

Harlequin Duck Harvest and Contamination in Québec

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ABSTRACT

Since 1990, the ban on Harlequin Duck (*Histrionicus histrionicus*) hunting has reduced the number of bird wings provided by hunters during the Species Composition Survey (SCS) conducted in eastern Canada by 78%. Nevertheless this reduction is not distributed equally between provinces. In Québec, information gathered on Harlequin Duck hunting and accidental killing between 1970 and 2004 showed that the latter is the primary cause of mortality for harlequins, followed by sport and subsistence hunting. Over 50% of birds killed originated from the North Shore of the St. Lawrence River. In order to better protect this species, communication strategies in isolated regions should be implemented. Concentrations of most organochlorine contaminants and of mercury, cadmium, arsenic, and selenium in Harlequin Ducks are lower than those known to cause health problems in birds. However, the only adult female captured in spring had a higher liver selenium concentration than the threshold value (3 µg/g; wet weight) beyond which reproductive problems are known to occur in birds under experimental conditions.

RÉSUMÉ

Depuis 1990, l'interdiction de la chasse à l'Arlequin plongeur (*Histrionicus histrionicus*) a permis de réduire de 78 % le nombre d'ailes remises par les chasseurs lors de l'Enquête sur la composition des prises par espèce (ECPE) dans l'est du Canada. Cependant, la répartition par province de cette réduction est inégale. Au Québec, les informations recueillies entre 1970 et 2004 sur la chasse ou la récolte accidentelle d'Arlequins plongeurs ont permis de constater que cette dernière est la principale source de mortalité, suivie de la chasse sportive et de celle de subsistance. Plus de 50 % des oiseaux abattus provenaient de la Côte-Nord du Saint-Laurent. Des efforts de communication dans les régions éloignées seraient souhaitables pour mieux protéger cette espèce. Les concentrations de la plupart des contaminants organochlorés, de mercure, de cadmium, d'arsenic et de sélénium chez l'Arlequin plongeur sont inférieures à celles qui occasionnent des problèmes de santé chez les oiseaux. Toutefois, la concentration en sélénium dans le foie de la seule femelle adulte capturée au printemps est supérieure au seuil (3 µg/g; poids frais) au-delà duquel on constate des problèmes de reproduction chez les oiseaux en laboratoire.

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INTRODUCTION

The Harlequin Duck is an uncommon species in eastern North America. It nests predominantly in Northern Québec, Nunavik (north of the 55th parallel), Newfoundland and Labrador, on Baffin Island and in Greenland, and also in northern New Brunswick, in Québec, in the Gaspé Peninsula and the lower North Shore (Robertson and Goudie 1999). The Harlequin Duck is found along streams with clear, swift-flowing and turbulent waters, where it feeds on insects (Robert and Cloutier 2001).

In 1990, the eastern population of the Harlequin Duck was listed as an *endangered* species by the Committee on the Status of Endangered Wildlife in Canada (COSEWIC) because of the decline this small population had been showing since the beginning of the eighties. This decline was attributed to oil spills, unfavorable climatic conditions and hunting (Thomas and Robert 2001). Coastal settlements, natural resource extraction, forestry, hydro-electric power projects, and disturbances can also have an impact on this species (Goudie 1989; Thomas and Robert 2001). After a knowledge acquisition period, the species' status was re-assessed: in 2001, the COSEWIC listed the Harlequin Duck as a *special concern* species, a lower risk category, due to an increasing population size at wintering grounds and the discovery of birds wintering on Greenland coasts. These two factors contributed to the significant increase of the total population size (Thomas and Robert 2001). Harlequin Ducks nesting in eastern North America and in Greenland are considered to be part of the same distinct population under the *Species at Risk Act*; however, controversy surrounds this status. Some biologists believe that both populations of Harlequin Ducks should be considered to be distinct from each other, each with its own status (Thomas and Robert 2001), especially since management measures to restore these populations are different (Thomas and McAloney in press).

Telemetry data on Harlequin Ducks suggest the existence of two different populations, based on their respective wintering areas (Thomas and Robert 2001; Brodeur et al. 2002). Firstly, the northeastern North American population includes birds nesting in northern New Brunswick, the Gaspé Peninsula, and Newfoundland. Known wintering grounds are predominantly located along the American East Coast, particularly in Maine, but small groups are also found in Nova Scotia and Newfoundland. Secondly, the Greenlandic population includes harlequins nesting in Northern Québec, Labrador and Greenland. The primary wintering site of this sub-population is located on the south-west coast of Greenland. However, exchanges between these two populations do take place, as some males of the northeastern population winter along Greenland coasts (Robert et al. in press). The latter population numbers approximately 1 800 birds, while the former includes between 5 000 and 10 000 individuals (Thomas and Robert 2001; Robert et al. in press; Boertman and Mosbech 2002).

In the past, hunting was an important cause of mortality for the eastern population of North America and it would have contributed to the low population size estimate in the eighties (Goudie, 1989). Since 1990, Harlequin Duck hunting is banned in the Atlantic Flyway. Nevertheless, this species is still not spared from the threat of hunting. Even if population size is increasing at some major wintering sites, losses (or accidental killings) related to hunting are being reported each year. These losses, which are difficult to estimate, are caused in large part by misidentifications, but the lack of awareness among hunters remains the major contributing factor (Thomas and McAloney, in press). One of the objectives of this study is to document accidental

killings of Harlequin Ducks in Québec. An additional objective is to determine if metals and organic contaminants are found in this species, particularly in Québec, since high metal concentrations are sometimes observed in sea ducks, and no information is currently available on contamination of this species.

MATERIAL AND METHODS

In order to gather as much information as possible on Harlequin Duck harvest, several information sources were examined. The SCS data from 1973 to 2004 (Gobeil and Collins 2003) were investigated, as well as reports on field bag checks undertaken in the field by Canadian Wildlife Service biologists between 1949 and 2004 (CWS, unpublished data). A literature review was conducted to find mentions of Harlequin Duck captures, and consultations with provincial and federal conservation officers were held to identify offences related to this species. Information on accidental killings of this species was gathered from various sources (hunters, wildlife technicians, etc.) by Canadian Wildlife Service biologists.

The specimens used for chemical analyses originated from accidental killings. These were sent to the National Wildlife Research Centre (NWRC) in Ottawa for analyses. Only liver tissue was used in the analyses. Metal concentrations are expressed in dry weight of tissue.

Mercury

Mercury was analysed using the method described in Adeloju and Mann (1987) (MET-CHEM-AA-03C). The samples (≈ 0.5 g) were digested in a mixture of nitric and sulfuric acids (1:2) at 70°C. Potassium dichromate was then added to the mixture to complete the organic mercurial compound oxidation. Mercury concentrations were determined using a cold vapor technique (CVAAS) using an atomic absorption spectrometer model 3030-AAS (Perkin-Elmer) equipped with a VGA-76 (Varian) hybrid generator and a PSC-55 autosampler.

Selenium and arsenic

Selenium and arsenic concentrations were determined using the method described by Julshamn et al. (1981) (MET-CHEM-AA-02C). Sample digestion was carried out in acidic media (concentrated nitric acid) at 100°C for 6 hours. Arsenic and selenium were analyzed by graphite furnace atomic absorption spectrometry (GFAAS, Perkin-Elmer 3030b with a deuterium background corrector) equipped with a HGA-300 graphite furnace with an AS-40 autosampler.

Cadmium

Cadmium concentrations were determined using a method published by the Perkin-Elmer company (1982) (MET-CHEM-AA-01C). Nitric acid was added to weighed samples (≈ 0.5 g). Digestion took place overnight. Samples were digested at 100°C for two hours, and analysed using flame atomic absorption spectrophotometry (Perkin-Elmer 3030b) equipped with an atom concentrator (ACT-80) (Hinderberger et al. 1981).

Synthetic Organic Compounds

Synthetic Organic Compounds: The chemical analysis method used for organochlorine (OC) pesticides and polychlorinated biphenyls (PCB) is described in Won et al. (2001). A total of 22 organochlorine compounds and 41 PCB congeners were sought. The PCB congener classification used here is that of the International Union of Pure and Applied Chemistry (IUPAC) (Ballschmiter and Zell 1980). The standard procedure which was used and is described

in the Laboratory Service Methods Manual as MET-CHEM-OC-04C. Brief principle of the sample cleanup: Neutral extraction of sample with 1:1 DCM:Hexane after sample dehydration with anhydrous Na₂SO₄. Removal of lipids and biogenic materials by Gel Permeation Chromatography, and further cleanup by Florisil column chromatography. Quantitative analysis of OCs and PCBs is performed using capillary gas chromatograph, coupled with a mass selective detector.

Quality control of chemical analysis

Quality control of organochlorine compounds was undertaken by the NWRC. The reference material used (Herring Gull's eggs, *Larus argentatus*) is regularly analysed at the NWRC as described in Wakeford and Turle (1997). Generally, the NWRC includes a reference sample for every five samples analysed. The reference material used to control metal analyses is provided by the NRCC (National Research Council of Canada), and consists of Spiny Dogfish (*Squalus acanthias*) muscle (DORM-2) and liver (DOLT-2) tissues. Analysis values of reference samples used for metal and organochlorine compound analyses fell within the confidence interval of the provided standard values. The coefficient of variation of liver samples analysed in duplicate was 4.9% for mercury, 10.3% for selenium, 4.1% for arsenic, and 5.7% for cadmium.

Statistical analysis

Descriptive statistics were obtained using SAS® (2002). Non-parametric statistics (Mann-Whitney and Spearman's rho) were used for some comparisons, as sample size was small and the data normality assumption was not always respected.

RESULTS

Arlequin ducks harvest

The data from the Species Composition Survey data (Gobeil and Collins 2003) indicate that 49% of all Harlequin Duck wings received in eastern Canada between 1973 and 2004 originated from Ontario (Table 1). In eastern Canada, the number of wings gathered has declined by 79% since hunting for that species was banned (42 vs. 9 wings), and this has occurred over a relatively comparable period (17 vs. 14 years). Prior to the ban, most wings received were from Ontario (59.5%) and Québec (19.1%) (Table 1). Since the ban, the largest number of wings gathered has been in Québec and Newfoundland (Table 1). The total number of Harlequin Ducks killed from sport hunting in eastern Canada between 1990 and 2004 represents only 18% of all specimens received between 1973 and 2004 (Table 1). Most birds aged were adults (70.8%) (Table 2). Sixty-two percent of birds sexed were male.

Table 1 Number of Harlequin Duck wings received during the Species Composition Survey from 1973 to 2004.

Province	Legal Hunting		No Hunting		1973-2004	
	n	%	n	%	N	%
New Brunswick	1	2.4	0	0	1	1.9
Newfoundland	2	4.8	3	33.3	5	9.8
Nova Scotia	6	14.3	2	22.2	8	15.7
Ontario	25	59.5	0	0	25	49.2
Québec	8	19.1	4	44.4	12	23.5
Total	42	100	9	100	51	100

Table 2 Age and gender of Harlequin Ducks for which wings were received during the Species Composition Survey.

Age	Female	Male	Unknown	Total
Adult	13	18	3	34
Immature	2	7	5	14
Unknown			3	3
Total	15	25	11	51

In Québec, from 1973 to 1989, when sport hunting of this species was legal, eight wings were obtained through the SCS, in comparison with four wings between 1990 and 2004 (Tables 1 and 3). Due to the efforts deployed to gather information on Harlequin Duck sport or subsistence hunting, as well as on accidental killings, 27 specimens were reported between 1990 and 2004, compared to 10 specimens prior to 1990 (Table 3). Among all specimens, 21 (57%) came from accidental killing, nine (24%) from legal sport hunting, six (16%) from subsistence hunting practiced by natives, and one specimen died after having been fitted with a satellite transmitter. Of these 37 Harlequin Ducks, 19 (51%) came from federal hunting district B on the North Shore,

nine (24%) from districts E and J covering the Gaspé and the Magdalen Islands, and four (11%) from district F, located between Québec and Rivière-du-Loup.

Table 3 Capture dates and localities of Harlequin Ducks reported in Québec.

Year	Capture month	Location/ Origin	Hunting district	Reason	Bird number
2001	November	Saint-Pierre Lake	G	Accidental killing	2
2001	Fall	National survey ¹	E	Accidental killing	1
1998	Fall	Iles-de-la-Madeleine	J	Accidental killing	1
1997	November	Rimouski ²	E	Accidental killing	2
1996	April	Port-Daniel ²	E	Scientific study	1
1996	April	Little Mecatina River ²	B	Aboriginal harvest	3
1994	December	La Romaine ²	B	Accidental killing	1
1994	November	National survey	B	Accidental killing	2
1993	October	Cap Tourmente	F	Accidental killing	1
1993	November	Wabouchagamou Lake ³	B	Aboriginal harvest	1
1993	May	Olomane River ³	B	Aboriginal harvest	1
1993	June	La Romaine ³	B	Accidental killing	1
1993	October	Little Mecatina River ³	B	Accidental killing	1
1993	October-November	Tête-à-la-Baleine ³	B	Accidental killing	8
1991	October	National survey	F	Accidental killing	1
1987	September	National survey	E	Legal hunting	1
1987	Fall	Bag check	E	Legal hunting	1
1987	September	National survey	D	Legal hunting	2
1987	September	National survey	F	Legal hunting	1
1987	September	National survey	H	Legal hunting	1
1986	October	National survey	F	Legal hunting	1
1986	October	National survey	E	Legal hunting	1
1983	September	Wabouchagamou River ³	B	Aboriginal harvest	1
1977	September	National survey	E	Legal hunting	1

¹ Species Composition Survey (SCS).

² Specimens used for chemical analyses. Additional specimen from Newfoundland not included.

³ Taken from D'Astous 1994.

Arlequin ducks contamination

In total, eight birds were used for chemical analyses. These birds had been gathered between 1994 and 1997. The locations of these individual capture sites are shown in Figure 1 (seven birds in Québec, one in Newfoundland). Six specimens were accidentally killed by hunters or during subsistence hunting by natives and were given to conservation officers or biologists. Another died after it was fitted with a satellite transmitter (M. Robert, CWS, pers. comm.), and one was received from Newfoundland, with no known cause of mortality. Among the eight individuals, six juveniles (four males and two females), one adult female, and one individual of unknown sex and age (Newfoundland) were numbered.

The mean mercury concentration in liver tissue was 3.3 µg/g (Table 4). Only three mercury values were above 3 µg/g and these were found in juveniles from Little Mecatina River. In fact, these values are above those from the other harlequins that were harvested (Mann-Whitney, p=0.04). If these three values are excluded, the mean mercury concentration was 1.49 µg/g. Selenium concentrations were considerably higher than mercury; two were above 15 µg/g. These were measured in an adult from Port-Daniel (31.1 µg/g) and a juvenile from Rimouski

(18.6 µg/g). Liver [Hg] / [Se] ratios were below 1.1 (\bar{x} =0.41). No relationship between selenium and mercury concentrations could be uncovered (r =-0.43; p =0.28).

Table 4 Mean metal concentrations (µg/g; dry weight) in Harlequin Duck livers.

Metals	\bar{x}	Standard Deviation	n	Range
Mercury	3.30	3.05	8	0.72 - 9.72
Arsenic	0.42	0.23	8	d. l. - 0.83
Cadmium	1.59	1.12	8	0.62 - 3.63
Selenium	12.70	8.7	8	3.67 - 31.1

d. l.=detection limit

The mean cadmium concentration was low, with a value of 1.6 µg/g (Table 4). The highest cadmium concentration (3.6 µg/g) was found in the adult female. Arsenic was detected in only six samples. The average concentration was 0.42 µg/g; the highest value was found in a juvenile from Little Mecatina River (0.83 µg/g). The two samples in which arsenic was not found were from the Port-Daniel adult female and the Newfoundland individual.

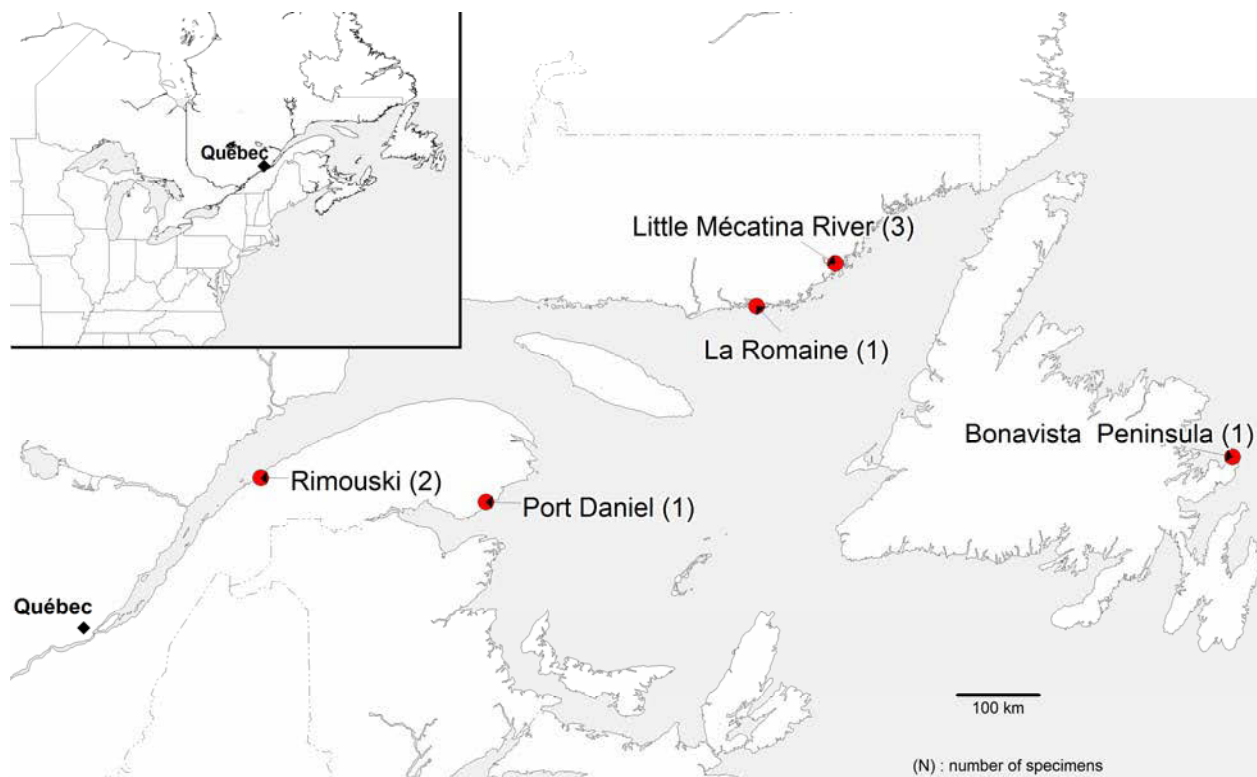


Figure 1 Location of the Harlequin Duck harvest sites in Québec and Newfoundland (number of individuals).

Detection percentages for organochlorine compounds are shown in Table 5. No single compound was detected in all samples. Six compounds (*p,p'*-DDE, oxychlordane, PCB, dieldrin, heptachlor epoxide, and hexachlorobenzene) were found in more than six individuals, while β -hexachlorocyclohexane was detected in only one sample. Fifteen compounds were not found or were detected only in trace amounts, these were: 1,2,3,4-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, *p,p'*-DDD, *p,p'*-DDT, photo-mirex, mirex, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, α -hexachlorocyclohexane, γ -hexachlorocyclohexane, octachlorostyrene, and tris(4-chlorophenyl)methanol.

Table 5 Percentage of detection and concentration ($\mu\text{g}/\text{kg}$; wet weight) of organochlorine compounds in Harlequin Duck livers.

Organochlorine Compounds	Percentage of Detection (%) (n=8)	Concentration		
		\bar{x}	Standard Deviation	Range
Hexachlorobenzene	75	1.5	0.7	0.5 - 3
<i>p,p'</i> -DDE	88	6.1	3.3	0.5 - 16
Oxychlordane	75	2.1	1.2	0.5 - 7
Heptachlor epoxide	75	1.3	0.5	0.5 - 2
Dieldrin	88	2.9	1.2	0.5 - 4
Polychlorinated biphenyls	75	59.8	40.4	0.5 - 233
β -Hexachlorocyclohexane	13	0.4	0.3	d.l. - 2

d. l.=detection limit

All organochlorine compound concentrations measured were below 300 $\mu\text{g}/\text{kg}$ (Table 5). PCBs and the DDT summation (Σ) (*p,p'*-DDD, *p,p'*-DDT, *p,p'*-DDE) represented more than 60% of the concentration sum. Oxychlordane, DDE and PCB concentrations were correlated ($r_s > 0.75$; $p < 0.04$). The average ratio of DDE to PCB concentrations was 0.24. The highest DDE (16 $\mu\text{g}/\text{kg}$) and PCB (233 $\mu\text{g}/\text{kg}$) concentrations were measured in two of the three juveniles killed at Little Mecatina River in Québec. Other concentrations above 10 $\mu\text{g}/\text{kg}$ were found in Port-Daniel samples (DDE: 13 $\mu\text{g}/\text{kg}$; PCB: 79 $\mu\text{g}/\text{kg}$) and in Little Mecatina River samples (DDE: 10 $\mu\text{g}/\text{kg}$; PCB: 150 $\mu\text{g}/\text{kg}$, and 11 $\mu\text{g}/\text{kg}$). Concentrations for all other compounds were less than 8 $\mu\text{g}/\text{kg}$. No significant difference in organochlorine compound and metal concentrations was found between samples from Little Mecatina River and those from elsewhere, except in the case of oxychlordane (Mann-Whitney, $p < 0.017$). Oxychlordane concentrations in birds from Little Mecatina River were five times higher than those in individuals from other localities (4.3 $\mu\text{g}/\text{kg}$ vs. 0.8 $\mu\text{g}/\text{kg}$).

PCB homologues with five and six chlorine atoms were the most abundant (Figure 2). They constituted more than 80% of total PCBs. The most abundant congeners were, in decreasing order, numbers 153, 138, 118, 187, 180, and 146. They represented more than 62% of total PCBs. It should be noted that no PCBs were detected in two of the specimens; the birds harvested at La Romaine and in Newfoundland.

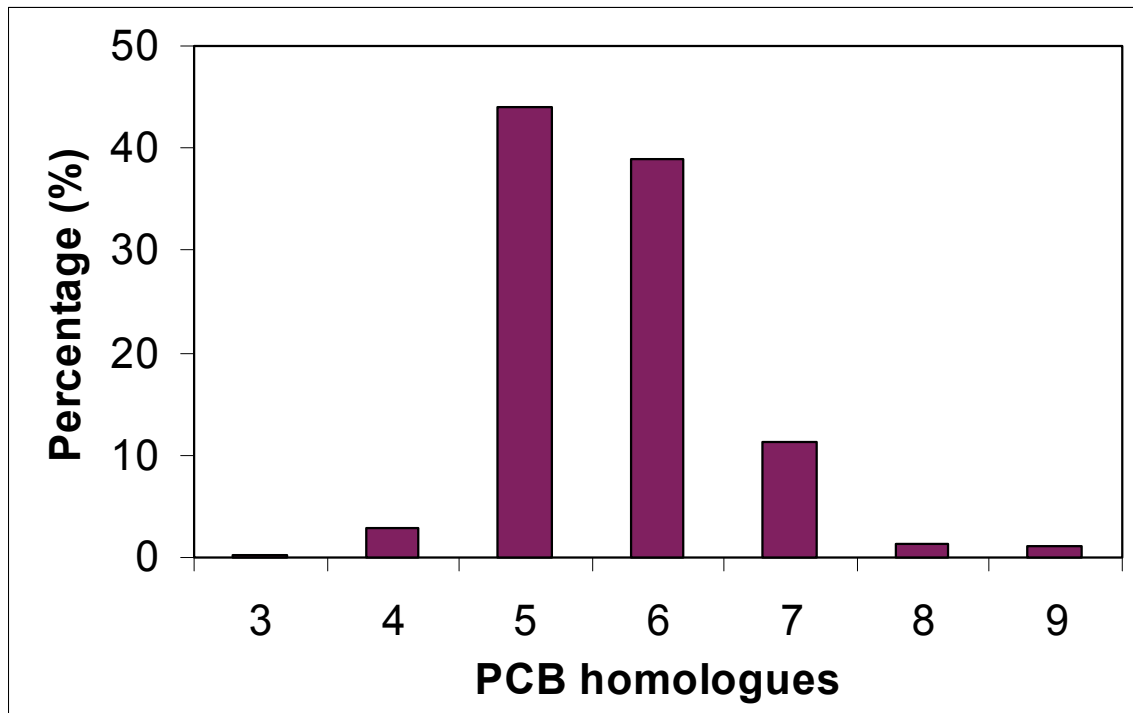


Figure 2 Distribution of PCB homologues in Harlequin Duck livers.

DISCUSSION

The number of Harlequin Ducks killed by hunters in eastern Canada between 1990 and 2004 represented only 14% of all specimens received between 1974 and 2004 during the SCS (Table 1). These results confirm that the ban on hunting was an effective management measure for this species. Nevertheless, it is surprising that no Harlequin Duck wing was received from Ontario between 1990 and 2004, and this, despite the fact that more than 59.5% of wings came from this province when hunting was still allowed. However, Harlequin Ducks are indeed present in Ontario; this species has been observed each fall in this province since the 1980's (Bain 2000, 2001, 2002, 2003; Elder 2004; Goodwin 1981, 1982; Ridout 1993, 1994, 1995, 1996, 1997, 1998; Weir 1983, 1984, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992). Furthermore, this species has been inventoried every year since 1970 during the Christmas Bird Count (CBC), with the exception of 1986 (Website: www.audubon.org/bird/cbc/index.html).

There are two reasons that may explain why it is difficult to estimate the number of Harlequin Ducks accidentally killed in eastern North America. The first is species identification: the darker juvenile and female plumages make species identification more difficult for hunters, whose abilities may vary greatly between species (Lederer and Fickett 1974; Neiman et al. 1987). The second is related to hunters' reaction when they accidentally kill protected duck species; they may attempt to discard the prey in order to avoid prosecution. Examples of this behaviour were observed in western Canada when legal restrictions related to the Redhead (*Aythya Americana*) were in effect (Hochbaum and Caldwell 1977). Nevertheless, some hunters have, in the past, turned over to biologists Harlequin Ducks that had been accidentally killed, on the condition that no legal action would be taken against them. In fact, if conservation officers in Québec catch a hunter in possession of a Harlequin Duck, they always investigate the case before laying charges. If they believe that the killing was involuntary, and if the hunter has no record, they may, at their discretion, simply issue a warning or take appropriate legal actions (F. Daigle, CWS, pers. comm.). If, during the SCS, the Canadian Wildlife Service, Québec Region, receives the wing of a protected species, a letter is sent to the hunter, notifying him or her of the error committed (P. Brousseau, CWS, pers. comm.). The significant difference between the number of Harlequin Ducks killed before and after 1990 in Québec is probably amplified since real information on specimens killed prior to 1990 has been lost or forgotten.

Goudie et al. (1994) estimated that the Harlequin Duck population can withstand a harvest rate between 3% and 5% without being affected. Thus, for a population of 1 800 individuals, the sustainable harvest is between 54 and 90 birds per year. Despite the limited information available on yearly accidental kills of Harlequin Ducks, it is unlikely that these reach the threshold value in Québec only.

Four of the specimens harvested for chemical analyses (those from La Romaine (1994) and those from Little Mecatina River (1996)) were received a few years after a meeting with natives and non-natives that was aimed at determining Harlequin Duck occurrences on the Lower North Shore in 1993 (D'Astous 1994). These specimens were made available because of the success of awareness-raising activities on the species' status conducted among some members of these remote communities. But despite increased awareness, accidental killings still occur. The remote communities of the Lower North Shore and Northern Québec, being located within Harlequin Duck breeding areas and migratory corridors in Québec, should be targeted for the application of

a specific awareness strategy, to be conducted through the organisation of meetings since these communities are difficult to reach with traditional methods (leaflets, newspapers, television, etc.).

There is apparently no published study on metal levels in the Harlequin Ducks. Mercury concentrations in Harlequin Ducks measured in this study were below those known to cause health problems in other bird species (Thompson 1996). Mean mercury concentrations in Harlequin Duck livers were higher than those in Great Blue Heron juveniles (*Ardea herodias*) along the St. Lawrence River, but lower than those in adults (Rodrigue et al. 2005). These concentrations were on average ten times higher than those published on many dabbling duck species in the Prairies (Vermeer and Armstrong 1972; Driver and Derksen 1980), but five to eight times lower than those in some Common Mergansers (*Mergus merganser*) and Common Loons (*Gavia immer*) in eastern Canada (Scheuhammer et al. 1998). Mercury does not seem to cause problems for Harlequin Ducks, perhaps not only because most bird species can demethylate methylmercury (a detoxification mechanism) (Norheim and Frosli 1978), but also because of the presence of sufficient amounts of selenium to combine with mercury and thus protect against the toxic effects of mercury. The [Hg] / [Se] ratio of 0.41 is below the Hg / Se (1:1) molar ratio of 2.54.

Selenium is an essential growth nutrient in animals and is mostly found in the kidneys and liver (Underwood 1971; Arthur 1972; Eisler 1985; Leonzio et al. 1986). It builds up through the aquatic food chain (Ohlendorf et al. 1986; Mora and Anderson 1995); high selenium concentrations are observed in several sea duck species (Ohlendorf et al. 1989; Henny et al. 1991). Selenium concentrations in Harlequin Ducks were lower than those in some species of dabbling ducks in California (Paveglio et al. 1992); however, they are similar to those in Common Mergansers in eastern Canada (Scheuhammer et al. 1998). In Québec, the mean selenium concentration measured in the liver of three adult scoter species was 25.8 µg/g (dry weight) (J. Rodrigue, pers. comm.); thus lower than that measured in the adult Harlequin Duck (31.1 µg/g) (dry weight). However, selenium concentrations for these three scoter species have been found to be very high: 14.6% were above 50 µg/g (J. Rodrigue, pers. comm.).

All selenium concentrations in livers were below the threshold value for sublethal effects in birds, that is, below 10 µg/g (wet weight) (Heinz 1996). Nevertheless, the concentration in the adult female captured in the spring was 9.11 µg/g (wet weight); thus higher in the liver than the threshold value (3 µg/g; wet weight), above which reproductive problems are known to occur in adult females (Heinz 1996). Comparison between species is difficult because of interspecific differences related to toxicity thresholds (Smith et al. 1988). These thresholds are based on a continuous intake of selenium, which does not apply to individuals in a natural environment, as the selenium concentration in freshwater environment, and therefore at breeding and rearing areas, is usually lower than in the marine environment (probably due to very different diets). In the summer, Harlequin Ducks feed almost exclusively on insects; in marine environment, crustaceans and molluscs (Goudie and Ankney 1986). Added to this is the suppression of selenium in the diet, which has been shown to cause a reduction of 50% in concentrations in livers of Mallards (*Anas platyrhynchos*) in 18.7 days (Heinz et al. 1990). It thus seems very likely that a decline in concentration occurs during the transition of birds from a marine to a freshwater environment, and that the extent of this decline depends on the number of days between the date of arrival at the breeding site and the date when the first egg is laid in May (Savard et al. in press). Finally, bird age and breeding status must also be considered. Diving ducks, in particular, do not necessarily breed during their second year, nor do they do so annually (Coulson 1984). However, it would be

interesting to obtain tissue samples of adults who died or were killed accidentally in order to increase the number of samples to analyse.

Cadmium is bioaccumulated throughout life, particularly in the kidneys and liver, two organs that contain together almost 80% of the organism's body burden (Scheuhammer 1991). Cadmium concentrations in Harlequin Duck livers were lower than those measured in three scoter species in Québec: $\bar{x} > 10.4 \mu\text{g/g}$ (J. Rodrigue, pers. comm.). Cadmium concentrations that are known to cause problems are much higher than those detected in Harlequin Ducks (White and Finley 1978; White et al. 1978).

Arsenic concentrations measured in organisms living in freshwater environments are typically below $1 \mu\text{g/g}$ (Eisler 1988). These low concentrations are probably due to the fact that arsenic does not biomagnify in the food chain (Eisler 1988). Arsenic concentrations in Harlequin Duck livers are similar to those measured in fish taken from Saint-Pierre Lake ($< 0.05 \mu\text{g/g}$ - $0.34 \mu\text{g/g}$; wet weight) (Langlois and Sloterdijk 1989), and higher than those measured in kidneys of young herons along the St. Lawrence River ($\bar{x} = 0.06 \mu\text{g/g}$; dry weight) (Rodrigue et al. 2005).

Organochlorine contaminant concentrations were very low, and below those known to cause health problems in other species (Eisler 1986; Noble and Elliott 1990). The only published results found on Harlequin Duck contamination come from the west coast of Greenland in 1972. The p,p'-DDE and PCB levels measured in fat were respectively 1.1 mg/kg and 1.2 mg/kg (Braestrup et al. 1974). In the Harlequin Duck, DDE, the main metabolite of DDT accounts for almost 100% of the total sum of DDT and its metabolites. High proportions are also observed in belugas (*Delphinapterus leucas*) (79% to 94%) of the St. Lawrence River (Massé et al. 1986), and in Great Blue Herons along the St. Lawrence (84% to 97%) (Rodrigue et al. 2005). The authors of these studies explain this high ratio by DDT metabolic decomposition, and the absence of recent DDT intake. The mean DDE and PCB concentrations in the liver of young herons along the St. Lawrence estuary and the gulf are between four and five times higher than those of Harlequin Ducks (Rodrigue et al. 2005), but are similar to those of American Black Ducks captured in 1986 in Lake Saint-Pierre (Laporte 1987).

PCB concentrations and congener signatures can vary according to the type of PCBs present in the environment, gender, size, metabolic rate and health status, as well as the time elapsed since the ingestion of the compound (Norstrom et al. 1978). Because the number of chlorine atoms impacts on degradation rate, low chlorinated homologues are quickly metabolized. An important number of PCB homologues with five or six chlorine atoms suggest a low PCB intake, which is usually the case in freshwater reaches of the St. Lawrence (Rodrigue et al. 2005). The congeners numbers 138, 153, and 180 found in the Harlequin Duck are among those most often detected in wildlife (Focardi et al. 1988; Elliott et al. 1989; Turle et al. 1991).

Exposure sources of the Harlequin Duck to organochlorine compounds are limited not only because of its diet that is low in contaminants (benthics and insects) compared to piscivorous birds, but also because of the species distribution. Indeed, the Harlequin Duck winters in the northern United States, in Canada, or in Greenland, where organochlorine pesticides have been less used than in South America. If the downward trend of PCB and DDE concentrations in wildlife since the last twenty years is also considered (Hodson et al. 1994; Renaud et al. 1995; Ion et al. 1997; Pekarik and Weseloh 1998), then the low concentrations measured in this study

are not surprising. However, the situation is different for metals. It is generally accepted that concentrations of some metals are higher in birds living in salt water than those living in fresh water. Part of the variation in concentrations is not only related to the age of the individual, but also to physiological processes that change according to seasons, such as the capture date of the specimen, for example.

CONCLUSION

Between 1974 and 2004, accidental harvest of Harlequin Ducks in Québec was a more important cause of mortality than legal subsistence sport hunting. Over 50% of birds killed originated from the North Shore of the St. Lawrence River. In order to better protect this species, communication strategies adapted to isolated regions should be implemented. Concentrations of most organochlorine contaminants and of mercury, cadmium, arsenic, and selenium in Harlequin Ducks are low. Nevertheless, since the majority of individuals are juveniles, it is likely that, in general, contaminant concentrations are greater in adults. Moreover, the only adult female used in the study had a liver selenium concentration higher than the threshold value (3 µg/g; wet weight), above which reproductive problems are known to occur in some birds.

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