se can protect against the neurotoxicity of MeHg, and correlations between Hg and Se have been reported in fish-eating wildlife species (Scheuhammer et al. 2008). There was no relationship between Hg and Se in livers of goldeneyes from the St. Lawrence. The mean molar ratio of Hg to Se was 1:4.5 in Charlevoix, 1:3.6 in Manicouagan, and 1:33 in Chaleur, which indicates that Hg levels are lower than toxic levels (Scheuhammer et al. 2008). Although metal contamination of Chaleur Bay from various industries has been well documented (Fraser et al. 2011), no data could be found on sources of Se.

Pollock and Machin (2008) observed that the adverse effect of Se on seminiferous tubule morphology in male lesser scaups was partially offset by an interaction with Cd in a range of concentrations that overlapped what we measured in Chaleur. If sensitivity of Barrow's goldeneyes to Se toxicity compares with that of lesser scaup, the male birds wintering in Chaleur Bay may have decreased fitness and fertility due to Se intoxication, although the problem may be attenuated by the presence of Cd.

Cd levels are also magnified across trophic levels and are typically high in sea birds and mollusc-eating birds (Furness 1996; Henny et al. 1995). Cd concentrations in our samples were lower than the threshold of 100 mg/kg dw Cd in kidney for toxic effects (Furness 1996) or the conservative risk level of 65 mg/kg ww proposed by Wayland and Scheuhammer (2011). The latter investigators also suggest a liver threshold level between 45 and 70 mg/kg ww, which is also higher than the levels observed in this study (Wayland and Scheuhammer 2011). The high ratio of renal to hepatic Cd concentration we found is consistent with published figures. A ratio closer to or less than one would be indicative of Cd-induced renal disruption (Furness 1996). Juvenile birds showed consistently low Cd levels, likely due to the absence of maternal transfer of Cd to eggs and a lack of time to bioaccumulate Cd (Furness 1996).

As and Pb levels in sea duck tissues are often low or not detected (Custer et al. 2003; Franson et al. 1995, Trust et al. 2000). Pb levels in goldeneyes in this study correspond to background levels in birds (Scheuhammer 1987). No difference was found between sexes despite a greater intestinal Pb absorption in female birds concurrent with increased absorption of Ca for eggshell formation (Scheuhammer 1987).

PCB levels were generally low. The only individuals with significant PCB levels were those collected within 40 km of the PCB-contaminated shoreline of Baie des Anglais in Manicouagan (Lee et al. 1999; Lacroix et al. 2001); the highest total PCB concentration (525.9 ng/g) was measured in the liver of a juvenile male bird collected there in early January 2006. This level is lower than levels causing reproductive impairment (Elliott and Martin 1998; Hoffman et al. 1996). Few data exist on PCBs in liver of Barrow's goldeneye or similar species. Liver in Barrow's goldeneye from the Pacific coast (Elliott and Martin 1998) and common goldeneyes (*Bucephala clangula*) from the Detroit River (Smith et al. 1985) had 138 ng/g and 7.6 µg/g ww PCBs, respectively.

DDT was widely used in forestry management in Eastern Canada to control spruce budworm outbreaks before its ban in 1974 (Kerswill 1967). Barrow's goldeneyes collected in Chaleur had greater total DDT and *pp*'-DDT levels and lower relative contribution of DDE than the ones collected in the Estuary, indicating that Chaleur Bay has been exposed to more recent inputs of DDT than the St. Lawrence Estuary (Aguilar 1984). The DDE levels found in Barrow's goldeneyes of the Eastern North American population are six times greater than those reported by Elliott and Martin (1998) in liver of Barrow's goldeneyes from the Pacific coast. This contrast is consistent with Braune and Malone (2006b), who found generally greater values of contaminants in sea ducks from Eastern than Western Canada. Nevertheless, levels of DDT and metabolites observed were much lower than those causing decreased eggshell thinning and hatching failure (Blus 2011). All of the other pesticides were generally found in low concentrations.

Cormorants (*Phalacrocorax carbo*) from England had 1.8 to 140 ng/g ww Σ PBDEs in liver (Law et al. 2002). Black guillemots (*Cepphus grylle*) from southern Greenland had 46 ng/g lipid PBDEs in liver (Vorkamp et al. 2004). The mean Σ BFRs in common eider eggs from the Gulf of St. Lawrence was 24.09 ng/g ww (Lavoie et al. 2010). Transformed by lipid weight, the mean Σ PBDEs in the Barrow's goldeneyes from the St. Lawrence is 106.07 ng/g lipid weight, which is lower than that from cormorants and greater than that of black guillemots. Although levels of these contaminants are low relative to other bird species, it is worth mentioning they were detected in a duck species nesting in boreal forest and consuming marine invertebrates in its wintering habitat.

Several aspects in winter resource selection of Barrow's goldeneye in the St. Lawrence marine ecosystem likely protect it against severe contamination. First, its preferred feeding habitat is mostly wave-beaten rocky intertidal habitat (J. F. O. [unpublished data]). These environments are typically poor in fine-grained sediments and organic matter, both of which bind contaminants. Second, the species feeds only on invertebrates and occupies thereby a relatively low trophic level, which lessens its exposure to biomagnification. Finally, important bioaccumulators, such as filter-feeding organisms, are poorly represented in its winter diet (Bourget et al. 2007; JFO [unpublished data]). Apart from Se in Chaleur, all contaminants measured in this study were either low in tissues or not known to be transferred to eggs by female birds. It is then not probable that eggs and embryos would be exposed to toxic levels of contaminants.

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References

Aguilar A (1984) Relationship of DDE/DDT in marine mammals to the chronology of DDT input into the ecosystem. Can J Fish Aquat Sci 41:840–844

Blus LJ (2011) DDT, DDD, and DDE in birds. In: Beyer WN, Meador JP (eds) Environmental contaminants in biota: Interpreting tissue concentrations, 2nd edn. CRC Press, Boca Raton, pp 425–445

Bourget D, Savard JPL, Guillemette M (2007) Distribution, diet and dive behavior of Barrow's and common goldeneyes during spring and autumn in the St. Lawrence Estuary. Waterbirds 30:230–240

Braune BM, Malone J (2006a) Mercury and selenium in livers of waterfowl harvested in Northern Canada. Arch Environ Contam Toxicol 50:284–289

Braune BM, Malone J (2006b) Organochlorines and mercury in waterfowl harvested in Canada. Environ Monit Assess 114:331–359

Committee on the Status of Endangered Wildlife in Canada (2010) Canadian wildlife species at risk. http://www.cosewic.gc.ca/eng/sct0/rpt/rpt_csar_e.cfm. Accessed: 2011

Cossa D, Gobeil C (2000) Mercury speciation in the Lower St. Lawrence Estuary. Can J Fish Aquat Sci 57:138–147

Custer CM, Custer TW, Anteau MJ, Afton AD, Wooten DE (2003) Trace elements in lesser scaup (*Aythya affinis*) from the Mississippi Flyway. Ecotoxicology 12:47–54

DeVink JMA, Clark RG, Slattery SM, Wayland M (2008) Is selenium affecting body condition and reproduction in boreal breeding scaup, scoters, and ring-necked ducks? Environ Pollut 152:116–122

Elliott JE, Martin PA (1998) Chlorinated hydrocarbon contaminants in grebes and seaducks wintering on the coast of British Columbia, Canada—1988-1993. Environ Monit Assess 53:337–362

Elliott JE, Harris ML, Wilson LK, Smith BD, Batchelor SP, Maguire J (2007) Butyltins, trace metals and morphological variables in surf scoter (*Melanitta perspicillata*) wintering on the south coast of British Columbia, Canada. Environ Pollut 149:114–124

EPA Method 7473 (1998) Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrometry (Rev). http://www.leco.com/products/organic/ama_254/pdf/7473.pdf

Franson JC, Koehl PS, Derksen DV, Rothe TC, Bunck CM, Moore JF (1995) Heavy metals in seaducks and mussels from Misty Fjords National Monument in southeast Alaska. Environ Monit Assess 36:149–167

Fraser M, Surette C, Vaillancourt C (2011) Spatial and temporal distribution of heavy metal concentrations in mussels (*Mytilus edulis*) from the Baie des Chaleurs, New Brunswick, Canada. Mar Pollut Bull 62:1345–1351

Furness RW (1996) Cadmium in birds. In: Beyer WN, Heinz GH, Redmon-Norwood AW (eds) Environmental contaminants in wildlife. Lewis, New York, pp 447–458

Hebert CE, Keenleyside KA (1995) To normalize or not to normalize? Fat is the question. Environ Toxicol Chem 14:801–808

Heinz GH (1996) Selenium in birds. In: Beyer WN, Heinz GH, Redmon-Norwood AW (eds) Environmental contaminants in wildlife. Lewis, New York, pp 447–458

Heinz GH, Pendleton GW, Krynitsky AJ, Gold LG (1990) Selenium accumulation and elimination in mallards. Arch Environ Contam Toxicol 19:374–379

Henny CJ, Rudis DD, Roffe TJ, Robinson-Wilson E (1995) Contaminants and sea ducks in Alaska and the circumpolar region. Environ Health Perspect 103(Suppl 4):41–49

Hoffman DJ, Rice CP, Kubiak TJ (1996) PCBs and dioxins in birds. In: Beyer WN, Heinz GH, Redmon-Norwood AW (eds) Environmental contaminants in wildlife. Lewis, New York, pp 165–207

Kerswill CJ (1967) Studies on effects of forest sprayings with insecticides, 1952–63, on fish and aquatic invertebrates in New Brunswick streams: introduction and summary. J Fish Res Board Can 24:701–708

Lacroix A, Fournier M, Lebeuf M, Nagler JJ, Cyr DG (2001) Phagocytic response of macrophages from the pronephros of American plaice (*Hippoglossoides platessoides*) exposed to contaminated sediments from Baie des Anglais, Quebec. Chemosphere 45:599–607

Lavoie RA, Champoux L, Rail JF, Lean DRS (2010) Organochlorines, brominated flame retardants and mercury levels in six seabird species from the Gulf of St. Lawrence (Canada): relationships with feeding ecology, migration and molt. Environ Pollut 156:2189–2199

Law RJ, Allchin CR, Bennett ME, Morris S, Rogan E (2002) Polybrominated diphenyl ethers in two species of marine top predators from England and Wales. Chemosphere 46:673–681

Lee K, Nagler JJ, Fournier M, Lebeuf M, Cyr DG (1999) Toxicological characterization of sediments from Baie des Anglais on the St. Lawrence estuary. Chemosphere 39:1019–1035

Miller EK, Vanarsdale A, Keeler GJ, Chalmers A, Poissant L, Kamman NC et al (2005) Estimation and mapping of wet and dry mercury deposition across northeastern North America. Ecotoxicology 14:53–70

Neugebauer EA, Sans Cartier GL, Wakeford BJ (2000) Methods for the determination of metals in wildlife tissues using various atomic absorption spectrophotometry techniques. Technical Report Series no. 337E. Canadian Wildlife Service, Headquarters, Hull, Québec, Canada

Ohlendorf HM, Heinz GH (2011) Selenium in birds. In: Beyer WN, Meador JP (eds) Environmental contaminants in biota, 2nd edn. CRC Press, Boca Raton, pp 669–701

Ouellet JF, Guillemette M, Robert M (2010) Spatial distribution and habitat selection of Barrow's and common goldeneyes (*Bucephala islandica*, *B. clangula*) wintering in the St. Lawrence marine system. Can J Zool 88:306–314

Parsons MB, Cranston RE (2006) Influence of lead smelter emissions on the distribution of metals in marine sediments from Chaleur Bay, eastern Canada. Geochem: Explor Environ, Anal 6:259–275

Pollock B, Machin KL (2008) Effects of cadmium, mercury, and selenium on reproductive indices in male lesser scaup (*Aythya affinis*) in the western boreal forest. Arch Environ Contam Toxicol 54:730–739

Robert M, Savard JPL (2006) The St. Lawrence River Estuary and Gulf: a stronghold for Barrow's Goldeneyes wintering in eastern North America. Waterbirds 29:437–450

Robert M, Benoit R, Savard JPL (2000) COSEWIC status report on the eastern population of the Barrow's Goldeneye (*Bucephala islandica*) in Canada. Committee on the Status of Endangered Wildlife in Canada, Ottawa

Robert M, Benoît R, Savard JPL (2002) Relationship among breeding, molting, and wintering areas of male Barrow's Goldeneye in eastern North America. Auk 119:676–684

Robert M, Drolet B, Savard JPL (2008) Habitat features associated with Barrow's Goldeneye breeding in Eastern Canada. Wilson J Ornithol 120:320–330

Saucier JF, Roy F, Gilbert D, Pellerin P, Ritchie H (2003) Modeling the formation and circulation processes of water masses and sea ice in the Gulf of St. Lawrence, Canada. J Geophys Res 108:1–20

Scheuhammer AM (1987) The chronic toxicity of aluminium, cadmium, mercury, and lead in birds: a review. Environ Pollut 46:263–295

Scheuhammer AM, Meyer MW, Sandheinrich MB, Murray MW (2007) Effects of environmental methylmercury on the health of wild birds, mammals, and fish. Ambio 36:12–17

Scheuhammer AM, Basu N, Burgess NM, Elliott JE, Campbell GD, Wayland M et al (2008) Relationships among mercury, selenium, and neurochemical parameters in common loons (*Gavia immer*) and bald eagles (*Haliaeetus leucocephalus*). Ecotoxicology 17:93–101

Shore RF, Pereira MG, Walker LA, Thompson DR (2011) In: Beyer WN, Meador JP (eds) Environmental contaminants in biota (2nd ed). CRC Press, Boca Raton, FL, pp 609–624

Smith VE, Spurr JM, Filkins JC, Jones JJ (1985) Organochlorine contaminants of wintering ducks foraging on Detroit River sediments. J Great Lakes Res 11:231–246

Trust KA, Rummel KT, Scheuhammer AM, Brisbin IL, Hooper MJ (2000) Contaminant exposure and biomarker responses in spectacled eiders (*Somateria fischeri*) from St. Lawrence Island, Alaska. Arch Environ Contam Toxicol 38:107–113

Uthe JF, Chou CL, Loring DH, Rantala RTT, Bewers JM, Dalziel J et al (1986) Effect of waste treatment at a lead smelter on cadmium levels in American lobster (*Homarus americanus*), sediments and seawater in the adjacent coastal zone. Mar Pollut Bull 17:118–123

Vorkamp K, Christensen JH, Glasius M, Riget FF (2004) Persistent halogenated compounds in black guillemots (*Cepphus grylle*) from Greenland—Levels, compound patterns and spatial trends. Mar Pollut Bull 48:111–121

Wayland M, Scheuhammer AM (2011) Cadmium in birds. In: Beyer WN, Meador JP (eds) Environmental contaminants in biota, 2nd edn. CRC Press, Boca Raton, pp 645–667