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Contaminants in Lesser and Greater Scaup Staging on the Lower Great Lakes

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Abstract. The decrease and subsequent lack of recovery of the North American scaup population has increased concerns about contaminants acquired during migration. We collected 189 fall- and spring-migrant lesser (*Aythya affinis*) and greater scaup (*A. marila*) on the lower Great Lakes (LGL) to determine if organic contaminants and trace elements in scaup livers were increased and to evaluate sources of variation in selenium (Se) burdens. We found that all organic contaminants were below toxic levels. Of 18 trace elements, only Se was detected at increased (>10-ppm dry-mass) levels. Se in lesser scaup increased but remained constant in greater scaup throughout fall; levels were increased in 14% of lesser scaup and 46% of greater scaup. During spring, Se increased in lesser scaup but decreased slightly in greater scaup; levels were increased in 75% of lesser scaup and 93% of greater scaup. We suggest that Se may be problematic for some breeding female scaup after departing the LGL, but more research is needed to determine the extent to which it affects scaup demographics.

The North American population of lesser (*Aythya affinis*) and greater scaup (*A. marila*) decreased substantially between the mid-1980s and late 1990s, and numbers remain low (Afton and Anderson 2001). Scaup population recovery may be limited by factors affecting female scaup reproduction or survival, one of which may be related to acquisition of contaminants at major wintering or staging areas (Austin *et al*. 2000). The lower Great Lakes (LGL) provide important staging and wintering habitat for scaup (Dennis *et al*. 1984), much of which lies close to highly populated and industrialized areas. The LGL have been subjected to, and altered by, several anthropogenic stressors, including contaminants and introduction of exotic species (Sweet *et al*. 1988; Mills 1993). Either the independent or combined effects of these stressors may have major population level impacts for scaup using the LGL.

Zebra mussels (*Dreissena polymorpha*) were introduced to the LGL in the mid-1980s, and the closely related quagga mussels (*D. bugensis*) were introduced in the early 1990s (hereafter, dreissenid mussels) (Herbert *et al*. 1989; May and Marsden 1992). Dreissenid mussels rapidly spread throughout the LGL and now dominate the benthic macroinvertebrate community (Griffiths *et al*. 1991; MacIsaac *et al*. 1991). In response, both scaup species switched from a diet of mainly native gastropods to one dominated by zebra mussels (Ross *et al*. 2005). Dreissenid mussels are prolific filter-feeders and can bioaccumulate contaminants more readily than gastropods (Brieger and Hunter 1993; deKock and Bowmer 1993). These organisms can facilitate the trophic transfer of contaminants to scaup and other diving ducks (Custer and Custer 2000) and ultimately may decrease their reproductive output or survival (de Kock and Bowmer 1993).

Since dreissenid mussel colonization, the total number of staging scaup, and their duration of stay, has increased greatly on the LGL (Petrie and Knapton 1999). Thus, dreissenid mussels, by way of trophic transfer of organic contaminants and trace elements, could have major demographic implications for scaup. Custer and Custer (2000), for example, found that 95% of scaup collected near industrialized sites on the LGL had increased to potentially harmful concentrations of liver selenium (Se), a trace element that can cause reproductive (>10-ppm dry-mass) and health-related (>33-ppm dry-mass) problems in some waterfowl (Heinz 1996). Additional study into the contaminant burdens of fall- and spring-migrant lesser and greater scaup on the LGL is warranted because the North American scaup population is currently near all-time low levels, and there is concern that birds are acquiring unhealthy levels of contaminants outside the breeding season (Austin *et al*. 2000; Custer and Custer 2000).

We had several main objectives for our research. First, we sought to determine if scaup were acquiring increased levels of any organic contaminants or trace elements during fall or spring. Because previous studies have shown that Se was increased in lesser scaup on the United States side of the LGL (Custer and Custer 2000; Custer *et al*. 2000a, 2003), we were most interested in identifying sources of variation in Se burdens of scaup collected from major stopover sites in Canada. A second objective was to determine if seasonal Se levels differed between collection locations, species, and ages and to evaluate within-season temporal dynamics of Se. Third, we tested for differences in Se burdens in lesser and greater scaup staging on Lake Ontario during fall 1986 and 1999.

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Materials and Methods

Sample Collection

We collected female lesser and greater scaup from the Ontario sides of Lakes St. Clair, Erie, and Ontario throughout fall 1999 (October 4 to December 31) and spring 2000 (March 4 to May 3) (Figure 1). Birds were shot with shotguns using steel shot over decoys. After collection, we injected 10% formalin solution into the esophagus of each bird to preserve food items. For each bird we recorded sex, collection date, and location. We then labeled birds and froze them in plastic bags.

In the laboratory, we thawed and dissected birds, as described in Badzinski and Petrie (2000b), to ascertain age (bursa of Fabricius = immature) and to obtain a sample (approximately 15 g) of liver tissue. Liver samples were wrapped in hexane-rinsed foil, frozen, and sent to the Great Lakes Institute of Environmental Research in Windsor, Ontario, Canada, for contaminant analyses. This tissue was analyzed so results could be directly compared with several other contaminant studies of scaup that reported liver contaminant burdens (*e.g.*, Cohen *et al*. 2000; Custer and Custer 2000; Custer *et al*. 2000a, 2003). The remaining liver tissue was frozen and sent to the University of Western Ontario for proximate analyses to determine lipid content (Badzinski and Petrie 2006b).

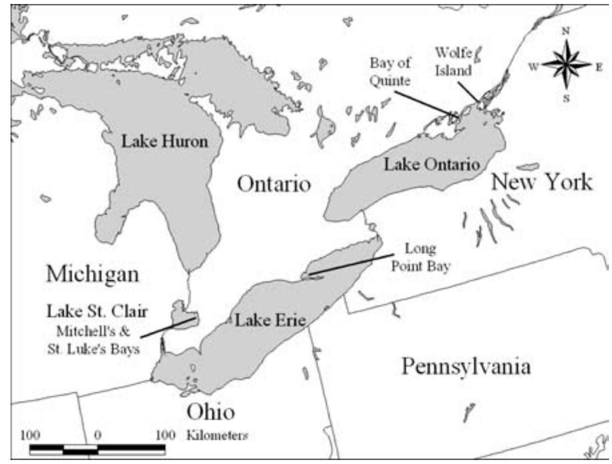

Fig. 1. Geographic distribution of locations (Mitchell's and St. Luke's Bays, Lake St. Clair; Inner and Outer Long Point Bays; Lake Erie; and Bay of Quinte/Wolfe Island area, Lake Ontario) in Ontario, Canada, where lesser and greater scaup were collected during fall 1999 and spring 2000

Contaminant Analyses

We used liver samples (approximately 5 g) from 24 female lesser scaup collected during spring 2000 from lakes Erie (n = 6), Ontario (n = 8), and St. Clair (n = 10) to determine organochlorine pesticide and polychlorinated concentrations using analytic methods described by O'Rourke *et al*. (2004). Organochlorine analysis included determination of the following:

1. chlorobenzenes (*e.g.*, 1,2,3,4-tetrachlorobenzene [1,2,3,4-TCB], 1,2,4,5-TCB pentachlorobenzene [QCB], and hexachlorobenzene [HCB]);
2. hexachlorocyclohexanes [HCHs] (*e.g.*, alpha-HCH, beta-HCH, and gamma-HCH isomers);
3. chlordane-related compounds (*e.g.*, sum chlordane = oxychlordane + *trans*-chlordane + *cis*-chlordane + *trans*-nonachlor + *cis*-nonachlor);
4. dichloro-diphenyl-trichloroethane [DDT] and its metabolites (*e.g.*, 4,4′-(2,2,2-trichloroethane-1,1-diyl)bis(chlorobenzene); sum DDT = p,p'-DDT + p,p'-DDE + p,p'-DDD);
5. octachlorostyrene (OCS);
6. Mirex; and
7. polychlorinated biphenyls [PCB] (*e.g.*, sum PCBs = sum of IUPAC nos. 31/28, 52, 49, 44, 42, 64 + 47 + 71, 74, 70 + 76, 66 + 95, 56 + 60, 90 + 101, 99, 87, 110, 151, 149, 118, 146, 153 + 132, 105, 141, 138, 158, 129, 182 + 187, 183, 185, 174, 171, 200, 172, 180, 170 + 190, 201, 203, 195, 194, and 206).

We analyzed another liver sample (approximately 5 g) from 64 lesser scaup as follows: (Erie: adult = 11, juvenile = 9; Ontario: adult = 14, juvenile = 11; and St. Clair: adult = 8, juvenile = 11) and 41 greater scaup as follows: (Erie: adult = 10, juvenile = 9 and Ontario: adult = 12, juvenile = 10) collected during fall and 56 lesser scaup (Erie = 20; Ontario = 19; and St. Clair = 17) and 28 greater scaup (Erie = 20 and Ontario = 8) collected during spring for the following trace and macro elements—Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se, V, Zn, and Hg (total)—using methods described by Mallory *et al*. (2004). Zebra mussel soft tissues, collected from the upper digestive tract of scaup, were combined into 4 pooled spring samples (11 lesser scaup from Lake Ontario) and 5 pooled fall samples (12 greater scaup and 5 lesser scaup from Lake Ontario; 8 lesser scaup from Lake St. Clair; and 7 lesser scaup from Lake Erie) and were analyzed for trace elements. We obtained liver samples (approximately 15 g) from greater (n = 26) and lesser (n = 29) scaup collected by the Canadian Wildlife Service during fall 1986 on eastern Lake Ontario, which we also subjected to trace element analyses.

Statistical Analyses

We first inspected species-specific data matrices of analytes and assessed their frequencies of nondetection values. After doing this, we identified which analytes had ≥60% detection rates and replaced nondetection values with random numbers generated from a log normal distribution with a mean and SD corresponding to that derived for the method detection limit. All data were log transformed to normalize error distributions of data in statistical analyses.

We used multivariate analysis of variance (MANOVA) to test for among-lake differences in major organochlorine groups (sum chlordanes, HCB, OCS, Mirex, sum PCB, and sum DDT) in spring-staging female lesser scaup. We also used species- and season-specific MANOVA to determine if trace elements in lesser and greater scaup collected during fall 1999 and spring 2000 differed among lakes or between age classes (fall only); an interaction between lake and age also was included in models for fall analyses. We made these evaluations to simplify presentation of summary statistics and to identify which contaminants were increased or of biological concern. We used MANOVA to test for differences between fall Se burdens in both scaup species collected at Lake Ontario during 1986 and 1999.

We used general linear models (GLMs) in four sets (lesser-fall, lesser-spring, greater-fall, greater-spring) of preliminary analyses to determine if collection location (lesser = Erie, Ontario, and St. Clair; greater = Erie and Ontario) explained variations in Se burden and age (class, fall only). Date (Julian date; continuous) main effects, plus the interactions lake × age and age × date (both *fall* only), were also included in models. Each of these four analyses showed that lake main effects (and relevant interactions) were not significant ($p > 0.05$), so we combined data across lakes in subsequent season-specific analyses. We analyzed Se data separately by season because (1) this element has greater implications for female scaup migrating to breeding areas where Se can be incorporated into eggs and possibly affect reproduction (Heinz 1996); (2) scaup diets differ between seasons on the LGL (Badzinski and Petrie 2006a); and (3) age could not be confidently assigned during spring. We thus used a GLM to test for differences between species and ages (plus species × age interaction) and to assess temporal trends (date + species × date and age × date effects) in fall Se burdens. We also used a GLM to assess the following sources of variation in Se burdens in spring-staging scaup: species + date and species × date.

All initial models were reduced in a backward stepwise manner, sequentially removing the highest-order effects at $p > 0.05$ to obtain decreased models. We evaluated significance of F-tests (type III sums of squares) in univariate analyses, whereas Wilks' lambda was the test statistic for multivariate analyses. We made all post hoc comparisons of means for effects included in final models using Tukey-Kramer (T-K) tests (Zar 1996). Geometric means and other parameter estimates, unless otherwise stated, are reported with lower and upper 95% confidence limits. Log-transformed concentrations were back-transformed for presentation and easier interpretation. Unless otherwise stated, concentrations are reported as ng/g (ppb) wet liver mass for organic contaminants or μg/g (ppm) dry liver mass for trace elements. Throughout, we consider Se levels "increased" at >10 ppm dry liver mass (3-ppm wet-weight basis) given that some waterfowl experienced reproductive impairment or health-related problems above that level (Heinz *et al*. 1989; Heinz 1996). Statistical analyses were made using SAS analytic software (SAS Institute, Cary, NC).

Results

Organic Contaminants

Organic contaminants with infrequent detection in lesser scaup included tetrachlorobenzenes (1,2,3,4- and 1,2,4,5-TCB, $n \leq 2$) and HCHs ($n = 1$). QCB was above the method detection limit concentration (0.30 ppb wet mass) in one, two, and three birds from Lakes St. Clair, Ontario, and Erie, respectively. For samples in which QCB was detected, levels were near the detection limit of 0.30 ppb. The aforementioned organochlorines were not included in subsequent data analyses or interpretation.

There were no differences in mean liver lipid content among female lesser scaup from different lakes (ANOVA: $F_{2,23} = 0.31$, $p = 0.7394$), so analyses were made using wet-weight concentration data. Overall, concentrations of six major groups of organochlorines in lesser scaup did not differ among lakes (MANOVA: Wilks' $\lambda = 1.45$, $p = 0.1908$). Geometric mean (95% confidence interval [CI]) concentration of sum PCBs was 49.1 [37.0 to 65.0] ppb and ranged from 8.11 to 180 ppb. Sum DDT concentration averaged 15.1 [2.80 to 81.4] ppb and ranged from 3.30 to 69.6 ppb. The geometric mean OCS level in liver tissues was 4.67 [3.08 to 7.14] ppb; 7 birds had values below the method detection limit of 0.30 ppb, and the maximum concentration was 28.9 ppb. Sum chlordane levels averaged 3.54 [0.64 to 18.7] ppb; 5 birds had values at or below the detection limit of 0.50 ppb, and the maximum concentration was 32.4 ppb. HCB levels averaged 1.04 [0.88 to 1.22] ppb, and the maximum level recorded was 2.92 ppb. Geometric mean Mirex concentration was 0.61 [0.50 to 0.75] ppb; 7 birds were below the detection limit of 0.50 ppb, and the maximum recorded level was 1.48 ppb.

Trace Elements

Several trace elements—including As, Co, Cr, Ni, Pb, and V—had low frequencies of detection in all lake-season species–age groupings of birds and thus were not included in analyses. Three (Ontario = 2, St. Clair = 1) fall-collected lesser scaup had nondetection values for Se, and two adult lesser scaup (one in each season) had nondetection values for Al. All 11 remaining elements were detected at 100% frequency and, along with Se and Al, were included in analyses.

For lesser scaup collected during fall, concentrations (ppm dry liver mass) of several trace elements differed by lake (MANOVA: Wilks' $\lambda = 0.48$, $p = 0.022$) and age (Wilks' $\lambda = 0.38$, $p < 0.001$). Al was higher in birds at Lake Erie (804 [44 to 1460] ppm) compared with those at Lake Ontario (141 [83.0 to 240] ppm) (T-K $p = 0.002$) but similar to levels in birds at Lake St. Clair (335 [182 to 617] ppm) (T-K $p > 0.05$); Lake Ontario and Lake St. Clair birds had similar Al burdens (T-K $p > 0.05$). K levels in birds at Lake Ontario (10,100 [9720 to 10,400] ppm) were higher than those at Lake Erie (9210 [8860 to 9570] ppm) (T-K $p = 0.004$) but were similar to those at Lake St. Clair (9560 [9190 to 9940] ppm) (T-K $p > 0.05$); Lake St. Clair and Lake Erie birds had similar K concentrations (T-K $p = 0.3195$). Cd overall was higher in adult (2.91 [2.36 to 3.59] ppm) than in juvenile scaup (0.79 [0.64 to 0.98] ppm) (T-K $p < 0.001$). The remaining 10 trace elements showed no among-lake (T-K all $p > 0.05$) or age-related variation (T-K all $p > 0.05$) during fall (Table 1).

For lesser scaup collected during spring, concentrations of some elements differed among lakes (MANOVA: Wilks' $\lambda = 0.40$, $p = 0.010$). Birds at Lake Ontario (20.6 [18.7 to 22.2] ppm) had slightly higher Mn levels than did those at both lakes Erie (16.3 [14.8 to 17.9] ppm (T-K $p = 0.003$) and St. Clair (17.2 [15.7 to 18.9] ppm (T-K $p = 0.042$); birds at the latter two lakes had similar Mn levels (T-K $p = 0.707$). Hg levels in birds were higher at Lake Erie (1.89 [1.41 to 2.52] ppm) than at Lake Ontario (1.05 [0.78 to 1.42] ppm) (T-K $p = 0.0224$) but were similar to those at Lake St. Clair (1.53 [1.12 to 2.10] ppm) (T-K $p > 0.05$); levels did not differ (T-K $p > 0.05$) in birds at Lakes Ontario and St. Clair. The remaining 11 elements showed no among-lake variation (T-K all $p > 0.05$) (Table 1).

For greater scaup collected during fall, concentrations of several trace elements differed between lakes (MANOVA: Wilks' $\lambda = 0.24$, $p < 0.001$) and ages (Wilks' $\lambda = 0.35$, $p = 0.001$). Al was higher in birds from Lake Erie (963 [684 to 1360] ppm) compared with those from Lake Ontario (113 [82.1 to 155] ppm) (T-K $p < 0.001$). Birds from Lake Ontario (439 [327 to 588] ppm) had higher Ca levels than did those from Lake Erie (238 [174 to 325] ppm) (T-K $p = 0.008$). K was higher in birds from Lake Ontario (9070 [8560 to 9620] ppm) relative to those from Lake Erie (8200 [7700 to 8740] ppm) (T-K $p = 0.028$). Birds from Lake Ontario (768 [725 to 813] ppm) had higher Mg levels than did birds from Lake Erie (694 [653 to 738] ppm) (T-K $p = 0.023$). Cd levels in birds

Table 1. Geometric mean concentrations (μg/g dry mass [ppm]), 95% CIs, and ranges of trace elements in liver tissues of female lesser and greater scaup collected at Lakes Erie and St. Clair, Ontario, Canada during fall 1999 and spring 2000. Values were combined across lakes and ages within species and seasons

		Fall		Spring	
Element	Detection limit	Lesser scaup (n = 64)	Greater scaup (n = 41)	Lesser scaup (n = 56)	Greater scaup (n = 28)
Al	11.0	314 [b]	309 [b]	153	174
		(217 – 455)	(206 – 461)	(110 – 213)	(118 – 257)
		(1nd[c]–3990)	(46.1 – 4520)	(1nd – 3280)	(13.8 – 2230)
Ca	6.25	332	331 [b]	418	326
		(279 – 394)	(263 – 416)	(358 – 489)	(279 – 382)
		(134 – 8290)	(119.6 – 7800)	(178 – 9340)	(129 – 809)
Cd	0.15	1.54 [c]	1.99 [b,d]	ND [e]	ND
		(1.24 – 1.92)	(1.59 – 2.51)		
		(16nd – 14.4)	(15nd – 8.68)	(17nd – 18.8)	(16nd – 12.5)
Cr	1.10	0.88	1.02	ND	ND
		(0.77 – 1.02)	(0.81 – 1.28)		
		(2nd – 2.32)	(3nd – 4.12)	(56nd – 0.36)	(28nd – 0.62)
Cu	0.99	77.6	720	70.8	98.1
		(70.4 – 85.4)	(64.3 – 80.6)	(64.7 – 77.6)	(87.8 – 110)
		(26.8 – 221)	(22.8 – 137)	(29.6 – 153)	(38.9 – 186)
Fe	1.06	1490	1190	2200	1540
		(1330 – 1660)	(1070 – 1320)	(1820 – 2660)	(1330 – 1790)
		(544 – 4490)	(518 – 2390)	(295 – 20300)	(842 – 4630)
Hg (total)	0.04	1.53	0.76	1.45 [b]	0.77
		(1.35 – 1.73)	(0.64 – 0.91)	(1.24 – 1.70)	(0.68 – 0.88)
		(0.39 – 3.87)	(0.30 – 4.76)	(0.16 – 5.62)	(0.32 – 1.70)
K	14.2	9630 [b]	8640 [b]	9760	9400
		(9410 – 9860)	(8250 – 9040)	(9450– 10100)	(8980 – 9840)
		(7690 – 11900)	(5250 – 11200)	(7600 – 13000)	(7410 – 12100)
Mg	4.36	796	733 [b]	835	787
		(776 – 816)	(702 – 765)	(811 – 860)	(764 – 811)
		(616 – 1160)	(544 – 1100)	(621 – 1050)	(636 – 918)
Mn	0.17	15.3	13.6	17.9 [b]	16.3
		(14.3 – 16.3)	(12.6 – 14.8)	(17.0 – 18.9)	(15.2 – 17.5)
		(9.13 – 28.7)	(8.94 – 31.5)	(10.0 – 33.5)	(11.0 – 24.1)
Na	11.4	3220	3110	3390	3270
		(3120 – 3330)	(2990 – 3240)	(3300 – 3490)	(3150 – 3400)
		(2380 – 6310)	(2360 – 3900)	(2620 – 4720)	(2790 – 4700)
Se	1.61	5.98	9.63 [d]	15.6	22.6
		(4.91 – 7.28)	(7.82 – 11.9)	(13.4 – 18.1)	(19.7 – 26.0)
		(3nd – 26.1)	(3.17 – 35.5)	(1.77 – 56.4)	(7.40 – 59.7)
Zn	0.53	116	101	131	131
		(110 – 123)	(95.4 – 106)	(124 – 138)	(124 – 139)
		(75.2 – 253)	(70.2 – 145)	(82.3 – 220)	(85.6 – 172)
Moisture [f]		68.0	67.5	68.1	68.6

[a] Denote lake- or age-related differences.
[b] See results for among-lake differences.
[c] Number before nd indicates nondetection values.
[d] See results for age-related differences.
[e] ND = detectable residues measured in < 60% of birds.
[f] Moisture content of liver tissue reported as the mean percentage.

from Lake Erie (2.37 [1.89 to 2.96] ppm) were higher than those from Lake Ontario (1.60 [1.30 to 1.97] ppm) (T-K $p = 0.016$); adult birds (3.31 [2.69 to 4.08] ppm) also had higher levels than did juvenile birds (1.14 [0.91 to 1.43] ppm) at both lakes (T-K $p < 0.001$). Se was higher in adult (12.6 [9.65 to 16.4] ppm) compared with juvenile scaup (7.11 [5.36 to 9.43] ppm) (T-K $p = 0.006$). There were no among-lake (T-K all $p > 0.05$) or age-related (T-K all $p > 0.05$) differences in the seven remaining trace elements (Table 1).

There were no differences in trace element levels between greater scaup staging at lakes Erie and Ontario during spring (MANOVA: Wilks' $\lambda = 0.41$, $p > 0.05$). Summary statistics for the 13 elements are presented in Table 1.

Inspections of trace element concentrations showed that nearly all were either below detection limits or at background levels in both scaup species during fall and spring (Table 1). Se, however, was consistently at levels of biological concern in both species (Table 1). In the later analyses, we evaluate

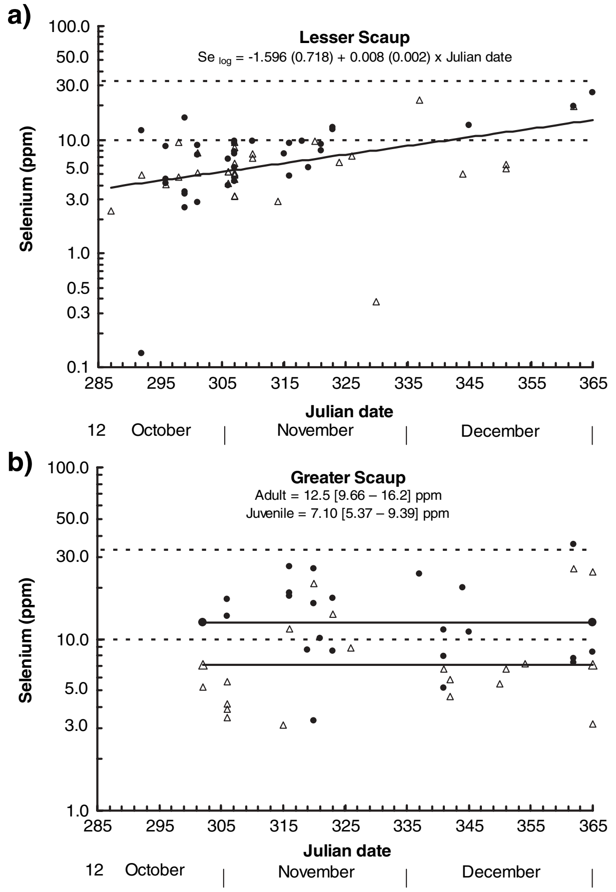

Fig. 2. Temporal dynamics of Se concentrations (μg/g dry mass [ppm]) in liver tissues of (**a**) lesser scaup and (**b**) greater scaup during fall 1999 on the LGL in Ontario, Canada. Values for adult and juvenile birds are represented by solid circles and open triangles, respectively. The horizontal dashed lines at 10 and 33 ppm represent the thresholds above which mallards may experience reproductive impairment and health-related problems, respectively

species- and age-related differences and within-season temporal dynamics in liver Se concentrations.

Sources of Variation and Temporal Dynamics of Se During Fall

Analyses showed that species, age, and date, as well as the interaction between species and date, were important sources of variation in fall Se concentrations in scaup on the LGL (model: $R^2 = 0.24$, $F_{4,100} = 7.91$, $p < 0.001$; effects: $p_{\text{Species}} = 0.014$, $p_{\text{Age}} = 0.008$, $p_{\text{Date}} = 0.005$, and $p_{\text{Species} \times \text{Date}} = 0.043$). Because of the interaction between species and date, we assessed temporal trends in Se burdens using species-specific regression models testing both age and date effects. In doing so, we found that Se in lesser scaup did not differ between adult and juvenile scaup but did increase from 3.82 [2.77 to 5.27] ppm to 14.9 [8.43 to 26.4] ppm throughout fall ($R^2 = 0.15$, $F_{1,62} = 10.96$, $p = 0.002$; Figure 2a). Se in greater scaup, however, did not vary with date, but adult birds (12.5 [9.66 to 16.2] ppm) had higher levels than juvenile birds (7.10 [5.37 to 9.39] ppm) ($R^2 = 0.18$, $F_{1,39} = 8.52$, $p = 0.006$; Figure 2b). Overall, we found that 46% of greater scaup (19 of 41; 34% adult and 12% juvenile) and 14% of lesser scaup (9 of 64; 11% adult and 3% juvenile) had increased Se burdens. Furthermore, 44% (7 of 19 greater; 5 of 8 lesser) of scaup collected in December had increased Se burdens.

Sources of Variation and Temporal Dynamics of Se During Spring

Analyses showed that species and date, as well as the interaction between species and date, were important sources of variation in scaup burdens during spring (model: $R^2 = 0.13$, $F_{3,80} = 4.11$, $p = 0.009$; effects: $p_{\text{Species}} = 0.010$, $p_{\text{Date}} = 0.370$, and $p_{\text{Species} \times \text{Date}} = 0.027$). Because of the significant species × date effect, we evaluated temporal trends in spring Se levels using species-specific regression models. In doing so, we found that Se in lesser scaup increased from 10.7 [6.72 to 17.0] ppm to 26.1 [14.1 to 48.1] ppm throughout spring ($R^2 = 0.05$, $F_{1,54} = 2.97$, $p = 0.090$; Figure 3a). In greater scaup, however, Se showed a slight decreasing trend but was essentially stable at approximately 22.6 [4.79 to 107] ppm throughout spring ($R^2 = 0.10$, $F_{1,26} = 2.83$, $p = 0.105$; Figure 3b). Based on estimates from these models, lesser scaup had lower Se levels than did greater scaup from arrival (early March) until late March and early April, after which both species generally had similar Se burdens (Figure 3). It also was notable that 75% (42 of 56) of lesser scaup and 93% (26 of 28) of greater scaup had increased Se burdens during spring.

Comparison of Fall 1986 and 1999 Se Levels in Lake Ontario Scaup

Se concentrations in greater scaup differed between fall 1986 and fall 1999 (ANOVA: $R^2 = 0.17$, $F_{1,35} = 7.05$, $p = 0.012$); Se burdens were higher in 1999 (9.40 [5.98 to 14.8] ppm) than in 1986 (3.59 [2.07 to 6.21] ppm). Lesser scaup in 1986 (9.33 [5.98 – 14.8] ppm) and 1999 (5.96 [4.41 to 8.07] ppm) had similar Se burdens (ANOVA: $R^2 = 0.07$, $F_{1,33} = 2.31$, $p = 0.131$). Geometric means, 95% CIs, and ranges of trace elements for scaup collected during fall 1986 are provided in Appendix 1.

Fall and Spring Se Levels in Zebra Mussels

The geometric mean concentration (ppm dry soft tissue mass) of Se in zebra mussel tissues during spring 2000 was 5.27 (95% CI 1.00 to 27.7; detection limit 1.63) ppm. Se was detected in two of the five fall 1999 samples but at a detection limit of 3.18 ppm.

Discussion

Organic Contaminants

Organochlorines in lesser scaup from the LGL were similar to levels reported for this species in other studies (Mazak *et al.*

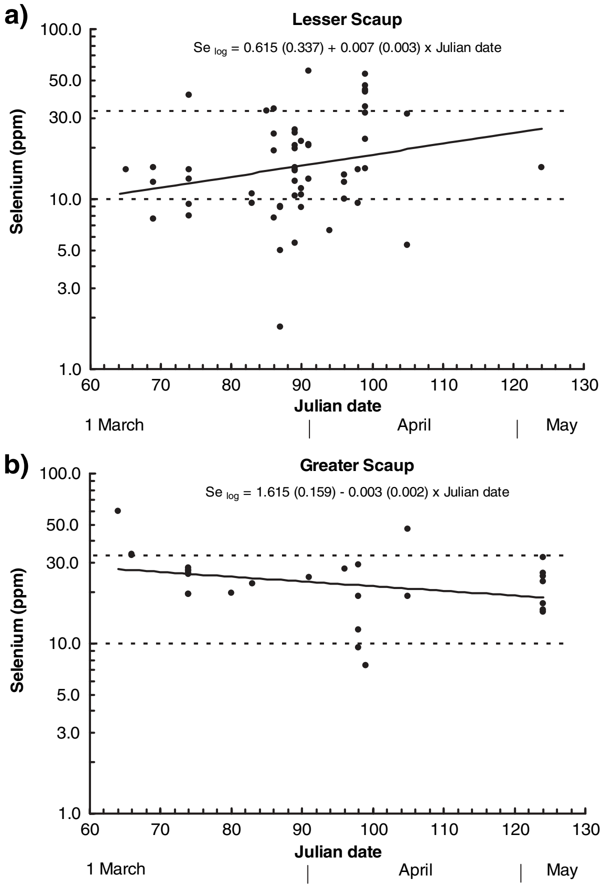

Fig. 3. Temporal dynamics of Se concentrations (μg/g dry mass [ppm]) in liver tissues of (**a**) lesser scaup and (**b**) greater scaup during spring 2000 on the LGL in Ontario, Canada. The horizontal dashed lines at 10 and 33 ppm represent the thresholds above which mallards may experience reproductive impairment and health-related problems, respectively

1997; Custer *et al.* 2000a; Fox *et al.* 2005). Lowest observed–effect levels (LOELs) for organochlorines were not available for lesser scaup, but guidelines exist for sum PCBs and sum DDT for other birds. For PCBs, the range of LOELs reported for reproductive impairment varies by species and ranged from 3500 to 7000 ppb wet mass in eggs (Hoffman *et al.* 1993; Yamashita *et al.* 1993; Bosveld and van den Berg 1994; Fisk *et al.* 2005). LOELs for *p,p*'-DDE, based on eggshell thinning in bald eagles (*Haliaeetus leucocephalus*) and American black ducks (*Anas rubripes*), ranged from 3000 to 6200 ppb wet mass (Longcore and Stendell 1977; Wiemeyer *et al.* 1984; Fisk *et al.* 2005). We lipid normalized the above LOELs (LOEL 15.5% [mean lesser scaup egg lipid; Fox *et al.* 2005]), which yielded a sum PCB LOEL of 22,580 ppb lipid mass and a sum DDT LOEL of 19,355 ppb lipid mass. Assuming liver lipid–normalized organochlorine concentrations are similar to those deposited in eggs (Braune and Norstrom 1989), geometric mean sum PCB and sum DDT concentrations in lesser scaup were 17- and 49-fold lower than their respective LOELs, whereas their maximum concentrations were 4- and 9-fold lower. These calculations suggest that sum PCBs and sum DDT likely are not causing reproductive problems in lesser scaup (see also Fox *et al.* 2005).

Trace Elements

Several trace elements that can be problematic for waterfowl, including As, Co, Cr, Ni, Pb, and V, were detected at low frequencies during fall and spring in both scaup species. Furthermore, levels of these six trace elements, plus Cd, were at or below background levels and thus were not of biological concern (Di Giulio and Scanlon 1984; Goede 1985; Scheuhammer 1987; Pain 1996; Custer and Custer 2000; Custer *et al.* 2000a, 2000b, 2003; Cohen *et al.* 2000). Hg also has been identified as a trace element of concern for scaup at some locations (Hothem *et al.* 1998). Hg was detected in all scaup we collected, but levels were well below those causing avian reproductive impairment or toxicosis (Fimreite 1974; Heinz 1979; Thompson 1996). Hg levels for lesser scaup in our study were similar to those of conspecifics at other Great Lakes locations (Custer and Custer 2000; Custer *et al.* 2000a) and throughout the Mississippi Flyway (Custer *et al.* 2003). Greater scaup we collected generally had liver Hg levels similar to conspecifics wintering at Long Island Sound (Cohen *et al.* 2000) but lower than birds wintering at San Francisco Bay, California (Hothem *et al.* 1998).

Se Levels

Of the 18 trace elements tested, only Se was detected in lesser and greater scaup at concentrations that could potentially affect reproductive output or survival. Se is a semimetallic element that is physiologically required by birds, but at increased levels it can become toxic and cause deleterious effects (Heinz 1996; Hoffman 2002). Background levels of Se in avian liver (dry) tissues range from 4 to 10 ppm (Ohlendorf 1989). In laboratory studies of mallards (*A. platyrhynchos*), Se concentrations >10 ppm dry liver mass can cause reproductive impairment, and burdens >33 ppm dry liver mass can adversely affect health and survival (Heinz *et al.* 1989; Heinz 1996). Increased levels of Se have been detected in scaup and other diving ducks at several major wintering and staging areas in North America (Ohlendorf *et al.* 1986; Hothem *et al.* 1998; Cohen *et al.* 2000), most notably including the LGL (Custer and Custer 2000; Custer *et al.* 2000a). Custer and Custer (2000) reported that 95% of 41 lesser scaup collected in industrial portions of western Lake Erie and Lake St. Clair in 1991 and 1993 (fall, winter, and spring combined) had increased, potentially harmful liver Se burdens. That value was slightly higher than the 93% (greater) and 81% (lesser) of spring-staging birds and much higher than the 46% (greater) and 14% (lesser) of the fall-staging scaup we collected from the Canadian side of the LGL in 1999 and 2000 with increased levels.

Although some lesser and greater scaup we collected during fall on the LGL had increased Se burdens, it is unlikely that reproductive output or survival would be greatly affected as a result. First, although 44% of scaup we collected during December had Se burdens considered sufficiently increased to impair reproduction (Heinz *et al.* 1987), the peak laying period was ≥5 months away for most of those birds. This would provide sufficient time for Se depuration to occur if birds winter in areas where they are exposed to background levels of this element (Heinz *et al.* 1990). Second, we found that only one greater and no lesser scaup collected during fall had Se levels high enough to potentially cause health-related problems.

Lesser scaup we collected on arrival in early March had background Se levels, but levels increased throughout spring and were increased in most birds by the end of the season. In contrast, greater scaup had relatively high Se levels in early March, and levels remained increased throughout spring. Waterfowl surveys conducted between 1990 and 2000 show that far more greater scaup (mean 17 876 ± 4205) than lesser scaup (mean 1504 ± 383) overwinter on the Canadian side of Lake Ontario (B. Edmunds, unpublished data). Thus, most of the lesser scaup we collected probably wintered on or near the Atlantic or Gulf coasts of the United States, whereas more of the greater scaup collected in early spring likely overwintered on the LGL and as a result had higher Se burdens in early March.

Compared with our fall data, 75% of spring-collected lesser scaup had Se levels that exceeded thresholds that may cause reproductive impairment, and 18% had levels associated with health-related problems (Heinz *et al*. 1987; Heinz 1996). Furthermore, 93% and 13% of greater scaup had Se burdens linked with reproductive and health-related problems, respectively. Spring Se acquisition on the LGL, therefore, could be sufficient to cause chronic health-related problems in some birds, possibly affecting survival later in migration. Also, if birds cannot depurate enough Se before ovulation, reproduction could be compromised as a result of teratogenic and embryotoxic effects (Heinz *et al*. 1987).

Data available to date allow for rudimentary calculations regarding effects that spring Se burdens may have on female lesser scaup after departing the LGL to breed. A laboratory study found that mallards can depurate Se relatively rapidly given its half-life of 18.7 days in liver tissues (Heinz *et al*. 1990). Fifteen lesser scaup implanted with satellite transmitters at Long Point, Lake Erie, during spring 2005 and 2006 spent an average of 26 (range 6 to 50) days in migration before arriving at their presumed breeding sites (S. Badzinski and S. Petrie, unpublished data). Nest initiation for female lesser scaup can occur from 15 to 60 days (mean 38 days) after arrival at breeding sites (Austin *et al*. 1998; Fox *et al*. 2005). Based on these values, Se burdens in female scaup potentially could thus decrease from 54% (21 days) to 98% (105 days) of their LGL departure levels by onset of egg laying. Based on the average time between LGL departure and nest initiation (64 days), it seems that even the maximum Se level we detected in lesser scaup liver (56.4 ppm) could decrease 91% to approximately 5.3 ppm, which is well below the 10-ppm reproductive impairment threshold in mallards (Heinz *et al*. 1987). It is notable that this value was consistent with the generally lower liver Se burdens in prebreeding and breeding female lesser scaup collected throughout the western portion of the species breeding range (Custer *et al*. 2003; Fox *et al*. 2005). Calculations based on minimum migration and nest initiation times, however, suggest that female scaup departing the LGL with >22.0-ppm Se burdens may be at risk of reproductive impairment; 29% of the female scaup in our study exceeded this level. Se burdens in this study likely were not at maximum levels because female scaup were collected throughout spring and represented various stages of residence times. Average Se levels may thus underestimate departure levels in birds, whereas maximum values may better represent those burdens. Based on this, it is possible that a sizeable number of female lesser scaup using the LGL, particularly those that spend less time in migration and nest in the eastern portion of the breeding range (or close to the LGL), or require less time to initiate nests, may experience decreased reproduction as a result of Se acquisition.

Zebra Mussel Contaminants

Most of the scaup population decrease occurred from the mid-1980s to the late 1990s, a period that coincides with the colonization and increase of dreissenid mussels in the LGL. Thus, it was notable that although lesser scaup generally had similar fall Se burdens in 1986 (9.3 ppm) and 1999 (6.0 ppm) on Lake Ontario, during the same times burdens in greater scaup increased from 3.6 to 9.4 ppm. This increase, in part, could have been caused by a dietary shift from native gastropods (and aquatic plants) to filter-feeding zebra mussels at that location (Ross *et al*. 2005; Badzinski and Petrie 2006a). Protein and methionine content in diets can affect Se toxicity in mallards (Hoffman *et al*. 1992). It currently is unknown if the diet shift to dreissenid mussels has resulted in substantial changes in dietary quality or nutritional composition, which could be important interacting factors ultimately affecting subsequent survival or reproduction in scaup.

Despite a relatively high detection limit for the fall sample, our data also suggest some seasonal variation in Se burdens within zebra mussel tissues. This apparent seasonal variation in zebra mussel Se may partially explain why Se burdens were higher in scaup during spring. Spring-collected zebra mussels (dry soft tissue) had a mean Se concentration of 5.27 ppm, whereas all fall-collected mussel samples were below the detection limit (3.08 ppm). Lemly (1995) proposed 3 ppm dry tissue mass as the toxic threshold for Se in aquatic prey; Ohlendorf (2003) reported an EC_{10} for decreased mallard hatchability of 4.9 ppm Se in the diet. Zebra mussels eaten by scaup on the LGL during fall contained only background levels of Se, whereas those eaten during spring may ultimately be toxic to waterfowl, particularly if birds consistently eat them during long periods of time. Although zebra mussels filter feed throughout the year, they produce veliger larvae only during late spring and summer (Sprung 1992). Mussels thus continually accumulate Se but can only depurate it into larvae during the summer months, thereby resulting in slightly higher soft tissue burdens in spring than fall. Spring runoff may also result in a flush of atmospherically deposited Se into aquatic habitats, which may become available for uptake by zebra mussels at that time (G. Fox, personal communication).

Conclusion

Based on our results, and on other research conducted within the region (Custer and Custer 2000; Custer *et al*. 2000a), a large proportion of lesser and greater scaup are acquiring potentially unhealthy Se burdens on the LGL. The effect this has on scaup populations is still speculative because very little information exists regarding the species-specific behavioral and physiologic responses to increased Se burdens while on the LGL, during spring migration, and especially after arrival on breeding grounds. Furthermore, it is currently unknown what the cumulative, long-term effects are for scaup that annually acquire high Se burdens while on the LGL. Few data also exist on the possible sublethal effects caused by increased Se burdens, such as decreased body condition (Heinz and Fitzgerald 1993) and oxidative stress (Hoffman and Heinz 1998; Custer *et al*. 2000b), or how repeated or prolonged exposure influences lifetime reproductive success or longevity of lesser and greater scaup. Se exposure and associated effects may be particularly critical for greater scaup using the LGL during spring given that >90% of birds had increased burdens. A large proportion of the greater scaup population in North America now winters on the LGL, so data on behavior, foraging, body condition, health, and survival of these birds may provide insight into factors contributing to the continental scaup decrease.

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Appendix

Appendix 1. Geometric mean concentrations (µg/g dry mass [ppm]), 95% CIs, and ranges of trace elements in liver tissues of lesser and greater scaup collected from eastern Lake Ontario in Prince Edward County, Ontario, Canada, during fall 1986

Element	Detection limit	Lesser scaup (n = 29)	Greater scaup (n = 26)
Al	12.3	ND [a]	ND
		(29nd [b])	(26nd)
As	0.84	3.65	4.96
		(3.38–3.94)	(4.26–5.78)
		(2.02–5.81)	(2.34–13.7)
Ca	30.0	415	405
		(372–464)	(346–474)
		(241–1130)	(174–1280)
Cd	0.10	1.56	1.95
		(1.37–1.78)	(1.63–2.32)
		(0.57–4.47)	(0.69–6.50)
Co	0.10	ND	ND
		(27nd–0.15)	(23nd–0.17)
Cr	1.79	ND	ND
		(24nd–10.3)	(20nd–6.14)
Cu	0.44	91.1	97.3
		(85.2–97.4)	(86.2–110)
		(49.2–139)	(34.3–164)
Fe	12.8	1220	2060
		(1120–1330)	(1630–2600)
		(757–2190)	(911–11300)
Hg (total)	0.03	1.70	0.76
		(1.50–1.86)	(0.61–0.96)
		(0.83–3.97)	(0.24–5.13)
K	7.36	8210	8650
		(8060–8360)	(8420–8900)
		(7350–9230)	(7040–9940)
Mg	3.79	715	807
		(699–731)	(774–842)
		(606–864)	(639–1070)
Mn	0.25	12.9	15.7
		(12.2–13.5)	(14.5–17.0)
		(9.90–17.2)	(9.66–32.5)
Na	23.3	3700	3610
		(358–3820)	(3390–3840)
		(2910–4660)	(2400–5200)
Ni	0.40	ND	ND
		(23nd–5.89)	(16nd–3.10)
Pb	1.30	ND	ND
		(29nd)	(25nd–4.08)
Se	1.54	9.39	3.39
		(8.88–9.94)	(2.08–5.52)
		(6.22–13.1)	(6nd–19.5)
V	0.31	ND	ND
		(29nd)	(26nd)
Zn	0.41	106	124
		(101–111)	(114–136)
		(71.5–144)	(75.5–248)

[a] ND = detectable residues measured in less than 60% of birds.
[b] Number before nd indicates nondetection values.

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