# Contaminants in Overwintering Canvasbacks (*Aythya valisineria*) and Resident Mallards (*Anas platyrhynchos*) in the Lake St. Clair/St. Clair River Area


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## Abstract

Overwintering canvasbacks and resident mallards were collected in the Lake St. Clair/St. Clair River area in the winters of 2008/09 and 2010, respectively, and livers were analyzed for organochlorines, brominated flame retardants, mercury (Hg) and selenium (Se). Hepatic concentrations of organochlorines, brominated flame retardants, and Hg in all birds were low and Hg concentrations were below levels associated with adverse effects on survival. Hepatic concentrations of Se were largely low but were more variable among birds with 25% of canvasbacks showing concentrations considered elevated and 5% (i.e., one bird) with a concentration exceeding the threshold associated with toxicity. Comparisons of contaminant burdens in mallards in 2010 with those in birds collected from the St. Clair River in 1985/86 revealed large declines in concentrations of organochlorines in liver with percent declines ranging from 80.0% - 99.9%. In canvasbacks, significant increases in hepatic concentrations of Hg and Se, sum PCBs, *p,p'*-DDE and other organochlorines were evident over the four month period of collection in which mean concentrations in January and/or February were significantly higher than mean concentrations in November when overwintering birds arrived in the study area. The largest increases were most often between December and January which also coincided with the period when birds from Lake St. Clair moved, following freeze-up of the lake, to the St. Clair River to forage. It is unclear to what extent possible changes in diet, level of contamination and/or declines in lipid reserves following movement to the St. Clair River contributed to observed temporal trends in overwintering canvasbacks. Overall, current hepatic concentrations of contaminants in these two species of waterfowl, including those birds collected within the St. Clair River Area of Concern, were likely not sufficiently high to significantly impact survival.

## Introduction

The lower Great Lakes and particularly Lake St. Clair provide important staging and wintering habitat for numerous waterfowl species, including diving ducks such as canvasbacks (*Aythya valisineria*; Mullie *et al.* 1996). Following breeding in the prairies, canvasbacks migrate to major staging areas on the upper Mississippi near Wisconsin in the fall and then migrate to secondary staging areas on the Great Lakes, including Lake St. Clair and the St. Clair and Detroit rivers (Mowbray 2002). While most continue their migration to the wintering locations along the Atlantic coast, some remain in open-water areas and rivers in the region. During winter, canvasbacks consume primarily plants such as tubers of wild celery (*Vallisneria americana*) and, when plant foods are limited, small clams and snails (Mazak *et al*. 1997; Mowbray 2002; Long Point Waterfowl Newsletter 2010). In March and April, birds begin their spring migration back to breeding grounds in the central and eastern prairies of northern US and Canada (Mowbray 2002).

Historical industrial and municipal point sources in the upper reaches of the St. Clair River have contributed significant loadings of pollutants to the river which have been detected in water, sediment, and biota as well as in regions downstream including Lake St. Clair (Oliver and Bourbonniere 1985; Pugsley *et al.* 1985; OMOEE and MDNR 1991, 1995). Contaminants of concern associated with these sources were identified and include hexachlorobenzene (HCB), octachlorostyrene (OCS), polychlorinated biphenyls (PCBs), and heavy metals such as mercury. Once introduced into the aquatic environment, many of these contaminants become available to biota, bioaccumulate in aquatic organisms and fish and then biomagnify through the food web. Following the designation of the St. Clair River as an Area of Concern (AOC) in 1985, restrictions on discharges, improved industrial and municipal practices as well as sediment remediation projects have reduced contaminant loadings to the river (Mayne 2008). However, recent evidence of elevated concentrations of mercury, PCBs and other organochlorines in juvenile spottail shiner (*Notropis hudsonius*) from the St. Clair River suggest that historically-contaminated sediment in the river might be a continued source of chemicals to the food web (Gewurtz *et al.* 2010). Waterfowl such as diving and dabbling ducks which forage on submerged plants and benthic invertebrates have more contact with sediment and consume sediment-based food. Consequently as a result of their foraging behaviour, these ducks might be at an increased risk of contaminant exposure particularly in areas of the river where sediment is highly contaminated.

The primary objective of this study was to determine the level of contamination in livers of overwintering canvasbacks in the Lake St. Clair and St. Clair River area over a four month period in 2008/09. If canvasbacks are accumulating contaminants in this area, are concentrations sufficiently high to warrant concern regarding survival of these birds feeding within the St. Clair River AOC? A small number (3) of resident mallards (*Anas platyrhynchos*) were also collected from the Walpole Delta in the lower portion of the St. Clair River in 2010 to examine exposure in relation to contaminant concentrations associated with potential effects on survival. As an indication of long-term temporal trends for contaminants in waterfowl in this area, current concentrations in mallards were also compared to concentrations in birds from an earlier collection period in the mid-1980s (Environment Canada (EC) unpublished).

## Methods

**Specimen Collection** - Specimen collection for this study was part of a large research project conducted by the Long Point Bird Observatory examining wintering ecology of canvasbacks and redheads (*Aythya americana*) on Lake St. Clair and the Detroit and St. Clair rivers. Canvasbacks (N=148) were shot by firearms over a four month period in 2008/09 on Lake St. Clair and the St. Clair River, collectively known in this report as the Lake St. Clair/St. Clair River study area. Specifically, birds were collected in November and December from Lake St. Clair where this species typically forages in shallow, open water habitats in the fall and early winter (Long Point Waterfowl Newsletter 2010). Following freeze-up of Lake St. Clair, birds move to the open, fast water areas of the St. Clair River where they were collected in January and February. Upon collection, livers were removed, wrapped in hexane-rinsed aluminum foil and frozen at -20$^{o}$C. A subsample of 30 birds consisting of five males and 25 females were selected for contaminant analyses. Collection months and numbers of birds were as follows: November (8), December (8), January (8) and February (6). Twenty of these birds were hatch year birds, i.e., birds that had hatched the previous spring. The remaining ten birds were adult female birds, the ages of which were confirmed upon internal examination by the absence of the cloacal bursa; collection months of these birds were November (2), December (2), January (2), and February (4). Birds from Lake St. Clair were collected near Mitchell's Bay with the exception of two birds which were collected approx. 1.6 km offshore in Anchor Bay in Michigan. Birds collected from the St. Clair River were from three main locations in Ontario: Stag Island/Corunna and adjacent to the Lambton Power Plant and the Terra Plant, which are approximately 10 and 13 kilometres downstream, respectively, from Stag Island. Three resident mallards were also collected from the study area within the Walpole Delta in the Walpole Island First Nations Territory in November of 2010. Resident mallards were distinguished from migratory birds by leg colouration and plumage.

**Contaminant Analyses** - Chemical analyses of liver for organochlorine contaminants were conducted at the Great Lakes Institute for Environmental Research at the University of Windsor, Ontario. Frozen liver samples were thawed and homogenized. Samples underwent neutral extraction, removal of lipids and then further cleanup by gel permeation chromatography. Quantitative analysis of organochlorine compounds including PCBs was performed by gas chromatography using a mass selective detector (GC/MSD) using standard solutions for quantifying organochlorines. Organochlorine compounds included: *p,p′*-DDE (dichlorodiphenyldichloroethylene), *p,p′*-DDT (dichlorodiphenyltrichloroethane), *p,p′*-DDD (dichlorodiphenyldichloroethane), oxychlordane, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, HCB, dieldrin, heptachlor epoxide (HE), OCS, and mirex. Sum DDT is based on the sum concentrations of *p,p′*-DDE, *p,p′*-DDT, and *p,p′*-DDD. Sum chlordane is based on the sum concentrations of oxychlordane, *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, and *trans*-nonachlor. Sum PCBs were based on the sum concentrations of 38 individual and co-eluting PCB congeners (IUPAC# 17, 18, 31/28, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 138, 149, 151, 153/132, 156, 158, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 205, 206, 208, and 209). Polybrominated diphenyl ethers (PBDEs) were measured in liver by gas chromatography high resolution mass spectrometry methods using a time-of-flight mass spectrometer (GC-MS-TOF). Sum PBDEs were based on the sum concentrations of 22 congeners (IUPAC# 3, 7, 15, 17, 28, 47, 49, 66, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183, 184, 191, 196, and 197). Great Lakes carp (*Cyprinus carpio*) homogenate or Standard Reference Material 1947 from NIST was also analyzed with each run for quality assurance purposes. Two standards, PCB #34 and BDE #71, were also analyzed to measure sample recovery efficiency and samples were not adjusted for recoveries. Detection limits for organochlorines including individual PCB congeners ranged from 0.006 ng/g to 0.178 ng/g wet weight (ww) and for individual PBDE congeners ranged from 0.052 ng/g to 0.426 ng/g ww.

Chemical analyses of liver for total mercury (Hg) and selenium (Se) were conducted at the Environmental Analytical Laboratories at Laurentian University in Sudbury, Ontario. Frozen liver samples were freeze dried, homogenized to a fine powder and stored at -15$^{o}$C prior to digestion. A 0.2 g liver sample was microwave digested with a mixed chemical reagent containing 2.0 mL 30% $H_2 0_2$ and 8.0 mL 15.0 M $HNO_3$. Digestion included a multi-step preheating process from room temperature to 85$^{o}$C, then to 145$^{o}$C and finally to 210$^{o}$C, sample mineralization at 210$^{o}$C for 10 minutes, and venting to cool samples. Determinations of total Hg and Se were made by cold vapor atomic fluorescence spectrometry and hydride generation atomic fluorescence spectrometry, respectively. Quality control was performed with DOLT-3 (dogfish liver) certified by the National Research Council of Canada. One DOLT-3 sample and one reagent blank were analyzed in parallel with every eight samples digested. Detection limits were equal to 0.0005 µg/g dry weight (dw) and 0.1 µg/g dw for Hg and Se, respectively. Values are reported in ng/g ww concentrations for organochlorines and PBDEs and µg/g dw concentrations for metals unless indicated otherwise.

**Statistical Analyses** - Student's *t*-tests or Analysis of Variance (ANOVA) tests were performed to examine differences in mean contaminant concentrations between species or among collection months, respectively. In cases where the ANOVA test was significant, the post-hoc Tukey HSD test for unequal size groups was employed. Data were log-transformed ($log_{10}$) to meet conditions of equal variance and normality for parametric analysis. If data failed these assumptions, a Kruskal Wallis one way analysis of variance by ranks followed by non-parametric multiple contrast tests for unequal sample size was employed (Zar 1984). To examine the possible influence of age of birds (i.e., adult vs hatch year) on temporal trends in contaminant concentrations, a two-way ANOVA was conducted. Concentrations of compounds found below the limit of detection were given a concentration of one-half of the detection limit for calculations of mean values. All results were considered significant at $p<0.05$.

## Results

Of the organochlorines, sum PCBs and *p,p'*-DDE were found most consistently at the highest concentrations in livers of canvasbacks and resident mallards in the Lake St. Clair/St. Clair River study area (Table 1). Mean hepatic sum PCBs and *p,p'*-DDE concentrations (±SD) in canvasbacks were 18.15 (±31.79) ng/g and 3.10 (±5.73) ng/g, respectively, while relatively lower mean concentrations of sum PCBs (4.51 ng/g) and *p,p'*-DDE (1.38 ng/g) were found in the three mallards collected from the Walpole Delta in 2010. Notably high mean concentrations of HCB (7.96 ng/g) and OCS (39.10 ng/g) were found in livers of canvasbacks from this area. These means, however, were largely influenced by one adult female collected in February with an elevated concentration of both HCB (184.67 ng/g) and OCS (1046.33 ng/g) which

Table 1. Mean concentrations (SD) of organochlorines and sum PBDEs (ng/g, wet weight) and metals (µg/g, dry weight) in livers of canvasbacks and resident mallards from the Lake St. Clair/St. Clair River study area in 2008/2009 and 2010, respectively. N denotes the number of individuals analyzed with the exception of sum PBDEs in canvasbacks where the mean shown is based on analysis of three individuals.

| **Species** | **Canvasbacks** | **Mallards*** |
|---|---|---|
| **N** | 30 | 3 |
| Percent lipid | 3.6 (1.1)% | 5.2 (2.5)% |
| Sum PCBs | 18.15 (31.79) | 4.51 (1.81) |
| *p,p'*-DDE | 3.10 (5.73) | 1.38 (1.64) |
| Sum DDT | 3.19 (5.78) | 1.43 (1.64) |
| Sum Chlordane | 0.68 (0.75) | 0.47 (0.43) |
| HCB | 7.96 (33.47) | 0.05 (0.06) |
| HCB – one high bird removed | 1.87 (2.53) | - |
| Mirex | 0.05 (0.08) | 0.05 (0.05) |
| Dieldrin | 0.89 (1.93) | 0.35 (0.45) |
| HE | 0.74 (1.27) | 0.10 (0.07) |
| OCS | 39.10 (190.72) | 0.06 (0.04) |
| OCS – one high bird removed | 4.36 (13.79) | - |
| Sum PBDEs | 0.19 (0.01) | 0.26 (0.16) |
| Mercury (µg/g, dw) | 0.58 (0.48) | 0.36 (0.26) |
| Selenium (µg/g, dw) | 9.07 (6.93) | 3.08 (0.27) |

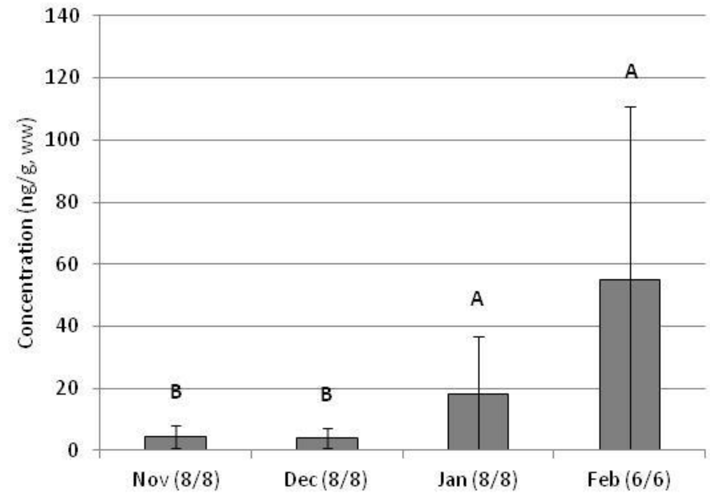
* Mallards collected from Walpole Delta

exceeded concentrations of these compounds in other birds by at least 22 and 14 fold, respectively. Removal of this one bird resulted in relatively lower overall mean concentrations (±SD) reported for HCB (1.87 (±2.53) ng/g) and OCS (4.36 (±13.79) ng/g) in canvasbacks. For the remaining organochlorines, concentrations were low and frequently below the limit of detection (see below) with means below 0.9 ng/g in canvasbacks and 0.5 ng/g in mallards. Sum PBDE concentrations were also very low in the three individuals of each species for which these were measured.

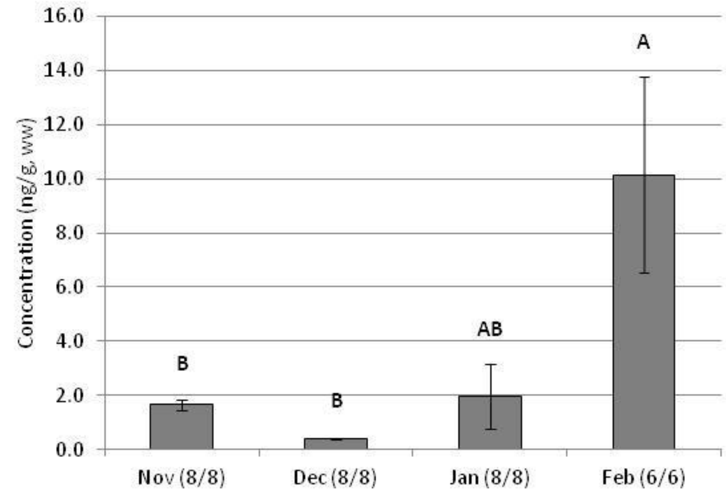
Hepatic mercury (Hg) and selenium (Se) in canvasbacks and mallards were found at relatively higher concentrations compared to organochlorines. On a dry weight basis, mean concentrations (±SD) of Hg and Se in canvasbacks were 0.58 (±0.48) µg/g and 9.07 (±6.93) µg/g, respectively (or 0.19 (±0.16) µg/g and 2.98 (±2.41) µg/g, respectively, on a wet weight basis). Mean concentrations (±SD) of Hg and Se in mallards were relatively lower at 0.36 (±0.26) µg/g and 3.08 (±0.27) µg/g, respectively (or 0.11 (±0.08) µg/g and 0.98 (±0.06) µg/g, respectively, on a wet weight basis). Hg concentrations in all birds were below 1.42 µg/g dw with the exception of one hatch year canvasback which exceeded this concentration (2.09 µg/g). Se concentrations in 30 canvasbacks were below 10 µg/g dw in 67% of birds (20), between 10-20 µg/g in 30% of birds (9) and above 20 µg/g in 3% of birds (1 hatch year individual; 36.60 µg/g). Hg and Se concentrations in the three mallards were low and below 0.66 µg/g and 3.34 µg/g, respectively. A highly significant correlation was found between Hg and Se concentrations in livers of canvasbacks ($r_s$=0.84, p<0.00001, N=30). The relationship was not examined in mallards due to small sample size. As a result of high variability in contaminant concentrations in canvasbacks, no significant differences in concentrations of organochlorines, sum PBDEs, and Hg were found between the two species. Se was the only exception in which concentrations were significantly higher in canvasbacks compared to mallards ($t_{31}$=2.33; p=0.03). Upon comparing the two species in the same collection month (i.e., November), no significant differences in concentrations were found for any contaminants.

A closer examination of contaminant concentrations in canvasbacks grouped by collection month revealed evidence of significant temporal trends in the study area from November to February in the winter of 2008/09 (Figure 1). Significant differences in mean hepatic contaminant concentrations of sum PCBs, *p,p'*-DDE, Hg and Se were consistently found among collection months (p<0.001). Birds collected in February from the St. Clair River had significantly higher concentrations of these compounds compared those collected in November from Lake St. Clair. Overall significant differences among collection months were also found for OCS, HCB, dieldrin, HE, sum chlordane and mirex which were detected at relatively lower concentrations and which were also frequently below the limit of analytical detection (p<0.03). Specifically, a greater numbers of birds had contaminant concentrations above the limit of detection in the last two months compared to the first two months, largely influencing the reported trends and apparent increases in concentrations between November and February when birds were collected from Lake St. Clair and the St. Clair River, respectively. Numbers of birds with concentrations above the detection limit by month are shown in Figure 1. In the case of OCS, dieldrin, and mirex, while significant temporal effects were found overall (p=0.025), no significant differences were evident between individual months in the post-hoc analysis. Upon comparing means of consecutive months, the greatest increases for sum PCBs, Hg, Se, HCB, dieldrin, and HE were found between December and January when birds moved from Lake St. Clair to the St. Clair River (range of increases between mean concentrations=2-14

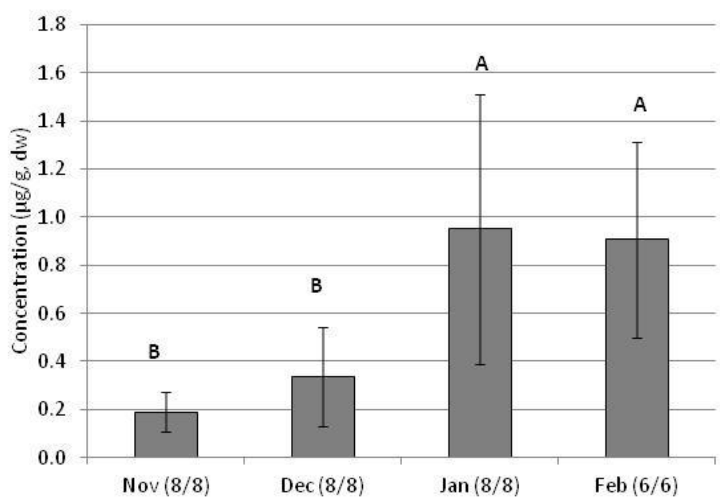
Figure 1. Mean concentrations (SD) of contaminants in livers of canvasbacks collected in November (N=8), December (N=8), January (N=8) and February (N=6) from Lake St.Clair and the St. Clair River in 2008/09. Ratios shown for each month represent the number of birds with a concentration above the level of detection relative to the total number of birds analyzed in that month. Detection limits are also provided for compounds found below the limit of detection. Different letters indicate significant differences in concentrations between collection months.



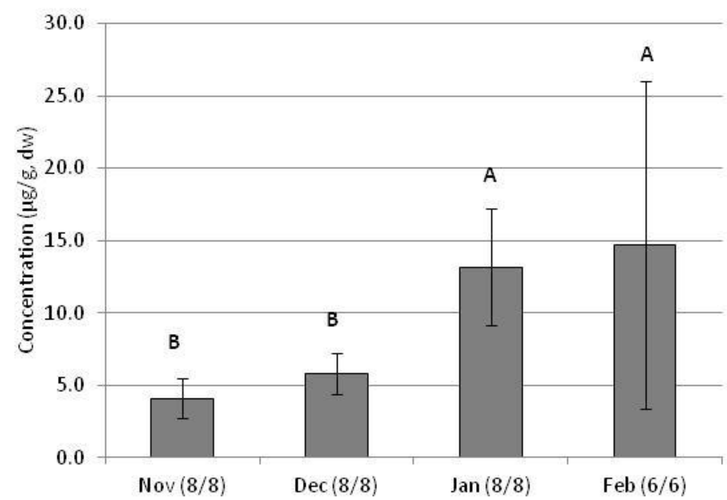

a) Sum PCBs – all birds above the limit of detection




b) *p,p'*-DDE - all birds above the limit of detection

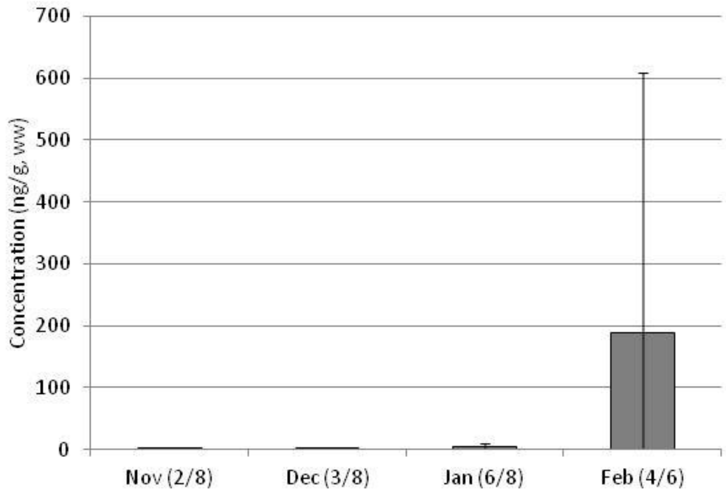



c) Mercury (Hg) - all birds above the limit of detection

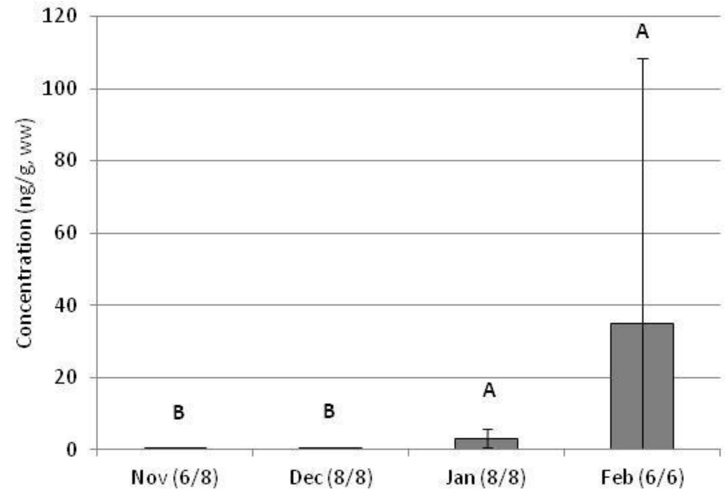



d) Selenium (Se) - all birds above the limit of detection

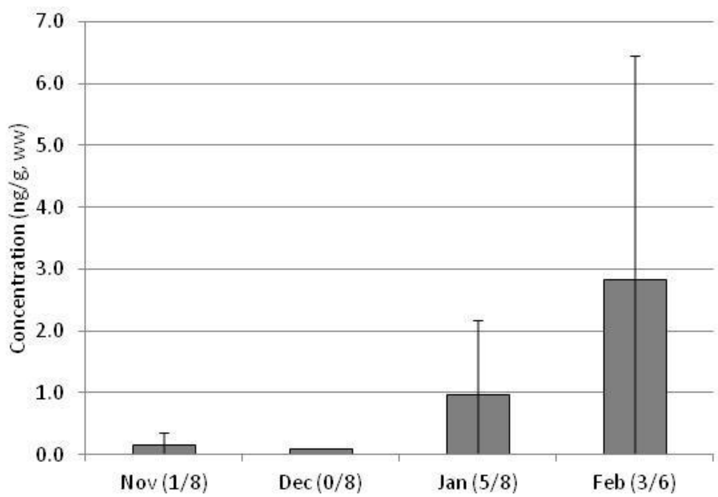
Figure 1 (continued)



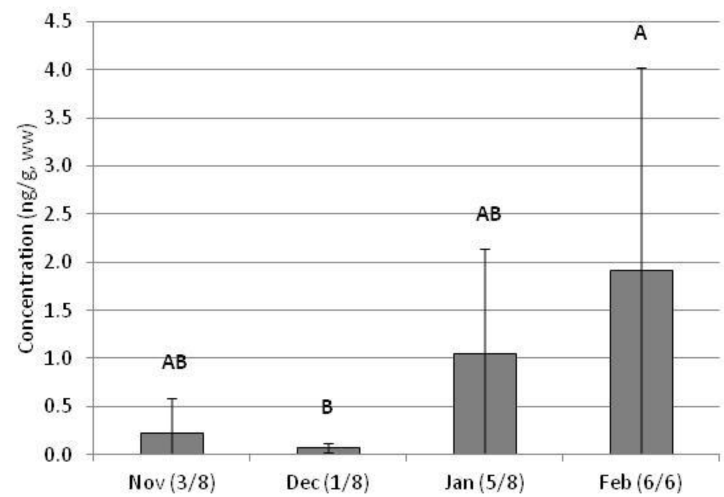

e) OCS – Overall significance found, but not detected between individual months; detection limit = 0.03 ng/g




f) HCB – Detection limit = 0.03 ng

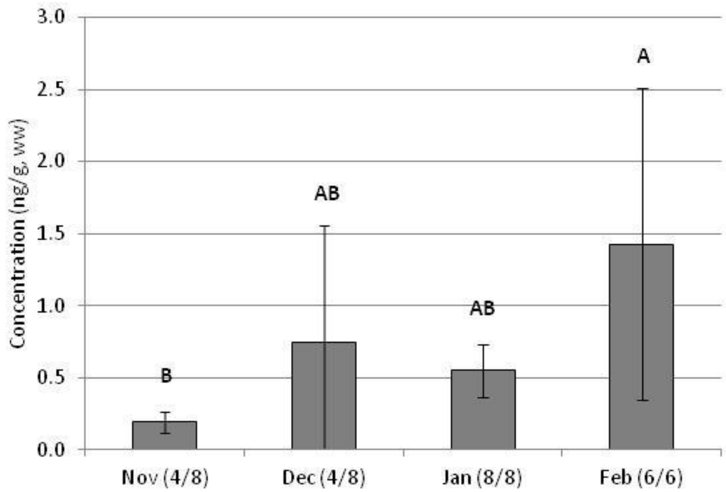



g) Dieldrin – Overall significance found, but not detected between individual months; detection limit = 0.18 ng/g

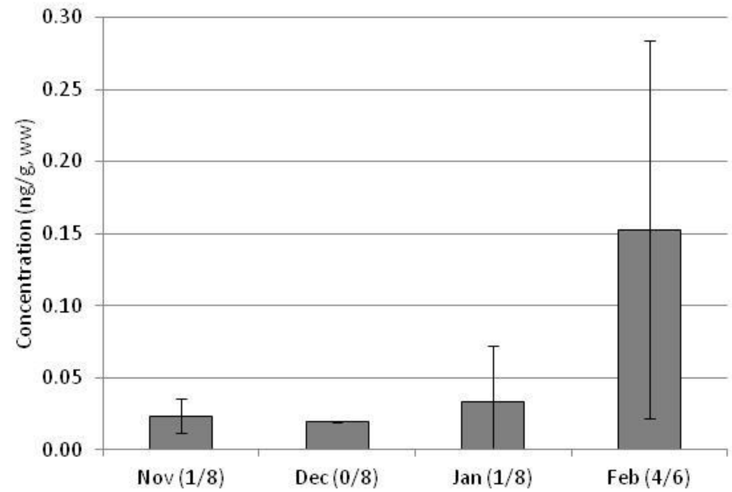



h) HE – Detection limit = 0.11 ng/g

Figure 1 (continued)




i) Sum Chlordane – Range in detection limits for oxychlordane and four metabolites = 0.03-0.12 ng/g



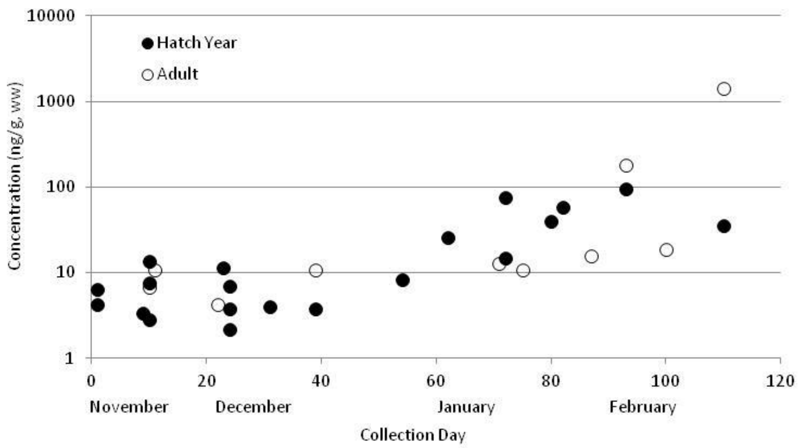

j) Mirex – Overall significance found, but not detected between individual months; detection limit = 0.04 ng/g times). For *p,p'*-DDE, OCS, and mirex, the greatest increases were found between January and February when the birds were foraging on the St. Clair River (range=5-40 times). For sum chlordane, the greatest increase was found between November and December when mean concentrations increased by four times. Mean percent lipid content (±SD) in liver of canvasbacks ranged from 3.3 (±1.5)% in December to 3.9 (±1.1)% in November and was comparable among the four collection months ($F_{(3,26)}$=0.45; p=0.72). The post-hoc results for OCS and HCB analyses were identical when the one adult February bird with the extremely high concentrations of these two compounds was removed from the temporal trend analyses.

Upon partitioning out the potential influence of age of birds in this study, no significant differences in temporal patterns were found between hatch year and adult birds and no significant interactions between collection month and age were found for any contaminants. To illustrate this, concentrations of sum of eight organochlorines (including PCBs), Hg and Se are shown for the individual 20 hatch year birds and 10 adult (female) birds by collection day in Figure 2. Similar to the hatch year birds, hepatic levels in adults were low (and comparable to hatch year birds) upon arrival in November and then increased over the winter. Two adults collected in February had notable high levels of sum organochlorines (note log scale) which were largely influenced by high OCS concentrations (1046 ng/g and 73 ng/g). Without OCS, sum concentrations for the remaining seven organochlorines would have been much lower in these birds (377 ng/g and 109 ng/g). Mean concentrations of compounds for hatch year birds and adult birds by collection month are provided in the Appendix.

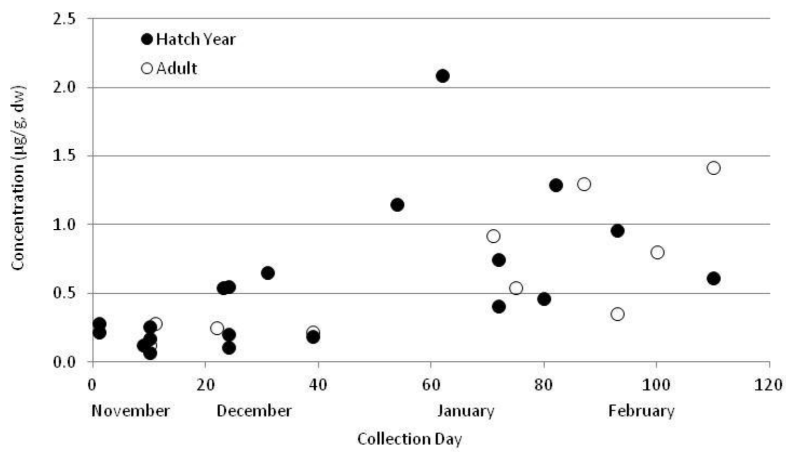
Historical organochlorine data for mallards collected from the St. Clair River area in 1985/86 are also available to examine long-term temporal trends for waterfowl in this area (EC unpublished). Twelve mallards were collected consisting of adult and immature birds (unknown numbers of each and status as either resident or migratory also unknown). Two pooled sets of liver samples were analyzed consisting of six individuals each. Since levels of contamination varied by a factor of at least two between the two pooled samples, concentrations are reported separately (Table 2). Concentrations of PCBs, which were quantified using an Aroclor 1254:1260 (1:1) mixture in the 1970/80s, were equal to 776.00 ng/g and 147.00 ng/g in the two pooled samples. Based on a conversion factor of 0.56 for Aroclor 1:1 to sum PCBs in muscle tissue of mallards collected from Great Lakes sites (EC unpublished), estimated sum PCBs concentrations in pooled liver samples in 1985/86 were equal to 434.56 ng/g and 82.32 ng/g. Among the remaining organochlorines, *p,p*-DDE, OCS and HCB were found at the highest concentrations. Mirex was not detected in either sample and is reported as one-half of the detection limit. Overall, large declines in concentrations were found in livers of mallards between 1985/86 and 2010 with percent declines ranging from 80.0% for mirex to 99.9% for OCS. Reported declines are based on comparisons to the pooled sample No. 2 which had relatively lower concentrations and provide a conservative estimate of change in contamination. Since chemical analyses for Hg and Se were not conducted in 1985/86 pooled liver samples, similar temporal comparisons cannot be performed.

Figure 2. Temporal trends in concentrations of sum of eight organochlorines which include sum PCBs, *p,p'*-DDE, OCS, HCB, dieldrin, HE, sum chlordane and mirex (a), Hg (b) and Se (c) for 20 individual hatch year birds and 10 adult female birds. Collection day is shown on the x-axis with day number 1 (November 10 2008) for collections on Lake St. Clair and day number 54 (January 2 2009) for collections on the St. Clair River.

a) Sum concentration of eight organochlorines




b) Hg




c) Se

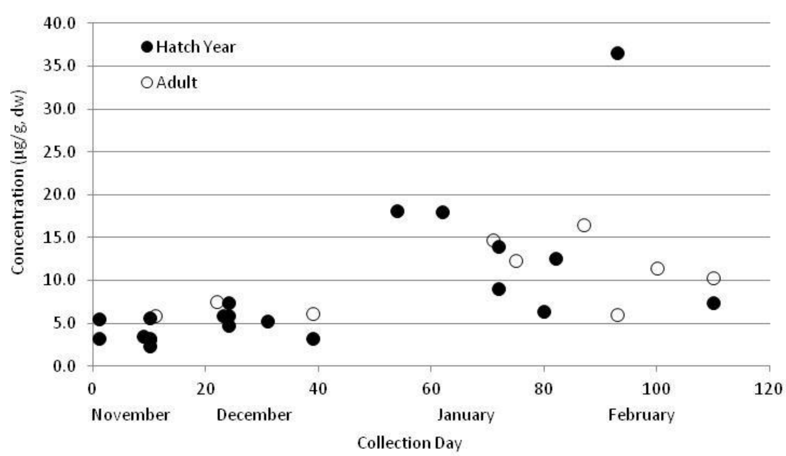


Table 2. Concentrations of organochlorines (ng/g, wet weight) in livers of mallards from the St. Clair River area in two time periods. Concentrations in two pooled samples of livers from birds collected in 1985/86 and mean concentrations (SD) for three birds collected within the study area (Walpole Delta) in 2010 (November) and analyzed individually are shown. Percent decline is relative to concentrations in pooled sample No. 2 and provides a conservative estimate of the relative change in concentrations between 1985/86 and 2010.

| **Year** | **1985/86 – Pooled Samples*** | | **2010 – Individuals** | **Percent Decline** |
|---|---|---|---|---|
| | No. 1 | No. 2 | 3 | 1985/86 & 2010 |
| Sum PCBs | 434.56** | 82.32** | 4.51 (1.81) | 94.5% |
| *p,p′*-DDE | 42.00 | 18.00 | 1.38 (1.64) | 92.3% |
| Sum DDT | 49.00 | 20.00 | 1.43 (1.64) | 92.9% |
| Sum Chlordane | 28.25 | 6.75 | 0.47 (0.43) | 93.0% |
| HCB | 311.00 | 11.00 | 0.05 (0.06) | 99.5% |
| Mirex | 0.25 | 0.25 | 0.05 (0.05) | 80.0% |
| Dieldrin | 42.00 | 8.00 | 0.35 (0.45) | 95.6% |
| Heptachlor Epoxide | 13.00 | 5.00 | 0.10 (0.07) | 98.0% |
| OCS | 493.00 | 41.00 | 0.06 (0.04) | 99.9% |

* Pooled sample No. 1 consists of six birds collected in December/January 1985/86 and No. 2 consists of six birds collected in February 1986.
** Estimated sum PCB concentration based on conversion factor of 0.56 for known Aroclor 1254:1260 PCB concentration (see text).

## Discussion

Based on a recent and extensive review of mercury in birds (Shore *et al*. 2011), Hg concentrations in canvasbacks and mallards were well below hepatic concentrations of 2 µg/g and 20 µg/g (wet weights) suggested as thresholds for adverse effects on reproduction and bird survival, respectively. The maximum Hg concentration in this study was 0.70 µg/g ww (or 2.09 µg/g dw). Se concentrations were relatively higher in birds, ranging widely and occasionally exceeding threshold levels. Se concentrations in the large majority of canvasbacks (67%) were below the threshold concentration of 10 µg/g (dry weight) associated with background exposure; 30% of birds had Se concentrations in the range of 10-20 µg/g which are considered elevated; and 3% (i.e., one bird) had a Se concentration of 36.60 µg/g which exceeded the 20 µg/g threshold associated with toxicity in birds (Ohlendorf and Heinz 2011). All three mallards had Se concentrations consistent with background exposure.

Hepatic Hg and Se concentrations were low overall in wintering canvasbacks from the study area in 2008/09 relative to concentrations in other studies of wintering canvasbacks and other diving duck species in the Great Lakes. For example, Hg and Se concentrations in livers of canvasbacks in this study (as geometric means, 0.41 µg/g and 7.34 µg/g, respectively) were one-half of those in three canvasbacks collected from western Lake Erie between 1991-1993 (2.16 µg/g and 20.0 µg/g dw, respectively; Custer and Custer 2000). Similarly, canvasbacks wintering at historically-contaminated sites on San Francisco Bay in California had relatively higher hepatic concentrations of Hg (range in geometric means, 0.29-5.44 µg/g) and Se (5.66-14.2 µg/g; Hothem *et al.* 1998). While 33% of canvasbacks in this study had Se concentrations suggestive of increased exposure (i.e., greater than 10 µg/g), this threshold was exceeded in livers of 99% of greater scaup (*Aythya marila*) wintering in Hamilton Harbour, Lake Ontario in 2006/07 and many of those birds had hepatic Se concentrations that exceeded the 20 µg/g dw threshold associated with toxicity (Ware *et al.* 2011). Petrie *et al.* (2007) reported substantial percentages of greater scaup collected from lakes St. Clair, Erie and Ontario in fall 1999 and spring 2000 with increased Se exposure (46% and 93%, respectively). High Se exposure was also found in lesser scaup (*A. affinis*) collected in the fall and spring from the same study where 14% and 75% of birds, respectively, exceeded this threshold. Elevated Se concentrations were found in lesser scaup wintering on the Indiana Harbour Canal on Lake Michigan in 1994 in which 14 of 16 birds (88%) had increased Se exposure and 8 of 16 birds (50%) birds had Se concentrations above 33.0 µg/g dw (Custer *et al*. 2000). Higher Se burdens in scaup species may be due to consumption of zebra mussels (*Dreissena polymorpha*) relative to canvasbacks which eat primarily vegetation (Petrie *et al.* 2007). It is unclear what effect might be evident in the one hatch year bird collected in February with a toxic Se concentration although, as reported above, concentrations considered toxic have been reported in staging and wintering Great Lakes waterfowl; further studies of short- and long-term health effects of elevated Se exposure are necessary. Hepatic Hg concentrations in canvasbacks were comparable or lower than concentrations reported in canvasback and scaup species in other studies (Custer and Custer 2000; Custer *et al.* 2000; Petrie *et al.* 2007; Ware *et al.* 2011). While Hg has been identified as a contaminant of concern in the St. Clair River due to historical industrial discharges in the upper reaches of the river (OMOEE and MDNR 1995), current concentrations reported in waterfowl collected at downstream sites were low and below concentrations associated with adverse effects. Se can protect against neurotoxicity of methylmercury and correlations between Hg and Se in liver have been found in other avian species (Scheuhammer *et al.* 2008).

Hepatic PCB and DDT concentrations in canvasbacks and mallards were also low and were below concentrations that resulted in death of avian species in laboratory feeding studies (Hoffman *et al.* 1996; Blus 2011). Concentrations of sum PCBs, total DDT and OCS in lesser scaup collected in the spring from the lower Great Lakes were more comparable to respective concentrations in canvasbacks collected in February versus earlier collection periods (based on comparisons of geometric means; Petrie *et al.* 2007). In contrast, HCB concentrations were at least nine times higher in canvasbacks in February compared to lesser scaup collected in the lower Great Lakes in the spring (Petrie *et al.* 2007). The mean HCB concentration in canvasbacks from the Lake St. Clair/St. Clair River study area was also at least 10 times higher than mean concentrations in canvasbacks and redhead ducks at Fighting Island in the winter of 1993/94 (Mazak *et al.* 1997). This mean HCB concentration remained elevated and was at least two times higher than canvasbacks and redhead ducks at Fighting Island when the one St. Clair River bird with an elevated HCB concentration was not included in the comparison. Hepatic concentrations of PCBs, *p,p'*-DDE and dieldrin in canvasbacks from Chesapeake Bay in winter of 1973 were at least 59 times higher than respective means reported here (White *et al.* 1979). Hepatic total PCB and *p,p*-DDE concentrations in domestic (flightless) white Pekin ducks (*Anas platyrhynchos*) released at Walpole Island (within the St. Clair River AOC) in the summer of 1986 and then subsequently captured after two months of foraging in the area were ten- and two-times higher, respectively, than mean levels in overwintering canvasbacks in this study (Weseloh *et al.* 1994). Hepatic sum PBDE concentrations in canvasbacks and mallards were an order of magnitude lower than sum PBDE concentrations in Barrow's goldeneye (*Bucephala islandica*) from the St. Lawrence marine ecosystem (Ouellet *et al.* 2012). Despite their resident status, organochlorine concentrations in the three mallards analyzed were not notably elevated and were largely similar for all compounds. Mean hepatic concentrations of OCS and HCB in migratory and non-migratory mallards from Walpole Island in summer and fall 1986 and reported in Hebert *et al.* (1990) were within the range of concentrations reported in the two pools of mallards collected in the winter of 1985/86 shown in Table 2. Concentrations of organochlorines in the liver of birds can vary considerably among individuals and can be influenced by a number of parameters including nutritional status (see below); consequently it is difficult to assign threshold concentrations in liver associated directly with toxicity. Overall, current hepatic concentrations of PCBs, *p,p'*-DDE, HCB, and OCS in birds in this study are low and likely not sufficiently elevated to significantly impact survival. A detailed assessment of exposure and threshold levels associated with reproductive impairment in females is not relevant here since birds were collected outside of the breeding season. Given the relatively long half lives for many of these compounds (see below), it is possible that contaminants acquired on wintering grounds could be deposited in eggs when birds return to the prairies to breed. To our knowledge, no studies have examined contaminant concentrations in eggs of canvasbacks breeding at sites in central and eastern prairies of northern US and Canada.

Historical industrial loadings by petrochemical plants situated in the upper 10km of the St. Clair River have been identified as the primary sources of organochlorines, metals and other contaminants to the River (UGLCCS 1988). Evidence based on caged clam studies and water quality and fish monitoring programs in the mid-1980s indicated that chlorinated organics, including OCS and HCB, were highest within a 2-km section of the waterfront from the Cole Drain to the Dow Chemical/Suncor property line (EC and OMOE 1985). Mercury was also elevated in sediment in this area and was associated with discharge from cell chlor-alkali plants operated on the Dow Chemical site (UGLCC 1988). The largest likely source of OCS to the St. Clair River was Dow Chemical where it was produced as waste by the chlorination of tars used as binding agents in graphite electrodes (Kaminsky and Hites 1984). The impacts of these industrial sources were evident as far as 35 km downstream where elevated levels of OCS and HCB were found in caged clams after 3 weeks of exposure in 1982/83 (Kauss and Hamdy 1985). Contaminants including PCBs, Hg and Se were also found above background concentrations in samples of the attached algae *Cladophora* collected from shoreline sites near the Shell Canada/Ethyl Corp. of Canada/Petrosar industrial complex at Corunna in 1984 (EC and OMOE 1985). Loadings from municipal sources (e.g., water pollution control plants), urban runoff and tributaries have also contributed pollutants to the River (OMOEE and MDNR 1991).

Significant temporal increases in hepatic concentrations of all organochlorines, Hg and Se were found in canvasbacks foraging in the Great Lakes study area over a four month period. Wintering birds arrived on Lake St. Clair in November with low concentrations of contaminants often below the limit of detection and accumulated contaminants to concentrations which were at least five-fold higher prior to leaving the St. Clair River for spring migration in February/March. This pattern of rapid uptake and accumulation of contaminants has been demonstrated previously in numerous overwintering and migrating waterfowl species on the Great Lakes. Concentrations of PCBs, dieldrin, HCB and HE in fat of adult male common goldeneyes (*Bucephala clangula*) increased significantly from the time the birds arrived on their wintering grounds on the upper Niagara River (Nov-Dec) to the time just prior to spring migration (Feb-March; Foley and Batcheller 1988). Significant accumulation of Se has been also found in greater scaup overwintering in Hamilton Harbour (Ware *et al.* 2011); in fall and spring migrant populations of lesser scaup on the lower Great Lakes (Petrie *et al.* 2007); and in three species of wintering sea ducks, buffleheads (*Bucephala albeola*), common goldeneyes, and long-tailed ducks (*Clangula hyemalis*) in Lake Ontario (Schummer *et al.* 2010). Rapid uptake of Hg has been demonstrated in canvasbacks on San Francisco Bay where a three-fold increase in hepatic concentrations was found between the early and late-winter periods (Hothem *et al.* 1998). Canvasbacks appear to be acquiring increased hepatic contaminant burdens when the population overwinters in the Lake St. Clair/St. Clair River area, a pattern which is also consistent with other waterfowl species staging or overwintering on the Great Lakes

The rapid uptake and accumulation of many compounds over a relatively short period (i.e., few months), in overwintering canvasbacks was dramatic. This pattern of rapid uptake of organochlorines and metals was demonstrated previously by Weseloh *et al.* (1994) in a study of domestic white Pekin ducks released at three Great Lakes study sites. At Walpole Island, rates of uptake were particularly high for HCB and OCS in these flightless ducks where hepatic concentrations after one month were similar to concentrations observed one year prior in wild mallard and redhead ducks breeding on the island (Hebert *et al.* 1990). Sum PCBs in liver of white Pekin ducks also tripled between the one-month and two-month collection periods (Weseloh *et al.* 1994). Laboratory evidence suggests that Se accumulation in liver of birds is also very rapid. When adult mallards were fed high Se diets, Se in liver was predicted to reach 95% of equilibrium in just 8 days; the rate of loss was also rapid with a half-life of 19 days (Heinz *et al.* 1990). In addition, for birds feeding continually on a contaminated food source, particularly in the latter part of the winter as in this study, it is likely that a stable state equilibrium would likely not have yet been reached prior to birds migrating back to their breeding grounds. For methylmercury, as the most toxic form of total mercury, stable state equilibrium in liver of American kestrels (*Falco sparverius*) may be longer than 125 days (Nichols *et al.* 2010). Upon accumulating organochlorines, depuration would be expected to be slow with predicted half-lifes for *p,p'*-DDE (880 days), OCS (93 days), HCB (188 days) in wild juvenile herring gulls (*Larus argentatus*) which exceed the period of exposure in this study (Clark *et al.* 1987). It is striking that dramatic temporal increases were evident despite the low sample size of canvasbacks (6-8) analyzed in each month over the four-month period.

In addition to significant temporal trends found in overwintering canvasbacks utilizing this Great Lakes study area, notable spatial trends arising from the movement of birds from Lake St. Clair when the lake freezes in December to the St. Clair River where food is more readily available in January were also found. This movement corresponds to the period when the most pronounced increases in hepatic burdens for many compounds were evident. These data suggest that birds are foraging on a relatively less contaminated food base on Lake St. Clair in the first two months relative to the St. Clair River where they accumulate contaminants rapidly over the latter two months of the winter. Spatial (and temporal) increases could be related to major changes in diet in which birds are eating a greater proportion of animal matter (i.e., benthic invertebrates) in the St. Clair River compared to Lake St. Clair where their diet may be more vegetation-based. Alternately, if diet did not change significantly between the two regions, birds may be foraging on a relatively more contaminated food base in the St. Clair River as a result of its proximity to upstream St. Clair River AOC contaminant sources. Similar patterns for Hg, PCBs, OCS and HCB were also found in juvenile spottail shiners (*Notropis hudsonius*) in which significantly higher concentrations were found in shiners from the St. Clair River compared to those from nearshore areas of Lake St. Clair (Gewurtz *et al.* 2010). Some combination of both of these scenarios is possible. Future studies of diet of overwintering canvasback as well the degree of contamination in diet items of birds from both of these regions would be required to examine this further.

It is also possible that increases in hepatic concentrations of organochlorines could be due to accelerated lipid metabolism during conditions of food stress evident during the winter (Smith *et al.* 1985). Preliminary evidence suggests that food availability was not limited in Lake St. Clair canvasbacks in 2008/09 since total body fat, as an indicator of lipid reserves, increased in these birds by 164% between November and December (based on a collection of 64 birds; Bird Studies Canada, unpublished data). This is in contrast to the pattern observed in St. Clair River canvasbacks where total body fat decreased by 85% between January and February (N=63 birds) which coincides with the period of increased contaminant burdens in these birds. This decrease in total body fat was accompanied by a 17% decrease in fresh body weight, a pattern which may not be unusual for overwintering bird particularly in the latter part of winter when food is limited (Ryan 1972, Smith *et al.* 1985). In collaboration with Bird Studies Canada, more detailed statistical analyses of nutrient reserves in these birds are being conducted to determine the extent to which declines in lipid reserves may have contributed to the temporal increases in hepatic burdens observed. There is also the possibility that during a period of mobilization of body fat, concentrations found in liver could be indicative of endogenous reserves and thus lipophilic contaminants acquired elsewhere such as on breeding grounds. However given the propensity for uptake of many of these compounds including locally bioavailable compounds (notably HCB and OCS which have historically been of concern in the St. Clair River AOC), it is likely that hepatic concentrations reported here, particularly in the latter part of the winter, are largely reflective of local exposure.

Large temporal declines in concentrations of organochlorines were evident in liver of mallards from the St. Clair River area between 1985/86 and 2010 with percent declines ranging from 80.0% - 99.9% (as a minimum) between the two periods. These trends are consistent with dramatic declines in concentrations of many organochlorines observed in numerous sport fish from the Great Lakes including Lake St. Clair since the 1970s followed by rates of decline which have slowed or stabilized after the early or mid-1990s (Gewurtz *et al.* 2010). Declines in organochlorines were also most pronounced in herring gull eggs from Chantry Island, Lake Huron (upstream) and the Detroit River (downstream) during the mid 1970s to 1990s compared to recent years (EC unpublished). These trends are reflective of environmental legislation aimed at reducing upstream point source loadings to the St. Clair River and restrictions on usage of pollutants, improved industrial and agricultural practices as well as the effectiveness of remediation efforts in the AOC.

Age effects on contaminant uptake has not been consistently found between immature and adult wintering waterfowl species (Foley and Batcheller 1988; Mazak *et al.* 1997; Custer *et al.* 2000; Petrie *et* *al.* 2007; Ware *et al.* 2011; Ouellet *et al.* 2012). While the sample size was low, no significant age effect was found in this study and similar patterns of increased contaminant burdens were found in both hatch year birds and adults overwintering in this study area. Sex effects associated with metal and/or organochlorine burdens have been noted in some waterfowl species (Braune and Malone 2006) and not in others (Custer and Custer 2000; Ware *et al*. 2011; Ouellet *et al.* 2012). The influence of sex could not be ascertained in this study with only five males analyzed.

Based on the results of a waterfowl consumption survey conducted upstream in the St. Clair River in 1996, there is some evidence of human consumption of mallards and canvasbacks in the AOC (Dawson 2000). Mallards were most frequently consumed with 72% of 106 respondents surveyed having eaten at least one meal of the species in the previous 12 months. Canvasbacks were less frequently eaten with only 9% of respondents having eaten this species in the survey year. With regard to potential human health effects associated with consumption of aquatic wildlife, no guidelines have been developed for consumption of waterfowl species; consequently, it is not possible to speculate on human risks due to consumption of species in this study. Pectoral muscle which is typically consumed by humans is not considered a major target organ for accumulation of contaminants; the liver, as the tissue analyzed in this study, is where contaminants tend to accumulate (Hebert *et al.* 1990). It is encouraging that contaminant concentrations in livers of the few resident mallards collected were relatively low, particularly relative to concentrations in the mid-1980s. In addition, temporal increases observed here suggest that human health risk may be relatively lower earlier in the winter, which coincides with the end of the hunting season in early January, compared to later in the winter, post-hunting. Waterfowl with a piscivorous or benthic invertebrate-based diet, such as lesser scaup and bufflehead, would be expected to have higher concentrations of Hg and PCBs compared to canvasbacks and mallards which generally have a more vegetation-based diet (Mazak *et al.* 1997; Hall *et al*. 2009).

Bald eagles (*Haliaeetus leucocephalus*) wintering in the lower Great Lakes basin are opportunistic scavengers relying on waterfowl and mammals as important dietary items during the winter months (Ewins and Andress 1995; Lang *et al.* 1999). Evidence from this study suggests that wildlife consumers of canvasbacks and mallards, such as bald eagles, may be at an increased health risk due to elevated concentrations of Hg. Based on a mean percentage of 38.1% for concentrations of methylmercury to total Hg in liver of mallards (Fimreite 1974), estimated hepatic methylmercury concentrations in 20 of 30 canvasbacks (67%) and 1 of 3 mallards (33%) would exceed the methylmercury tissue residue guideline of 33.0 ng/g ww for the protection of wildlife consumers of aquatic biota (CCME 2001). Therefore, consumption of livers by bald eagles could potentially pose some health risk. Lower risks would be associated with consumption of other tissues such as pectoral muscle where Hg concentrations would be lower. Hepatic total DDT concentrations were well below the total DDT tissue residue guideline of 14.0 ng/g for the protection of wildlife consumers (CCME 2001). Similarly, using known concentrations for three dioxin-like PCBs which were quantified in this study (mono-*ortho* PCBs #105, 118 and 156), hepatic concentrations were well below TEQ guidelines for sum PCBs associated with the protection of avian consumers of aquatic biota (equal to 2.4 ng TEQ/kg; based on TEFs derived for birds from van den Berg *et al.* 1998; CCME 2001). Estimates of TEQs for sum PCBs in this study however were largely underestimated since non-*ortho* PCBs, which are relatively more toxic, were not quantified in this study.

Overall, hepatic concentrations of organochlorines, Hg and Se in overwintering canvasbacks and resident mallards in the Lake St. Clair/St. Clair River study area were low. Hepatic Hg concentrations in these two species, including birds found within the St. Clair River AOC, were below the level associated with an adverse effect on survival in birds. Current levels of organochlorines were likely not sufficiently elevated to significantly impact survival. The overwintering population of canvasbacks utilizing this area appears to be acquiring increased contaminant burdens over the winter. This pattern is consistent with both the propensity of rapid uptake of many of these compounds (including those locally bioavailable) as well as temporal patterns found in other waterfowl species staging or overwintering on the Great Lakes. It is unclear to what extent possible changes in diet, level of contamination and/or declines in lipid reserves following movement from Lake St. Clair to the St. Clair River contributed to temporal/spatial trends observed in overwintering canvasbacks and additional studies will provide some insight into these findings.

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## References

Blus, L.J. 2011. DDT, DDD, and DDE in birds. In: *Environmental contaminants in biota (2$^{nd}$ edition)*, eds. W.N. Beyer and J.P. Meador, pp. 425-444. CRC Press, Boca Raton, FL.

Braune, B.M. and B.J. Malone. 2006. Mercury and selenium in livers of waterfowl harvested in northern Canada. *Arch. Environ. Contam. Toxicol*. 50: 284-289.

Canadian Council of Ministers of the Environment (CCME). 2001. *Canadian tissue residue guidelines for the protection of wildlife consumers of aquatic biota: summary table*. Updated. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Clark, T.P., R.J. Norstrom, G.A. Fox, and H.T. Won. 1987. Dynamics of organochlorine compounds in herring gulls (*Larus argentatus*): II. A two-compartment model and data for ten compounds. *Environ. Toxicol. Chem*. 6: 547-559.

Custer, C.M. and T.W. Custer. 2000. Organochlorine and trace element contamination in wintering and migrating diving ducks in the southern Great Lakes, USA, since the zebra mussel invasion. *Environ. Toxicol. Chem*. 19: 2821-2829.

Custer, T.W., C.M. Custer, R.K. Hines, and D.W. Sparks. 2000. Trace elements, organochlorines, polycyclic aromatic hydrocarbons, dioxins, and furans in lesser scaup wintering on the Indiana Harbor Canal. *Environ. Pollut*. 110: 469-482.

Dawson, J. 2000. *Fish stories: a profile of fishing and fish consumption along the St. Clair River area*. Fish and Wildlife Nutrition Project. Health Canada. Ottawa, Ontario, Canada. Great Lakes Health Effects Program Project No. K341813.

EC and OMOE. 1985. *Pollution of the St. Clair River (Sarnia area). A situation report prepared by Environment Canada and the Ontario Ministry of Environment under the auspices of the Canada-Ontario Agreement respecting Great Lakes Water Quality.* November 18, 1985. https://ia600303.us.archive.org/5/items/pollutionofstcla00onta/POLLUTIONOFTHEST_00_SNSN_08466.pdf

Ewins, P.J. and R.A. Andress. 1995. The diet of bald eagles, *Haliaeetus leucocephalus*, wintering in the lower Great Lakes basin, 1987-1995. *Can. Field Nat*. 109: 418-425.

Fimreite, N. 1974. Mercury contamination in aquatic birds in northwestern Ontario. *J. Wildl. Manage*. 38: 120-131.

Foley, R.E. and G.R. Batcheller. 1988. Organochlorine contaminants in common goldeneye wintering on the Niagara River. *J. Wildl. Manage.* 52: 441-445.

Gewurtz, S.B., S.P. Bhavsar, D.A. Jackson, R. Fletcher, E. Awad, R. Moody and E.J. Reiner. 2010. Temporal and spatial trends of organochlorines and mercury in fishes from the St. Clair River/Lake St. Clair corridor, Canada. *J. Great Lakes Res.* 36: 100-112.

Hall, B.D., L.A. Baron, and C.M. Somers. 2009. Mercury concentrations in surface water and harvested waterfowl from the prairie pothole region of Saskatchewan. *Environ. Sci. Technol*. 43: 8759-9766.

Hebert, C.E., G.D. Haffner, I.M. Weis, R. Lazar, and L. Montour. 1990. Organochlorine contaminants in duck populations of Walpole Island. *J. Great Lakes Res*. 16:21-26.

Heinz, G.H., G.W. Pendleton, A.J. Krynitsky, and L.G. Gold. 1990. Selenium accumulation and elimination in mallards. *Arch. Environ. Contam. Toxicol*. 19: 374-379.

Hoffman, D. J., C.P. Rice, and T.J. Kubiak. 1996. PCBs and dioxins in birds. In: *Environmental contaminants in wildlife: interpreting tissue concentrations*, eds. W.N. Beyer, G.H. Heinz and A.W Redmon-Norwood, pp. 165-207. SETAC Special Publications, Lewis Publishers, Boca Raton, FL.

Hothem, R.L., D.G. Lonzarich, J.E. Takekawa, and H.M. Ohlendorf. 1998. Contaminants in wintering canvasbacks and scaups from San Francisco Bay, California. *Environ. Monitor. Assess.* 50: 67-84.

Kaminsky, R. and R.A. Hites. 1984. Octachlorostyrene in Lake Ontario: sources and fates. *Environ. Sci. Technol.* 18: 275-279.

Kauss, P.B. and Y.S. Hamdy. 1985. Biological monitoring of organochlorine contaminants in the St. Clair and Detroit rivers using introduced clams, *Elliptio complanatus*. *J. Great Lakes Res*. 11(3): 247-263.

Lang, A.L., R.A. Andress, and P.A. Martin. 1999. Prey remains in bald eagle, (*Haliaeetus leucocephalus*), pellets from a winter roost in the upper St. Lawrence River, 1996 and 1997. *Can. Field Nat.* 113: 621-626.

Long Point Waterfowl Newsletter. 2010. *Providing Answers to Conservation-based Questions*. Fall 2010 Volume 5. Accessed from internet: http://longpointwaterfowl.org/wp-content/uploads/2011/05/2010-LPW-Newsletter.pdf

Mayne, G. 2008. *St. Clair River Remedial Action Plan Progress Report. Volume 1. Synthesis report and environmental conditions and implementation actions (1998-2003)*. 164 pp.

Mazak, E.J., H.J. MacIsaac, M.R. Servos, and R. Hesslein. 1997. Influence of feeding habits on organochlorine contaminant accumulation in waterfowl on the Great Lakes. *Ecol. Appl.* 7: 1133-1143.

Mowbray, T.B. 2002. Canvasback (*Aythya valisineria*). *The Birds of North America Online* (A. Poole, Ed.). Ithaca: Cornell Lab of Ornithology. Retrieved from the Birds of North America Online: http://bna.birds.cornell.edu/bna/species/659.

Mullie, A., R.K. Ross and D.G. Dennis. 1996. *Overview of migrant waterfowl use of the Great Lakes Areas of Concern and other selected coastal sectors in southern Ontario*. Technical Report Series No. 261, Canadian Wildlife Service.

Nichols, J.W., R.S. Bennett, R. Rossman, J.B. French, and K.G. Sappington. 2010. A physiologically based toxicokinetic model for methylmercury in female American kestrels. *Environ. Toxicol. Chem.* 8: 1854-1867.

Ohlendorf, H.M. and G.H. Heinz. 2011. Selenium in birds. In: *Environmental contaminants in biota (2nd edition)*, eds. W.N. Beyer and J.P. Meador, pp. 669-701. CRC Press, Boca Raton, FL.

Oliver, B.G. and R.A. Bourbonniere. 1985. Chlorinated contaminants in surficial sediments of lakes Huron, St. Clair, and Erie: implications regarding sources along the St. Clair and Detroit River. *J. Great Lakes Res.* 11(3): 366-372.

OMOEE and MDNR. 1991. *The St. Clair River Area of Concern environmental conditions and problem definition*. Stage 1 Remedial Action Plan. 466 pp.

OMOEE and MDNR. 1995. *The St. Clair River Area of Concern, water use goals, remedial measures and implementation strategy. Remedial Action Plan Stage 2- recommended plan.* St. Clair River RAP Team. 121 pp.

Ouellet, J.F., L. Champoux, and M. Robert. 2012. Metals, trace elements, and 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. *Arch. Environ. Contam. Toxicol*. 63: 429-436.

Petrie, S.A., S.S. Badzinski, and K.G. Drouillard. 2007. Contaminants in lesser and greater scaup staging on the lower Great Lakes. *Arch. Environ. Contam. Toxicol.* 52: 580-589.

Pugsley, C.W., P.D.N. Hebert, G.W. Wood, G. Brotea, and T.W. Obal. 1985. Distribution of contaminants in clams and sediments from the Huron-Erie corridor. I – PCBs and octachlorostyrene. *J. Great Lakes Res*. 11(3): 275-289.

Ryan, R.A. 1972. Body weight and weight changes of wintering diving ducks. *J. Wildl. Manage*. 36: 759-765.

Scheuhammer, A.M., N. Basu, N.M. Burgess, J.E. Elliott, G.D. Campbell, M. Wayland, L. Champoux, and J. Rodrigue. 2008. Relationships among mercury, selenium, and neurochemical parameters in common loons (*Gavia immer*) and bald eagles (*Haliaeetus leucocephalus*). *Ecotoxicology* 17: 93-101.

Schummer, M.L., S.S. Badzinski, S.A. Petrie, Y.W. Chen, and N. Belzile. 2010. Selenium accumulation in sea ducks wintering on Lake Ontario. *Arch. Environ. Contam. Toxicol.* 58: 854-862.

Shore, R.F., M.G. Pereira, L.A. Walker, and D.R. Thompson. 2011. Mercury in nonmarine birds and mammals. In: *Environmental contaminants in biota (2nd edition)*, eds. W.N. Beyer and J.P. Meador, pp. 609-624. CRC Press, Boca Raton, FL.

Smith, V.E., J.M. Spurr, J.C Filkins, and J.J. Jones. 1985. Organochlorine contaminants of wintering ducks foraging on Detroit River sediments. *J. Great Lakes Res*. 11: 231-246.

UGLCCS. 1988. *Upper Great Lakes Connecting Channels Study. Volume 2.* 1988. http://www.epa.gov/greatlakes/uglcc/pdfs/uglcc-198812-vol2.pdf

Van den Berg, M., L. Birnbaum, A.T.C. Bosveld, B. Brunström, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X.R. van Leeuwen, A.K. Dijen Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, and T. Zacharewski. 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* 106: 775–792.

Ware, L.L., S.A. Petrie, S.S. Badzinski, and R.C. Bailey. 2011. Selenium concentrations in greater scaup and dreissenid mussels during winter on western Lake Ontario. *Arch. Environ. Contam. Toxicol.* 61: 292-299.

Weseloh, D.V., J. Struger, and C. Hebert. 1994. White Pekin ducks (*Anas platyrhynchos*) as monitors of organochlorine and metal contamination in the Great Lakes. *J. Great Lakes Res*. 20: 277-288.

White, D.H., R.C. Stendell, and B.M. Mulhern. 1979. Relations of wintering canvasbacks to environmental pollutants - Chesapeake Bay, Maryland. *Wilson Bull.* 91: 279-287.

Zar, J.H. 1984. *Biostatistical analysis*. Second Edition. Prentice–Hall, Inc. Englewood Cliffs, N.J.

Appendix. Mean concentrations (SD) of contaminants in livers of hatch year and adult canvasbacks collected in November, December, January, and February from Lake St.Clair and the St. Clair River in 2008/09. Twenty hatch year birds and ten adult (female) birds were analyzed in total. Ratios shown for each month represent the number of birds with a concentration above the limit of detection relative to the total number of birds analzyed in that month.

| | | **November** | **December** | **January** | **February** |
|---|---|---|---|---|---|
| Sum PCBs | Hatch Year | 4.12 (3.62) 6/6 | 4.15 (3.25) 6/6 | 22.57 (19.59) 6/6 | 36.52 (27.95) 2/2 |
| | Adult | 5.75 (5.31) 2/2 | 4.21 (4.23) 2/2 | 5.25 (0.42) 2/2 | 63.99 (67.96) 4/4 |
| *p,p'*-DDE | Hatch Year | 1.47 (2.01) 6/6 | 0.34 (0.24) 6/6 | 2.52 (2.41) 6/6 | 7.18 (3.05) 2/2 |
| | Adult | 2.21 (2.26) 2/2 | 0.56 (0.004) 2/2 | 0.34 (0.04) 2/2 | 11.63 (12.53) 4/4 |
| OCS | Hatch Year | 0.02 (0.02) 1/6 | 0.07 (0.09) 2/6 | 6.23 (6.24) 6/6 | 7.30 (1.66) 2/2 |
| | Adult | 0.05 (0.05) 1/2 | 0.36 (0.49) 1/2 | 0.02 (0.00) 0/2 | 279.86 (512.14) 4/4 |
| HCB | Hatch Year | 0.13 (0.15) 4/6 | 0.13 (0.13) 6/6 | 2.62 (2.95) 6/6 | 4.51 (1.33) 2/2 |
| | Adult | 0.20 (0.19) 2/2 | 0.55 (0.66) 2/2 | 4.82 (1.43) 2/2 | 50.37 (89.56) 4/4 |
| Dieldrin | Hatch Year | 0.18 (0.22) 1/6 | 0.09 (0.00) 0/6 | 1.20 (1.33) 3/6 | 4.31 (5.97) 1/2 |
| | Adult | 0.09 (0.00) 0/2 | 0.09 (0.00) 0/2 | 0.30 (0.05) 2/2 | 2.09 (2.80) 2/4 |
| HE | Hatch Year | 0.24 (0.44) 1/6 | 0.06 (0.00) 0/6 | 1.28 (1.17) 4/6 | 3.35 (3.35) 2/2 |
| | Adult | 0.16 (0.04) 2/2 | 0.12 (0.09) 1/2 | 0.33 (0.38) 1/2 | 1.20 (1.28) 4/4 |
| Sum Chlordane | Hatch Year | 0.16 (0.05) 2/6 | 0.46 (0.61) 2/6 | 0.55 (0.22) 6/6 | 1.88 (1.68) 2/2 |
| | Adult | 0.29 (0.08) 2/2 | 1.58 (0.94) 2/2 | 0.53 (0.05) 2/2 | 1.20 (0.90) 4/4 |
| Mirex | Hatch Year | 0.02 (0.01) 1/6 | 0.02 (0.00) 0/6 | 0.04 (0.05) 1/6 | 0.24 (0.15) 2/2 |
| | Adult | 0.02 (0.00) 0/2 | 0.02 (0.00) 0/2 | 0.02 (0.00) 0/2 | 0.11 (0.12) 2/4 |
| Mercury | Hatch Year | 0.19 (0.08) 6/6 | 0.37 (0.23) 6/6 | 1.03 (0.63) 6/6 | 0.79 (0.25) 2/2 |
| | Adult | 0.20 (0.11) 2/2 | 0.24 (0.02) 2/2 | 0.73 (0.27) 2/2 | 0.97 (0.49) 4/4 |
| Selenium | Hatch Year | 3.94 (1.33) 6/6 | 5.40 (1.41) 6/6 | 13.03 (4.70) 6/6 | 21.99 (20.65) 2/2 |
| | Adult | 4.50 (1.93) 2/2 | 6.83 (0.97) 2/2 | 13.51 (1.65) 2/2 | 11.05 (4.32) 4/4 |