Rapid Increase in Contaminant Burdens Following Loss of Body Condition in Canvasbacks (*Aythya valisineria*) Overwintering on the Lake St. Clair Region of the Great Lakes

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Abstract

Overwintering canvasbacks were collected in the Lake St. Clair region of the Great Lakes in the winter of 2008/09 and livers were analyzed for organochlorines, mercury (Hg), and selenium (Se). We found dramatic increases in hepatic concentrations of Hg, Se, sum PCBs, *p,p'*-DDE, and other organochlorines in canvasbacks in which concentrations in February were significantly greater than concentrations in November when overwintering ducks arrived in the study area. The increases in contaminant burdens were generally greatest between December and January which also coincided with the period when ducks from Lake St. Clair (LSC) moved following freeze-up of the Lake to forage on the St. Clair River (SCR), an area of known historic contamination, and upstream of LSC. Body condition and fat reserves (after controlling for body size) increased significantly in LSC ducks but subsequently decreased significantly in SCR ducks. This rapid loss of body condition was one factor likely driving the dramatic increase in contaminant burdens and particularly for organochlorines which were inversely related to body condition in SCR ducks. Increased exposure due to foraging in closer proximity to contaminant sources and changes in diet associated with the movement of ducks may have also contributed to temporal trends. Concentrations overall were below those associated with toxicity with the exception of Se for which 30% of ducks exceeded the Se threshold that is considered elevated and one duck exceeded the threshold associated with possible toxicity. There may be fitness consequences for overwintering canvasbacks as loss of body condition (fat reserves) might impact energetic requirements for successful migration to breeding sites and reproduction in the prairies and contaminant burdens may be transferred to eggs at these breeding sites. Food availability, ice cover, and movements of canvasbacks are additional factors influencing contaminant accumulation and body condition in waterfowl utilizing this important wintering location.

Keywords: waterfowl; Great Lakes; contaminants; body condition

1. Introduction

Following breeding in the prairies of North America, canvasbacks (*Aythya valisineria*) migrate to the upper Mississippi River and eastwards to the Great Lakes including areas on Lake St. Clair and the St. Clair and Detroit rivers among others (Dennis et al., 1984; Mowbray, 2002). Traditionally, most canvasbacks have wintered in Chesapeake Bay on the Atlantic Coast but changing water, food, and ice conditions resulted in many of these ducks remaining farther north and west during winter along their migration route (Baldassarre, 2014). Lake St. Clair and associated rivers is one of the most northerly wintering locations for canvasbacks where their abundance in November 2006–2010 averaged 137,414 ducks (Cordts, 2010) with decreases in winter to around 10,000 ducks (Weaver et al., 2015; Canadian Wildlife Service, unpublished data). While variable, numbers of overwintering canvasbacks in this area have not changed substantially since 2010 (MLS, pers. obs). During winter, canvasbacks consume primarily plants such as tubers of wild celery (*Vallisneria americana*) and, when vegetation is limited, small clams and snails (Mowbray, 2002). In March and April, ducks begin their spring migration back to the prairie breeding grounds (Mowbray, 2002). Given the relatively higher levels of PCBs and other legacy pollutants in the Great Lakes area compared to the prairies (Shen et al., 2006), concentrations of contaminants may increase in tissues of ducks overwintering on the Great Lakes.

Historical industrial loadings by petroleum refineries and petrochemical plants situated on the upper St. Clair River were identified as primary sources of organic contaminants and metals to the River in the 1980s (OMOEE and MDNR, 1995). Several chlorinated organics, including octachlorostyrene (OCS) and hexachlorobenzene (HCB), and mercury (Hg) were associated with effluent discharge and waste from these industries concentrated in the Sarnia-Corunna area in Ontario, Canada that impaired water quality downstream (EC and OMOE, 1985). Dow Chemical was likely the largest source of OCS to the St. Clair River where it was produced as waste from the chlorination of the tar used to bind graphite electrodes

(Kaminsky and Hites, 1984). In the early-mid 1980s, elevated concentrations of OCS and HCB were found in water and caged clams after three weeks of exposure along the industrial area of the shoreline and polychlorinated biphenyls (PCBs), Hg, and selenium (Se) were detected in samples of the attached algae *Cladophora* collected from several shoreline sites near the industrial complex at Corunna (EC and OMOE, 1985; Kauss and Hamdy, 1985). Hepatic concentrations of OCS, HCB, and PCBs in flightless white Pekin ducks (*Anas platyrhynchos domesticus*) increased dramatically over a one-month period following the release of these ducks in the lower reaches of the St. Clair River (Weseloh et al., 1994). Industrial loadings on the American side of the River, municipal point sources, urban stormwater and rural runoff were also sources of the pollutants to the River (OMOEE and MDNR, 1995). Following the designation of the St. Clair River as a Great Lakes Area of Concern (AOC) in 1987, several initiatives including restrictions on industrial discharges, improved industrial and municipal practices, and sediment remediation projects in the upper St. Clair River have largely reduced contaminant loadings, improved water and sediment quality, and contributed to significant temporal declines in concentrations of several compounds in collections of juvenile spottail shiner (*Notropis hudsonius*) from the River between 1999–2007 (Environment Canada, 2003; Gewurtz et al., 2010; Richman and Milani, 2010; Richman et al., 2018). The St. Clair River discharges into Lake St. Clair, contributing 98% of the water flow into the Lake, and consequently is a major source of contamination to the Lake (Kauss and Hamdy 1985; Gewurtz et al., 2007). Significant declines in concentrations of PCBs, Hg, OCS, and HCB in several sport fish species collected from Lake St. Clair (where sufficient data were available) from the late 1970s to 2007 suggest that exposure to these pollutants also likely decreased in fish and other biota upstream during this period (Gewurtz et al., 2010).

Since the mid-1980s/90s, rates of contaminant declines in fish have slowed however and historically-contaminated sediment likely continues to be a source of pollutants to the River and downstream areas to potentially impact the food chain (Gewurtz et al., 2010; Jia et al., 2010; Dove et al., 2012; Richman et al., 2018). For waterfowl such as diving and dabbling ducks that have more contact with sediment and consume sediment-based food (i.e., submerged aquatic vegetation and benthic invertebrates), these ducks might be at an increased risk of exposure and particularly in areas along the River where sediment is highly contaminated. Molluscivorous diving ducks that overwinter on the lower Great Lakes are known to acquire elevated levels of selenium (Petrie et al., 2007; Schummer et al., 2010; Ware et al., 2011); however, little is known about organochlorine and metal acquisition in primarily herbivorous waterfowl wintering on the Great Lakes (but see Schummer et al., 2011).

The objectives of our study are to: 1) determine hepatic burdens of Hg, Se, PCBs and several other chlorinated compounds in overwintering canvasbacks in Lake St. Clair and the St. Clair River; 2) assess temporal changes in burdens over the course of a winter; 3) examine whether burdens are related to changes in body condition and nutrient reserves during this period, and; 4) predict whether burdens might adversely impact survival of overwintering canvasbacks based on published effect-level threshold concentrations. These data provide information on exposure to pollutants in overwintering canvasbacks in this Great Lakes region and examine contaminant burdens in relation to changes in body condition when increased energetic expenditures are required due to harsh and often unpredictable environmental conditions.

2. Methods

2.1 Specimen Collection

Specimen collection for this study was part of a large research project conducted by the Long Point Waterfowl and Wetlands Research Program of Duck Studies Canada examining wintering ecology of canvasbacks and redheads (*Aythya americana*) on Lake St. Clair and the Detroit and St. Clair rivers. Canvasbacks (n=127) were collected using shotguns and non-toxic shot from November 2008 to February 2009 on Lake St. Clair and the St. Clair River. Specifically, ducks were collected in November and December 2008 from Lake St. Clair (hereafter "LSC") where this species typically forages in shallow, open water habitats in the fall and early winter. Following freeze-up of LSC, ducks moved upstream to the open, fast water areas of the St. Clair River (hereafter "SCR") where they were collected in January and February 2009. Fresh body mass of ducks was determined to the nearest 0.01 g and morphological parameters including body length, wing chord, tarsus length, bill width, skull length, and keel length were measured to the nearest 0.01 mm. Organs were removed, measured, weighed, and frozen at -20^{o}C with the remaining carcass. Livers were retained separately for contaminant analysis and carcasses were analyzed for body composition (see below).

2.2 Contaminant Analyses

For contaminant analysis, six or eight livers from 30 ducks (five males and 25 females) were randomly selected from each of the four collection months. Twenty of these ducks were juvenile ducks (i.e., ducks less than one year old based on the presence of a cloacal bursa, an immune system gland present in young ducks) and the remaining 10 ducks were adult females. Ducks from LSC (n=16) were collected near Mitchell's Bay with the exception of two ducks that were collected approx. 1.6 km offshore in Anchor Bay in Michigan. Ducks collected from the SCR (n=14) were from three main locations on the Ontario side of the River: on Stag Island near Corunna (in an area associated with contaminated sediment; Richman and Milani, 2010) and at two locations approximately 10 and 13 km downstream from Stag Island, at the Lambton Generating Station and the Terra International Inc., respectively (Figure 1).

Livers were chemically analyzed for organochlorine contaminants at the Great Lakes Institute for Environmental Research at the University of Windsor, Ontario. Frozen liver samples were thawed, homogenized, spiked with a PCB-34 recovery standard, and extracted with dichlormethane:hexane

Figure 1. Map of collection sites for overwintering canvasbacks analyzed for contaminants in liver. Sitxeen ducks were collected from Lake St. Clair (LSC) near Mitchell's Bay and Anchor Bay in November and December of 2008. Fourteen ducks were collected from the St. Clair River (SCR) at Stag Island near Corunna (Stag I./Corunna) and near the Lambton Generating Station and Terra International Inc. (Lambton/Terra) in January and February of 2009.

(50:50% v/v). One standard mixture of Aroclor 1242:1254:1260 (1:1:1) was used for quantifying PCBs and two standard solutions were used for organochlorines. Lipids were removed and sample clean-up was performed by gel permeation chromatography followed by activated Florisil chromatography. Fractions were analyzed separately for organochlorine compounds by gas chromatography with a mass selective detector operated in the electron impact mode and using selected ion monitoring (SIM). Organochlorine compounds reported are *p,p'*-DDE (dichlorodiphenyldichloroethylene), HCB, dieldrin, heptachlor epoxide (HE), OCS, mirex, and sum chlordane (sum concentration 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). For every batch of six samples run, a method blank and one in-house reference tissue (Great Lakes carp *Cyprinus carpio* homogenate or Standard Reference Material 1947 from NIST) were also run for quality assurance purposes. Blanks and reference tissues were in compliance with the quality assurance procedures. The mean percent recovery of the PCB standard in samples and reference materials was 91.2% (range=75.3%–107.3%) and samples were not adjusted for recoveries. Method detection limits (MDLs) ranged from 0.008 ng/g to 0.178 ng/g wet weight (ww).

Chemical analyses of liver for total Hg and 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°C prior to digestion. A 0.2 g liver sample was placed in a Teflon vial containing 2.0 mL 30% H_2O_2 and 8.0 mL 15.0 M HNO_3 and microwave digested. Digestion included a multi-step preheating process from room temperature to 85°C, then to 145°C and finally to 210°C, sample mineralization at 210°C for 10 minutes, and venting to cool samples. Total Hg and Se were determined by cold vapor atomic fluorescence spectrometry and hydride generation atomic fluorescence spectrometry, respectively. For every four samples digested, one standard reference material sample (DOLT-3 dogfish liver) and one reagent blank were analyzed in parallel. Mean recoveries of the reference material were 101.4% for Hg and 99.8% for Se and concentrations were not recovery-corrected. MDLs were equal to 0.0005 µg/g dry weight (dw) for Hg and 0.1 µg/g dw for Se. The mean (±SD) moisture content of canvasback liver samples was 67.4 (±2.5)%. Concentrations are reported in ng/g ww for organochlorines and µg/g dw concentrations for metals.

2.3 Nutrient Reserves Analysis

For all overwintering canvasbacks collected in this study, body condition (based on morphometric parameters) and nutrients, i.e., protein, lipid (fat), and mineral reserves, were determined in collections at LSC between 10 November – 18 December 2008 (n=62 ducks) and at SCR between 19 December 2008 – 27 February 2009 (n=65 ducks). Included with the SCR ducks are two additional ducks that were collected from LSC on February 20 2009. Analysis of nutrient reserves was performed on carcasses (excluding internal organs and external appendages) at the Long Point Waterfowl Avian Energetics Lab (Port Rowan, Ontario, Canada). Carcasses were dried in an oven at 65°C to attain constant moisture, homogenized, and then 10 g samples were extracted using a Soxhlet apparatus with petroleum ether. Extracted samples were ashed in a muffle furnace at 550°C and nutrients expressed as lean dry weights. For details, see Gorman et al. (2008) and references therein.

2.4 Statistical Analysis

We performed an Analysis of Variance (ANOVA) to examine differences in mean contaminant concentrations among collection months which, when significant, was followed by the post-hoc Tukey HSD test for unequal size groups. Data were log-transformed ($\log_{10}$) to meet conditions of equal variance and normality for parametric analysis. A Kruskal Wallis one-way analysis of variance by ranks followed by non-parametric multiple contrast tests was used if conditions for parametric testing were not met. A two-way ANOVA was conducted to assess if age of ducks (i.e., juvenile or adult) and collection month was related to contaminant concentrations. Pearson correlation coefficients (r) were calculated to examine relationships between hepatic concentrations of Hg and Se. Regression analyses were conducted to assess temporal trends in body condition, nutrient reserves, and contaminant burdens. Concentrations of compounds found below the MDL were given a concentration of one-half of the MDL for calculations of mean values. Statistical analyses were performed using Statistica (Version 7). All results were considered significant at $p<0.05$.

Linear regression analysis of thawed body mass and body length in ducks showed a better fit ($R^2=0.35$, $p<0.001$) compared to the regression between scores from a Principal Component Analysis derived from morphological measurements (body length, wing chord, tarsus length, bill width, skull length, and keel length) and body mass ($R^2=0.27$, $p<0.001$). Body condition was subsequently estimated using residuals calculated from the regression between body mass and body length. A strong relationship was also detected between body mass and total fat reserves ($R^2=0.75$, $p<0.001$) and total protein reserves ($R^2=0.70$, $p<0.001$) but not mineral reserves ($R^2=0.03$).

3. Results

3.1 Contaminant Burdens in Overwintering Canvasbacks

Hepatic concentrations of sum PCBs, *p,p'*-DDE, HCB, sum chlordane, and HE in canvasbacks collected in February were significantly greater than concentrations in November (or December for HE) when overwintering birds arrived in the area ($p<0.006$; Figure 2, only select compounds shown). For these five compounds, mean concentrations in birds were on average 56 times greater in February than in November (range=6–244). While we detected an overall significant difference among collection months for OCS, dieldrin, and mirex ($p<0.02$), no significant differences in concentrations were identified by post-hoc comparisons between months (Figure 2). Nonetheless, mean concentrations for these three

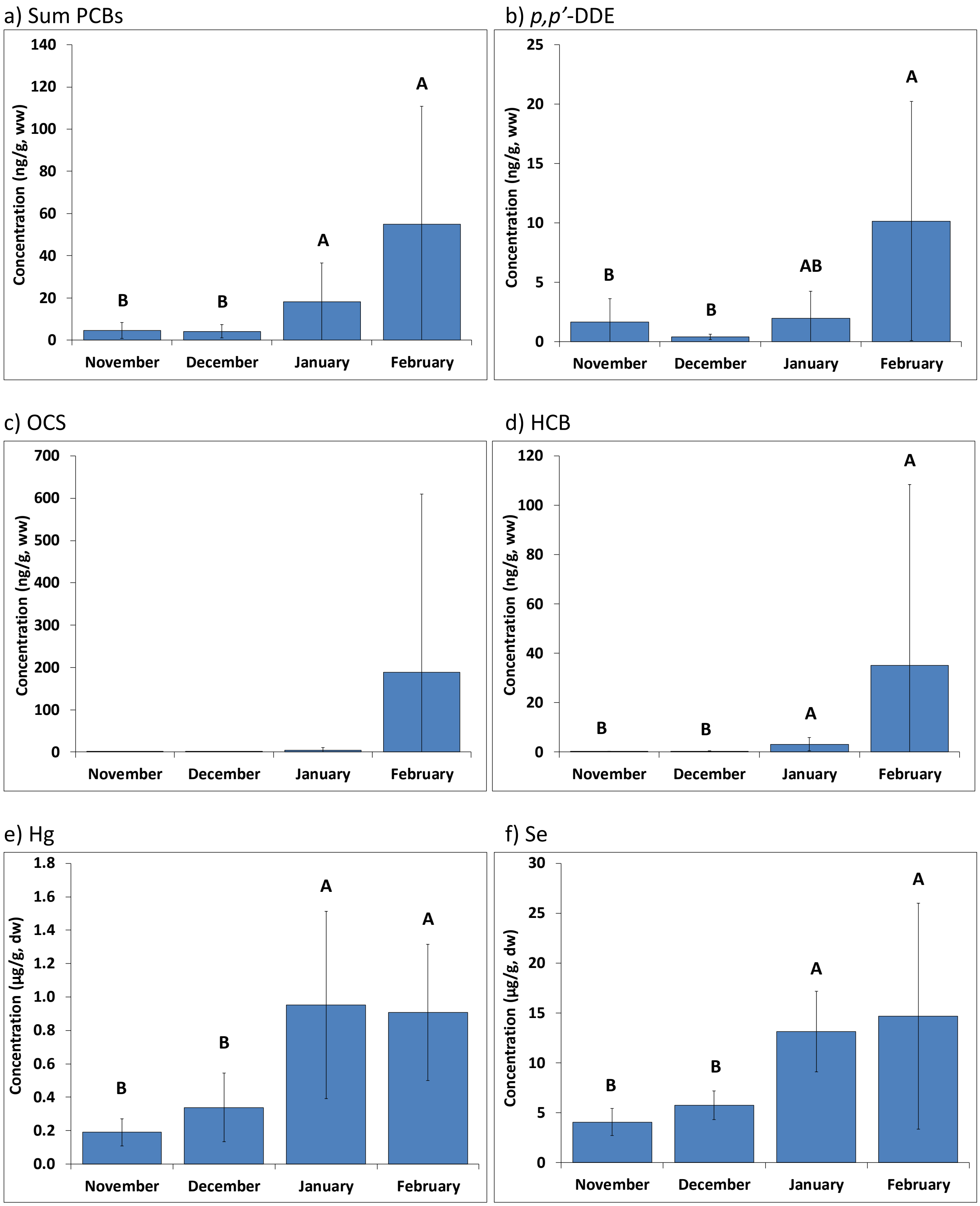


Figure 2. Mean hepatic concentrations (+SD) of sum PCBs (a), *p,p′*-DDE (b), OCS (c), HCB (d), Hg (e), and Se (f) in overwintering canvasbacks collected in November (n=8), December (n=8), January (n=8) and February (n=6) from Lake St. Clair and the St. Clair River in 2008/09. Concentrations are reported in ng/g wet weight for organochlorines and µg/g dry weight for metals. Different letters indicate significant differences in concentrations between collection months.

compounds were on average 1970 times greater in February than in November (range=7–5880). These dramatic increases were largely driven by relatively greater frequencies of November ducks with concentrations below respective MDLs compared to February ducks and the influence of one duck with a notably high OCS concentration in February (see below). Of all eight organochlorines quantified, sum PCBs and *p,p*'-DDE were detected at the greatest concentrations in livers. Mean sum PCB concentrations ranged from 4.2 ng/g in canvasbacks collected in December from LSC to 55 ng/g in canvasbacks collected in February from SCR. Similarly, mean *p,p'*-DDE concentrations ranged from 0.40 ng/g in December from LSC to 10 ng/g in February from SCR. Mean hepatic OCS concentrations ranged from 0.032 ng/g in canvasback collected in November to 190 ng/g in canvasbacks collected in February. Mean HCB concentrations ranged from 0.14 ng/g in November to 35 ng/g in February. Substantial variation for hepatic concentrations of HCB and OCS in February was largely due to one adult female from SCR with an elevated concentration of both HCB (180 ng/g) and OCS (1050 ng/g) which exceeded concentrations in other February ducks by at least an order of magnitude. Concentrations of HCB and OCS in this one duck were also greater than concentrations of all organochlorines (including sum PCBs) in other ducks. Removal of this duck resulted in relatively lesser overall mean concentrations for HCB (5.2 ng/g) and OCS (18 ng/g) in February ducks but did not change the post-hoc results for among-month comparisons. Mean percent lipid content ($\pm$SD) in liver of canvasbacks ranged from 3.3 ($\pm$1.5)% in December to 3.9 ($\pm$1.1)% in November and was statistically similar among collection months.

Hepatic concentrations of Hg and Se were also greater in ducks collected in January and February from SCR compared to ducks collected in the two preceding months from LSC (*p*<0.001; Figure 2). Mean Hg concentrations ranged from 0.19 µg/g in canvasbacks collected in November from LSC to 0.95 µg/g in canvasbacks collected in January from SCR. Hg concentrations in all ducks were below 1.4 µg/g dw with the exception of one juvenile female from SCR that exceeded this concentration (2.1 µg/g dw or 0.70 µg/g ww). Se concentrations were relatively greater with means ranging from 4.1 µg/g dw in liver of canvasbacks collected in November from LSC to 15 µg/g in canvasbacks collected in February from SCR. Se concentrations in 30 canvasbacks were below 10 µg/g dw in 67% of ducks (20), between 10–20 µg/g in 30% of ducks (9) and above 20 µg/g in 3% of ducks (1 juvenile female; 37 µg/g dw or 13 µg/g ww). A strong correlation was also detected between concentrations of Hg and Se in livers of canvasbacks (r=0.84, p<0.001).

Concentrations of sum PCBs, *p,p'*-DDE, Hg, and Se were above respective MDLs in all ducks while OCS concentrations were above the MDL in 50% (15/30) of study ducks. There was a general increase in the percentage of ducks with OCS concentrations above the MDL across months (in brackets) in November (25%), December (38%), January (75%), and February (67%). Upon comparing means of consecutive months, the greatest increases in concentrations of sum PCBs, HCB, Hg, and Se were detected between December and January when ducks moved from LSC to SCR while increases in *p,p'*-DDE and OCS concentrations were greatest between January and February in the SCR. In addition to sum PCBs, *p,p'*-DDE, HCB and OCS, hepatic concentrations of the less abundant organochlorines, i.e., dieldrin, HE, sum chlordane, and mirex, are provided in the supplemental information as means for adults and juvenile ducks by collection month (SI Table 1). When the age of ducks was considered (i.e., juvenile or adult), no effects of age or age by month interactions were detected for any organochlorines or metals. Temporal trends of concentrations of sum PCBs, sum of seven organochlorines, Hg, and Se were indistinguishable between juvenile and adult ducks indicating that age had little effect on concentrations of contaminants (SI Figure 1).

3.2 Body Condition and Nutrient Reserves

Distinct temporal changes in body condition were detected in canvasbacks collected from LSC and SCR (Figure 3). At LSC, body condition of canvasbacks increased between collection days 1–39 (R^2=0.42, p<0.001) while at SCR, a decrease in body condition was evident between collection days 40–110

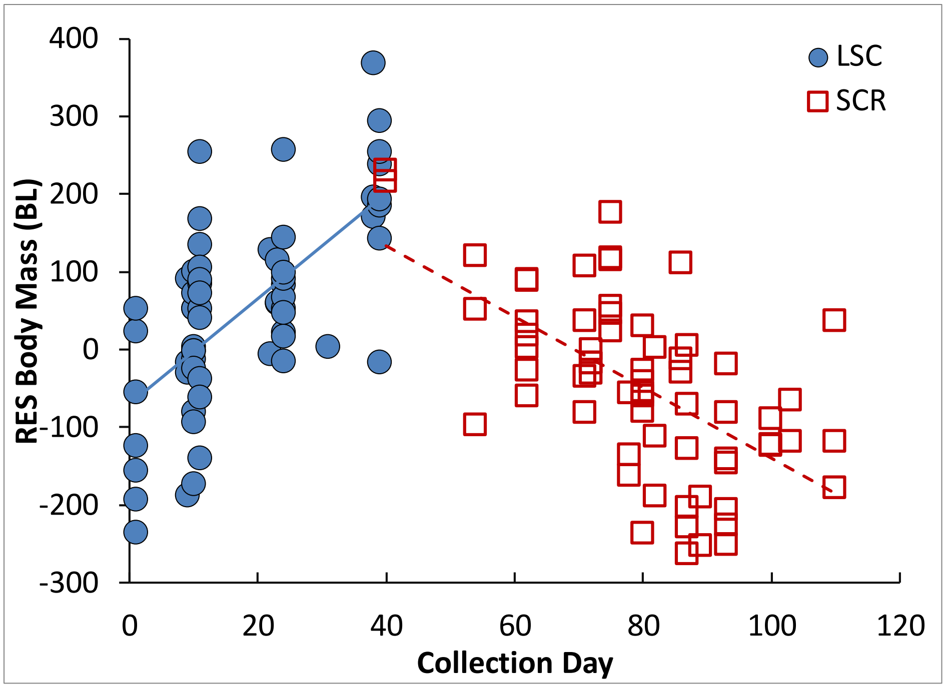


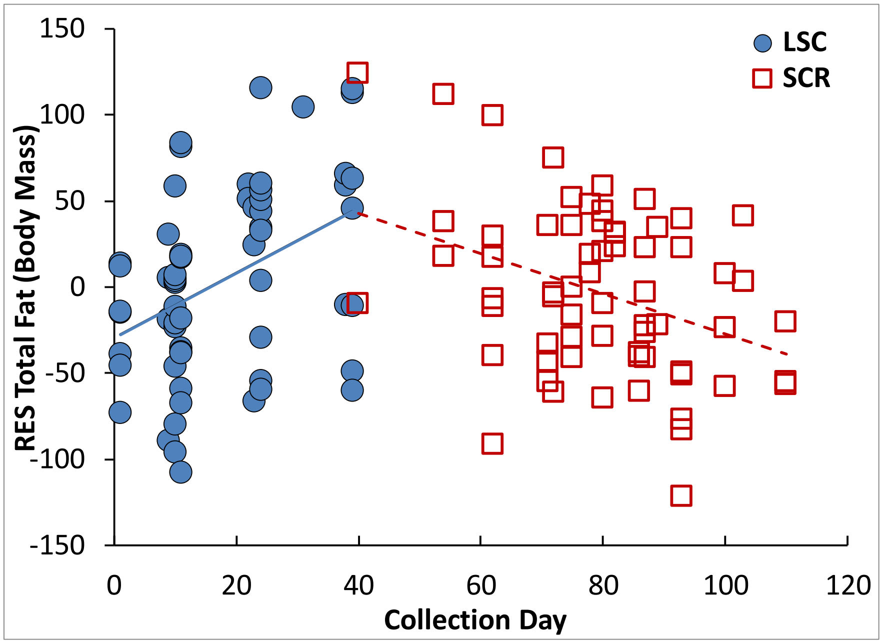
Figure 3. Signficant relationships between body condition (as an index determined as residuals of body length (BL) by body mass) and collection day for 127 overwintering canvasbacks collected from LSC (collection days=1–39) and from SCR (collection days=40–110).

(R^2=0.36, p<0.001). After controlling for body size, total fat reserves also increased in LSC ducks (R^2=0.17, p=0.001) and decreased in SCR ducks (R^2=0.13, p=0.003; Figure 4a). While an increase in protein reserves was detected in LSC ducks over time (R^2=0.17, p=0.001), no change in protein reserves were detected in SCR ducks (R^2=0.05, p=0.07; Figure 4b). Body condition and total fat reserves (both controlled for body size) in ducks were correlated although the coefficient of determination was low overall (R^2=0.06, p=0.006). No relationship was detected between body condition and total protein controlled for body size.

3.3 Contaminant Burdens and Body Condition

Similar spatial temporal trends were found when organochlorine concentrations in 30 ducks were examined in relation to body condition at the two study areas. While no relationships were detected between body burdens and body condition at LSC, a significant negative relationship was found between increasing concentrations of both sum PCBs (R^2=0.46, p=0.008; Figure 5a) and the sum of seven organochlorines (R^2=0.47, p=0.007; Figure 5b) and a decline in body condition at SCR. Relatively different spatial patterns were found for the two metals in relation to body condition at the two sites. For Hg, no significant relationships to body condition were found at either LSC or SCR (Figure 5c). For Se, a significant positive relationship was found between body burden and condition at LSC (R^2=0.43, p=0.005) but not at SCR (Figure 5d).

a) Total Fat



b) Protein

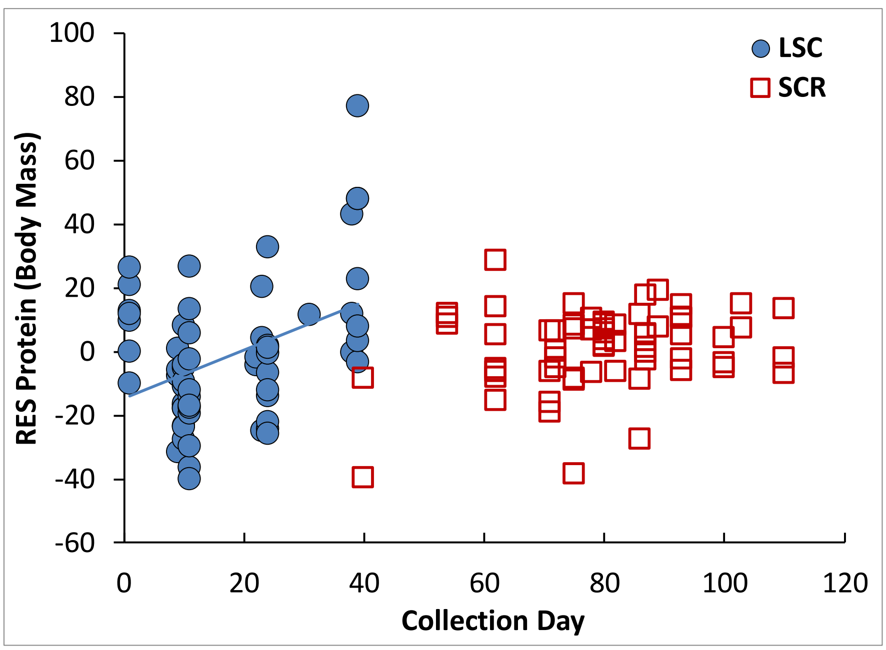


Figure 4. Relationships between total fat (a) and total protein (b) reserves (determined as residuals of fat or protein by body mass) and collection day for 127 overwintering canvasbacks collected from LSC (collection days=1–39) and from SCR (collection days=40–110). Regression lines indicate relationships that are significant.

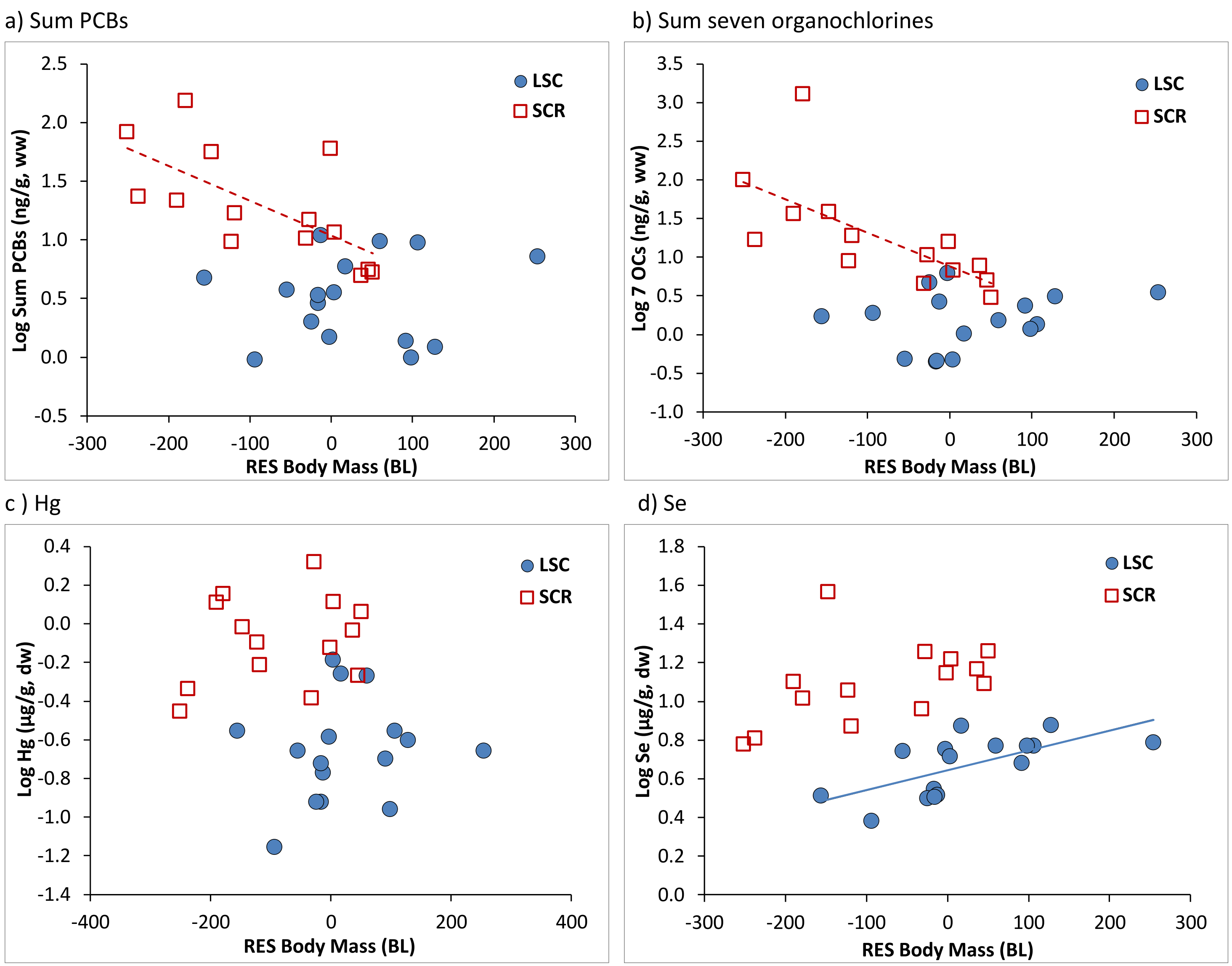


Figure 5. Relationships between hepatic concentrations of sum PCBs (a), sum of seven organochlorines (b), Hg (c), and Se (d) and body condition (as an index determined as residuals of body length (BL) by body mass) for 30 overwintering canvasbacks collected in LSC (collection days=1–39; n=16 ducks) and SCR (collection days=54–110; n=14 ducks). Regression lines indicate relationships that are significant.

4. Discussion

4.1 Temporal Changes in Burdens and Importance of Body Condition

We detected temporal increases in hepatic concentrations of eight organochlorines, Hg, and Se in overwintering canvasbacks foraging in this Great Lakes study area. Wintering ducks arriving on LSC in November had relatively low contaminant burdens that increased dramatically prior to leaving the SCR for spring migration in March. This pattern of rapid uptake and accumulation of contaminants has been demonstrated previously in several overwintering and migrating waterfowl species on the Great Lakes. Concentrations of sum PCBs and several other organochlorines increased significantly in fat of adult male common goldeneyes (*Bucephala clangula*) between the period when ducks arrived on their wintering grounds on the upper Niagara River (Nov–Dec) and the period just prior to spring migration (Feb–March; Foley and Batcheller, 1988). Accumulation of Se was also reported in fall and spring migrant populations of lesser scaup (*Aythya affinis*) on the lower Great Lakes and in overwintering populations of greater scaup (*A. marila*) and sea ducks including buffleheads (*Bucephala albeola*), common goldeneyes, and long-tailed ducks (*Clangula hyemalis*) on Lake Ontario (Petrie et al., 2007; Schummer et al., 2010; Ware et al., 2011). Uptake of Hg was also rapid in canvasbacks on San Francisco Bay where a significant increase in hepatic concentrations was detected between the early and late-winter periods (Hothem et al., 1998).

Two primary factors contributed to increasing concentrations of persistent organic pollutants (POPs) in this study. Loss of body condition is common in overwintering waterfowl due to depletion of fat reserves required for thermoregulation and restricted food intake (Mason et al., 2007; English et al., 2018). One consequence of loss of body condition is the redistribution of lipophilic contaminants among tissues following the consumption of fat stores (e.g., Bogan and Newton, 1977). Across a broad range of avian species, such increases in concentrations of POPs in tissues are not limited to periods of stress associated with winter periods (Anderson and Hickey, 1976; Smith et al., 1985) but also in breeding periods during egg laying and incubation when fat stores are being depleted (Henriksen et al., 1996; Bustnes et al., 2012). Furthermore during colder winters and poor feeding conditions, the mobilization of body fat reserves in female tawny owls (*Strix aluco*) was associated with both increased circulating contaminant concentrations and maternal transfer to eggs (Bustnes et al., 2011). Emaciated birds also tend to have greater burdens of POPs in liver or similar tissues in white-tailed eagles (*Haliaeetus albicilla*; Kenntner et al., 2003) and sparrowhawks (*Accipiter nisus*; Bogan and Newton, 1977). We also found that temporal increases of POPs in liver were associated with loss of body condition in overwintering canvasbacks in the SCR. The second factor influencing these temporal trends relates to increased exposure following the movement of ducks from LSC in December to SCR in January, an area associated with a relatively more contaminated food base due to its closer proximity to upstream SCR AOC contaminant sources. Greater concentrations of Hg, PCBs, OCS, and HCB were detected in juvenile spottail shiners collected from the SCR between 1999–2007 compared to shiners from nearshore areas of LSC (Gewurtz et al., 2010). Relative to reference sites, concentrations of Hg, OCS, and HCB were elevated in sediment in an area on the SCR near Corunna from 2006–2008 (Richman and Milani, 2010) where several canvasbacks were collected in this study. The adult female with the greatest concentrations of HCB and OCS, two notable organochlorines closely associated with the SCR AOC (OMOEE and MDNR, 1995), was collected on the east side of Stag Island, near Corunna. While this suggests that acquired hepatic burdens reflect local contaminant conditions, it is possible other sites of contamination (e.g., industrial holding ponds) may have contributed to burdens since these ducks are mobile and home range size in the winter has not been studied. In addition, a seasonal change in diet from one that is more vegetation-based in LSC (since plant matter senesces in winter) to one containing a greater proportion of benthic invertebrates in the SCR may have contributed to an increase in exposure. Such a shift was found in overwintering canvasbacks at Chesapeake Bay where ducks switched from a predominately vegetation-based diet in December to a diet dominated by Baltic clams (*Macoma balthica*) in February due to a decline in submerged aquatic vegetation (Haramis et al., 2001). Increased exposure directly through consumption of contaminated organic sediment in the SCR is also possible as plant matter is removed. Any or all of these scenarios are possible. Dietary studies of overwintering canvasbacks as well as the degree of contamination of diet items may elucidate potential sources and routes of exposure of pollutants in canvasbacks in this important overwintering area.

In contrast to organochlorines, relationships between body condition and Hg and Se in tissues may be related to concentrations as well as the metals themselves. While a negative correlation between hepatic Hg concentrations and body condition (based on fat content) has been reported in wild ducks (Wayland et al., 2002; Schummer et al., 2012), this was not evident in this study or in breeding female greater scaup (Badzinski et al., 2009), a difference that may be related to relatively lower Hg concentrations found in these ducks. Se is nutritionally required by waterfowl and the positive relationship between Se concentrations and body condition at LSC suggests that ducks are accumulating this essential metal in their diet as they consume more food. This positive association has been found in other studies of wild avian populations with similar Se concentrations (Anteau et al., 2007; Schummer et al., 2012). At sufficiently elevated Se concentrations however, a negative association may be evident since weight loss can be diagnostic of Se toxicosis (Ohlendorf and Heinz, 2011).

Our study is unique in that an estimated body condition index and quantified nutrient reserves were directly compared, a relationship that is often assumed but rarely tested when examining ecological variables of interest. Body mass was a good predictor of protein and fat reserves in overwintering canvasbacks which is in agreement with that found by Schamber et al. (2009) who compared combinations of several indices of body condition using assorted body size metrics with protein and fat reserves in five waterfowl species. Similar temporal patterns for body condition assessed using body metrics and fat reserves accounting for body size at the two sites (and significant correlation between these two variables) reflect, as expected, the importance of fat reserves in influencing body condition during the winter when food may be limited and temperatures are below freezing.

4.2 Potential Impact on Survival

Overall, hepatic concentrations of POPs and Hg in canvasbacks in this study were not notably elevated and were well below those associated with toxicity. Concentrations of PCBs and DDE in ducks were well below those resulting in death in laboratory feeding studies of birds (Hoffman et al., 1996; Blus, 2011). Hg concentrations were also well below hepatic concentrations of 2 µg/g and 20 µg/g (wet weights) suggested as thresholds for adverse effects on reproduction and survival, respectively, in non-marine birds (Shore et al., 2011). However, 30% of ducks exceeded the Se threshold concentration that is considered elevated (>10 µg/g) and one single February duck (3%) exceeded the concentration associated with possible toxicity in freshwater avian populations (20 µg/g, Ohlendorf and Heinz, 2011). Elevated Se exposure has been frequently reported in overwintering and staging Great Lakes waterfowl in several studies conducted between 1993–2007 (range in percentages of birds exceeding the lower threshold=14–99%; scaup species: Custer et al., 2000; Petrie et al., 2007; Ware et al., 2011; mute swan (*Cygnu olor*): Schummer et al., 2011) with a portion of these also exceeding the higher concentration associated with possible toxicity. While ducks may purge portions of their Se burdens on their breeding grounds, continued elevated Se exposure over the life of these individuals could be detrimental and further studies of short- and long-term health effects of elevated Se exposure in overwintering waterfowl on the Great Lakes would be informative.

4.3 Potential Impact on Fitness

Despite a predominantly vegetation-based diet, overwintering canvasbacks experienced rapid uptake and accumulation of contaminants over just a few months. For ducks feeding continually on a contaminated food source and notably in the latter part of the winter as in this study, it is unlikely that a steady state equilibrium would have been reached for most compounds prior to ducks migrating back to their breeding grounds. For methylmercury, a steady state condition was not yet evident in liver of American kestrels (*Falco sparverius*) at 125 days post exposure (Nichols et al., 2010). Se may be an exception since concentrations were predicted to reach 95% of equilibrium in just 8 days in liver of adult mallards (*Anas platyrhynchos*) fed a high Se diet; the rate of loss was also rapid with a half-life of 19 days (Heinz et al., 1990). Depuration rates of organochlorines however were slow in wild juvenile herring gulls based on predicted half-lives of OCS (93 days), and HCB (188 days), and *p,p'*-DDE (880 days; Clark et al., 1987). Evidence for a slow Hg depuration rate was found in breeding double-crested cormorants (*Phalacrocorax auritus*) on the Great Lakes that had migrated from winter locations with high Hg exposure compared to other locations (Lavoie et al., 2014). This may have fitness consequences for female canvasbacks because contaminants acquired on wintering grounds could be deposited in eggs. To our knowledge, only one study has examined contaminant concentrations in eggs of canvasbacks breeding at sites in central and eastern prairies of northern U.S. and Canada (Stendell et al., 1977). Irrespective of contaminant burdens, reduced body condition of migratory birds at overwintering sites may carry over to body condition upon their arrival to the breeding site (Hebert et al., 2008) and at the time of breeding can limit breeding propensity (Warren et al., 2014), reduce survivorship (Kaminski et al., 2013), and reduce productivity (Blums et al., 1997). Breeding canvasbacks require threshold nutrient reserves (i.e., fat and protein) for egg production and body maintenance which may be acquired from endogenous sources as well as local sources at the breeding site (Barzen and Serie, 1990).

Energetic requirements for successful migration and breeding may change from year to year as habitat and weather conditions change from one winter to the next. For example, canvasbacks would likely experience increased energetic expenditures while foraging and loafing in running water associated with the SCR relative to those in LSC. Consequently, loss of nutrient reserves and associated increases in contaminants may be more pronounced during years when LSC freezes thereby forcing birds to relocate to rivers. Thus, we do not think that habitat conditions (food availability and ice cover), nutrient reserves, and contaminant concentrations are mutually exclusive. Winter severity was found to influence movements of overwintering northern Great Lakes herring gulls and consequently contaminant accumulation in gulls (Hebert, 1998). Reduced Great Lakes ice cover (Wang et al., 2012) may increasingly allow canvasbacks to winter at LSC. However, extreme weather events and mass starvation, as reported in waterfowl with increased metal burdens at LSC in 2013/2014, may offset this as a predictable overwintering location for increased survival (van Zyl et al., 2015).

4.4 Conclusions

Our results suggest that a seasonal loss of body condition (fat reserves) and movement from LSC to the more contaminated SCR contributed to the rapid rise of contaminant concentrations in liver of overwintering canvasbacks. This species was effective in accumulating contaminants historically identified as compounds of concern, notably Hg, HCB, OCS, and PCBs, in the SCR AOC and provides evidence of ongoing exposure in this area. In addition, this pattern of increased contaminant burdens in overwintering ducks in the SCR/LSC study area is consistent with both the propensity of rapid uptake of many of these compounds and temporal patterns reported in other waterfowl species staging or overwintering on the Great Lakes. Although the effects of contaminants may be limited, loss of body condition in ducks from one of its most northerly wintering locations may have important consequences for meeting energetic demands required for successful migration to breeding sites and reproduction in the prairies. We suggest continued monitoring of abundances and spatial distributions of canvasbacks to examine habitat use and body condition of this species in this region during winter. As well, assessing contaminant burdens in eggs of canvasbacks at breeding sites would also be informative as there may be carry-over of burdens from overwintering Great Lakes locations where increased exposure to many legacy POPs and metals has been well-documented in biota.

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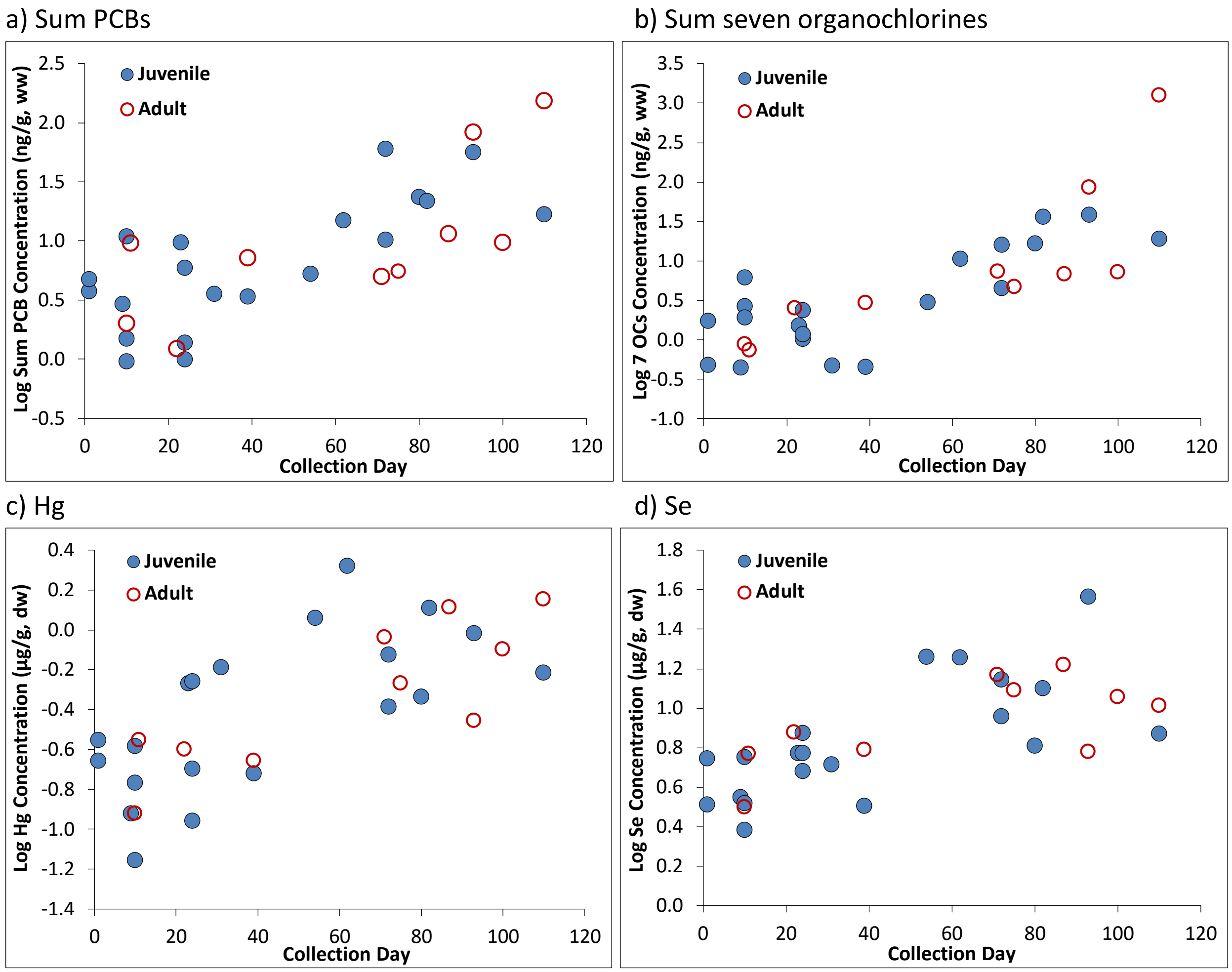
		November (LSC)	December (LSC)	January (SCR)	February (SCR)
No. of JUV/AD		6/2	6/2	6/2	2/4
Sum PCBs	JUV	4.1 (3.6) 100%	4.1 (3.2) 100%	23 (20) 100%	37 (28) 100%
	AD	5.8 (5.3) 100%	4.2 (4.2) 100%	5.3 (0.42) 100%	64 (68) 100%
p,p'-DDE	JUV	1.5 (2.0) 100%	0.34 (0.24) 100%	2.5 (2.4) 100%	7.2 (3.0) 100%
	AD	2.2 (2.3) 100%	0.56 (0.004) 100%	0.34 (0.043) 100%	12 (13) 100%
OCS	JUV	0.025 (0.018) 17%	0.071 (0.088) 33%	6.2 (6.2) 100%	7.3 (1.7) 100%
	AD	0.055 (0.053) 50%	0.36 (0.49) 50%	0.017 (0) 0%	280 (510) 50%
HCB	JUV	0.13 (0.15) 67%	0.13 (0.13) 100%	2.6 (2.9) 100%	4.5 (1.3) 100%
	AD	0.20 (0.19) 100%	0.55 (0.66) 100%	4.8 (1.4) 100%	50 (90) 100%
Dieldrin	JUV	0.18 (0.22) 17%	0.089 (0) 0%	1.2 (1.3) 50%	4.3 (6.0) 50%
	AD	0.089 (0) 0%	0.089 (0) 0%	0.30 (0.05) 100%	2.1 (2.8) 50%
HE	JUV	0.24 (0.44) 17%	0.056 (0) 0%	1.3 (1.2) 67%	3.4 (3.4) 100%
	AD	0.16 (0.039) 100%	0.12 (0.091) 50%	0.33 (0.38) 50%	1.2 (1.3) 100%
Sum Chlordane	JUV	0.16 (0.047) 33%	0.46 (0.61) 33%	0.55 (0.22) 100%	1.9 (1.7) 100%
	AD	0.29 (0.077) 100%	1.6 (0.94) 100%	0.53 (0.045) 100%	1.2 (0.90) 100%
Mirex	JUV	0.025 (0.014) 17%	0.019 (0) 0%	0.038 (0.046) 17%	0.24 (0.15) 100%
	AD	0.019 (0) 0%	0.019 (0) 0%	0.019 (0) 0%	0.11 (0.12) 50%
Hg	JUV	0.19 (0.082) 100%	0.37 (0.23) 100%	1.0 (0.63) 100%	0.79 (0.25) 100%
	AD	0.20 (0.11) 100%	0.24 (0.021) 100%	0.73 (0.27) 100%	0.97 (0.49) 100%
Se	JUV	3.9 (1.3) 100%	5.4 (1.4) 100%	13 (4.7) 100%	22 (21) 100%
	AD	4.5 (1.9) 100%	6.8 (0.97) 100%	13.5 (1.6) 100%	11 (4.3) 100%

SI Table 1. Mean hepatic concentrations (SD) of contaminants in juvenile (JUV) and adult (AD) canvasbacks collected in November, December, January, and February from LSC and the SCR in 2008/09. Twenty juvenile ducks and 10 adult (female) ducks were analyzed in total. Percentages represent the number of ducks with a concentration above respective MDLs relative to the total number of ducks collected in the month.



SI Figure 1. Temporal trends in hepatic concentrations of sum PCBs (a), sum concentration of seven OCs consisting of *p,p′*-DDE, OCS, HCB, dieldrin, HE, sum chlordane, and mirex (b), Hg (c) and Se (d) for 20 juvenile ducks and 10 adult female ducks. Collection day is shown on the x-axis with collection day 1 (November 10 2008) on LSC and collection day 54 (January 2 2009) on the SCR.