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Abstract. Previous research reported that concentrations of selenium in the livers of 88–95% of lesser scaup from locations in Lake Erie, Lake St. Clair, and Lake Michigan, USA were either elevated (10–33 μg/g dry weight [dw]) or in the potentially harmful range (>33 μg/g dw). In order to determine the geographic extent of these high selenium concentrations, we collected lesser scaup in Louisiana, Arkansas, Illinois, Minnesota, Wisconsin, and Manitoba and analyzed the livers for 19 trace elements. We found that all trace element concentrations, except for selenium, generally were low. Arsenic, which usually is not detected in liver samples, was detected in Louisiana and may be related to past agricultural usages. Chromium, which also is not usually detected, was only present in lesser scaup from Arkansas and may be related to fertilizer applications. Cadmium and mercury concentrations did not differ among locations and concentrations were low. Selenium concentrations in Arkansas (geometric mean = 4.2 μg/g dw) were significantly lower than those in Louisiana (10.7 μg/g dw), Illinois (10.5 μg/g dw), and Minnesota (8.0 μg/g dw); concentrations in Wisconsin and Manitoba were intermediate (6.6 and 6.5 μg/g dw). About 25% of lesser scaup livers contained elevated selenium concentrations; however, none were in the harmful range. We concluded that selenium concentrations in lesser scaup in the Mississippi Flyway are elevated in some individuals, but not to the extent that has been documented in the industrial portions of the Great Lakes.

Keywords: lesser scaup; *Aythya affinis*; trace elements; selenium; chromium

Introduction

Continental scaup populations (lesser [*Aythya affinis*] and greater [*A. marila*] scaup combined) have declined for the past 20 years (Allen et al., 1999; Afton and Anderson, 2001) in spite of the recovery by many other waterfowl species during this same time period (Dubovsky et al., 1997). Since 1985, scaup populations have remained below the population goal set by the North American Waterfowl Management Plan (NAWMP) (U.S. Fish and Wildlife Service and Environment Canada, 1986; Dubovsky et al., 1997). Record low numbers of breeding scaup (3.5 million) in 1998 were far below the goal (7.6 million) set by

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the NAWMP and led to a workshop in 1998 to discuss research and management needs for these species (Austin et al, 1999, 2000). Environmental contaminants were identified as one area where further research was needed, especially on lesser scaup.

Selenium, an essential trace element, has been identified as a contaminant of concern for lesser scaup (Custer and Custer, 2000; Custer et al., 2000). Background concentrations for selenium in avian liver tissue are 4–10 µg/g dry weight (dw) (Ohlendorf, 1989). Concentrations of 10 µg/g dw or higher have been associated with reproductive impairment in laboratory studies of mallards (*Anas platyrhynchos*) (Heinz et al., 1989; Heinz, 1996). The level of selenium in liver tissue that is deleterious may be species specific, however, and is unknown for lesser scaup.

Marine birds seem to have higher liver selenium concentrations, with no apparent ill effects, than do freshwater bird species (Henny et al., 1995; Trust et al., 2000). Lesser scaup migrate and breed primarily in freshwater systems, however they can winter in large numbers in marine environments such as coastal Louisiana, Texas, and California (Austin et al., 1998). It is unknown whether lesser scaup are more similar to marine or freshwater waterfowl species with respect to normal liver selenium levels.

Custer and Custer (2000) found that 95% of lesser scaup collected in Lake St. Clair, western Lake Erie, and Lake Michigan had elevated (>10 µg/g dw threshold based on laboratory studies of mallards) selenium concentrations in their liver tissue. In southern Lake Michigan, 14 of 16 lesser scaup had elevated liver selenium concentrations (Custer et al., 2000). All four of these Great Lakes sites are heavily industrialized. In California, one of two sampling locations along the coast had elevated selenium concentrations in lesser scaup livers as well (Hothem et al., 1998). The source for elevated selenium in the Great Lakes probably is burning of fossil fuels and industrial sources (Hodson et al., 1984), whereas in California it is the result of drainwater from seleniferous agricultural soils and/or industrial sources. There are also natural sources of selenium in certain geologic formations that provide sources for this essential trace element as well.

The Mississippi Flyway is one of the most important migration corridors for lesser scaup (Bellrose, 1976; Afton and Anderson, 2001). It is unknown whether the high selenium concentrations present in lesser scaup migrating through and wintering in the Great Lakes (Custer and Custer, 2000; Custer et al., 2000) are normal for this species and hence widespread in the Mississippi Flyway or whether the elevated concentrations are limited to industrial portions of the Great Lakes. It is also unknown whether selenium accumulated in the industrial portions of Great Lakes, if it occurs, persists until the birds reach their breeding grounds. If so, elevated selenium concentrations could be impairing reproduction.

Other trace elements, such as cadmium, lead, and mercury, can also be problematic in birds (see Eisler, 2000 for overall summary). Cadmium, lead, and mercury were accumulated over the winter period in lesser scaup in Indiana Harbor, Indiana (Custer et al., 2000), although to a lesser extent than selenium. It is therefore important to assess whether other trace elements are elevated elsewhere in the Mississippi Flyway and possibly contributing to lesser scaup population declines.

The objectives of this study were to determine the concentration of selenium and other trace element concentrations in lesser scaup liver tissue from the Mississippi Flyway. We also wanted to assess whether selenium, or other trace elements, could be contributing to declines in lesser scaup populations.

Materials and methods

We collected lesser scaup at five migration and wintering areas in the Mississippi Flyway and at one location at the southern end of their breeding distribution (Fig. 1). Collection locations were Lake Pelto, Terrebone Parish, LA (29.09°N, 90.70°W); near Lonoke, Lonoke Co., AR (34.78°N, 91.90°W); Keokuk Pool on the Mississippi River between Hamilton and Niota, Hancock Co., IL (40.62°N, 91.28°W); Point Sable, along the eastern shore of Green Bay, Lake Michigan, just north of Green Bay, Brown Co., WI (44.52°N, 88.02°W); northwestern Minnesota at Thief Lake and Roseau River Wildlife Management Areas and Agassiz National Wildlife Refuge, Marshall Co., MN (48.49°N, 94.82°W); and in the prairie-parklands breeding area west of Erickson, Manitoba (50.67°N, 99.92°W), Canada. All six locations were in non-industrial locations. We collected lesser scaup between 30 November 1999 and 15 May 2000 on their wintering areas or as they migrated north, except for Green Bay, where we

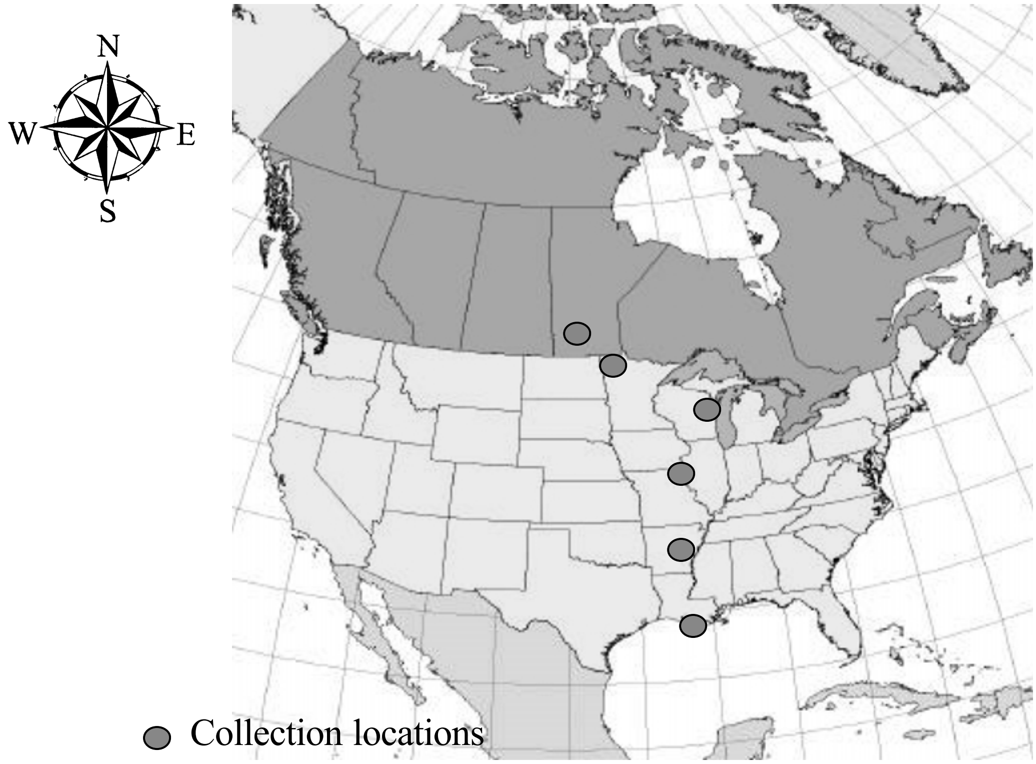

Figure 1. Collection locations for lesser scaup in 1997–2000. Locations, from north to south, are Erickson, Manitoba; northwestern Minnesota; Green Bay, Wisconsin; Keokuk Pool, Illinois; Lonoke, Arkansas; and Lake Pelto, Louisiana.

collected them between 27 October and 13 November 1997 as they migrated south. We collected only female lesser scaup except in Green Bay where we collected both males and females. We preferentially sampled females because high concentrations in their tissues could affect egg concentrations and subsequent hatching success. We froze the birds shortly after collection. Birds were later thawed and a liver sample (approx. 5 g) from 10 birds per location was dissected out, placed in a plastic whirl pack, and then refrozen.

All liver samples were analyzed by Research Triangle Institute (RTI), Research Triangle Park, NC for the standard suite of 19 trace elements. Trace elements analyzed, with nominal detection limits in parentheses on a μg/g dw basis, were aluminum (5), arsenic (0.5), barium (0.5), beryllium (0.1), boron (2), cadmium (0.1), chromium (0.5), copper (0.5), iron (10), lead (1), magnesium (11), manganese (0.4), mercury (0.02), molybdenum (0.5), nickel (0.5), selenium (0.5), strontium (0.2), vanadium (0.5), and zinc (1). Research Triangle Institute homogenized tissue samples and then digested them in the presence of nitric acid. They used inductively coupled plasma-atomic emission spectrophotometry for all elements, except mercury and selenium. Mercury was determined with cold vapor atomic absorption. Selenium was analyzed using graphite furnace atomic absorption. Blanks, duplicates and spikes were run at a frequency of at least 5% of the total number of samples. Reference material (NRCC TORT 2, lobster hepatopancreas) was used. Similarity with the certified material was as follows: arsenic 92.1%, cadmium 100%, chromium 93%, mercury 100%, and selenium 92%. Percent recoveries of spiked materials, for trace elements that can be problematic in birds, were arsenic 95.9, cadmium 101.7, chromium 102.2, lead 97.0, mercury 94.0, and selenium 94.0. Concentrations were not corrected for percent recovery. Moisture content of livers averaged 69.3% ± 0.35 (SE) for use in converting to wet weight if needed.

We statistically tested for location differences using analysis of variance (ANOVA) for those chemicals detected in >50% of the samples. Gender differences were tested with Wisconsin data only. Half the detection limit was used in analyses when including samples that were below the detection limit. We log transformed data to satisfy the homogeneity of variance assumptions of ANOVAs and to be consistent with previously published information. The Bonferroni method was used to test for differences among locations in trace element concentrations. A significance level of $P < 0.05$ was used. We present geometric means (antilog) and 95% confidence intervals (CI) in tables and text.

Results

There were no significant differences between the sexes in concentrations for the trace elements detected in >50% of samples (Green Bay, WI data only). *P*-values ranged between 0.17 and 0.78 for the ten trace elements present in >50% of samples (df = 1,8).

Table 1. Concentrations (μg/g dw) of trace elements in livers ($n = 10$ samples/site) of lesser scaup from six locations in the Mississippi Flyway that did not differ among collection locations. Samples were collected in 1997, 1999, and 2000

Chemical	Geometric mean	95% CI	Maximum value
Cadmium	0.62	0.54–0.70	3.3
Iron	1666	1572–1764	4509
Manganese	17.9	17.4–18.4	27.1
Mercury	0.96	0.89–1.04	3.2
Molybdenum	2.9	2.81–3.00	5.2

Non-essential trace elements

Barium, beryllium, and lead were not detected in any liver sample. Aluminum was detected in three livers, one each from Arkansas, Illinois, and Louisiana. Arsenic was detected in all livers from Louisiana (0.85 μg/g dw, 0.78–0.92) and two from Green Bay, but at no other location. Non-essential trace elements detected in >50% of samples were cadmium and mercury. These two elements did not vary by location (cadmium $P = 0.079$, mercury $P = 0.445$, Table 1), and both averaged < 1 μg/g dw. Boron and strontium varied among locations (Table 2). Boron was higher in Louisiana that in Arkansas or Wisconsin. Strontium was higher in Manitoba than in Illinois or Minnesota.

Essential trace elements

Nickel was not detected in any liver sample. Chromium was detected in all livers from Arkansas (0.89 μg/g dw, 0.79–1.01), but not at other locations. Essential trace elements detected in >50% of samples and which did not vary among locations were iron ($P = 0.803$), manganese ($P = 0.424$), and molybdenum

Table 2. Concentrations (geometric mean and 95% CI, μg/g dw) of trace elements in livers of lesser scaup collected from six locations in the Mississippi Flyway in 1997, 1999, and 2000 that differed among collection locations

	Location						
Chemical	Louisiana	Arkansas	Illinois	Minnesota	Wisconsin	Manitoba	*P* value[1]
Boron	5.85 a[2] 5.36–6.36	2.51 b 2.07–3.95	3.58 ab 2.94–4.36	3.72 ab 3.12–4.45	<1.0 c —[3]	4.97 a 4.52–5.46	<0.001
Copper	49.9 b 46.1–54.0	76.1 ab 64.6–89.8	79.5 ab 72.4–76.3	86.4 a 75.5–98.8	81.7 ab 73.6–90.7	81.9 a 75.2–89.3	0.015
Magnesium	733 ab 725–742	773 a 760–787	669 c 657–681	772 a 758–787	692 bc 681–705	792 a 766–1061	<0.001
Strontium	0.61 ab 0.57–0.66	0.36 abc 0.30–0.43	0.13 c 0.12–0.16	0.23 bc 0.19–0.29	0.38 ab 0.27–0.54	0.84 a 0.61–1.17	<0.001
Vanadium	1.02 a 0.98–1.06	0.99 a 0.93–1.06	0.98 a 0.94–1.02	0.91 b 0.84–0.97	<0.25 b —	0.93 a 0.88–0.97	<0.001
Zinc	140 ab[4] 135–146	133 ab 122–144	111 b 104–119	146 a 137–155	119 ab 112–126	137 ab 128–146	0.030

[1]*P*-values for one-way ANOVA comparing among locations, df = 5.54.
[2]Means sharing same letter were not significantly different among locations.
[3]— = all concentrations were below the detection limit.
[4]Means for zinc only differed at $P = 0.075$ by Bonferroni mean separation test.

Table 3. Concentrations (μg/g dw) of selenium in livers ($n = 10$ samples/site) of lesser scaup from six locations in the Mississippi Flyway in 1997, 1999, and 2000

Location	Geometric mean	95% confidence intervals	Minimum–maximum	Percent elevated (>10 μg/g dw)
Louisiana	10.7 a[1]	9.46–12.1	6.0–16	50
Arkansas	4.23 b	3.89–4.59	3.2–5.1	0
Illinois	10.5 a	9.49–11.7	4.9–17	50
Minnesota	7.99 a	6.84–9.33	4.0–19	30
Wisconsin	6.59 ab	5.92–7.32	4.6–20	20
Manitoba	6.51 ab	5.45–7.78	3.7–17	20

[1]Means sharing same letter are not significantly different. One-way ANOVA, $P < 0.001$, df = 5.54.

($P = 0.157$) (Table 1). Copper, magnesium, vanadium, and zinc concentrations varied among locations (Table 2). Copper was significantly higher in Manitoba than in Louisiana. Magnesium was higher in Manitoba than in either Illinois or Wisconsin. Vanadium was lower in Minnesota than anywhere else where it was detected. Zinc was higher in Minnesota than in Illinois.

Selenium concentrations differed significantly among locations (Table 3). Selenium concentrations in Louisiana, Illinois, and Minnesota were significantly higher than those in Arkansas. Selenium concentrations in Wisconsin and Manitoba did not differ from other locations. Selenium concentrations were in the elevated range (>10 μg/g dw) in 20–50% of samples, but no sample had concentrations >33 μg/g dw.

Discussion

Non-essential trace elements

Concentrations of the non-essential trace elements, arsenic, cadmium, mercury, and strontium, in this study were not considered toxic (see discussion below). Arsenic was detected in all livers from Louisiana, geometric mean = 0.85 μg/g dw, and at all four locations in the industrial portions of the Great Lakes (Custer and Custer, 2000). Arsenic was not detected at the other five areas in the Mississippi Flyway where scaup were collected for this study. Arsenic is rapidly metabolized and thus detectable concentrations in liver indicated recent exposure (Eisler, 1988, 2000). Arsenic has been used extensively in agricultural applications as an herbicide, insecticide, and defoliant (Eisler, 1988, 2000). This may explain why arsenic was present in Louisiana lesser scaup liver tissue, but nowhere else in the non-industrial areas of the flyway. Even in the Louisiana scaup, arsenic concentrations were not high enough to be problematic, however. Background concentrations generally are <1.5 μg/g dw; concentrations >33 μg/g dw confirms arsenic poisoning (Goede, 1985). Average concentrations of cadmium (0.62 μg/g dw) in our study were lower than the average values in the industrial portions of the Great Lakes (2–3 μg/g dw) (Custer and Custer, 2000; Custer et al., 2000) and did not vary among locations. Concentrations greater than 3 μg/g dw are considered elevated above background (Di Giulio and Scanlon, 1984; Scheuhammer, 1987; Furness, 1996). Mercury concentrations in the non-industrial portions of the Mississippi Flyway (0.96 μg/g dw) were similar to concentrations in the industrial portions of the Great Lakes (Custer and Custer, 2000; Custer et al., 2000), did not vary among locations, and are considered background as well (Fimreite, 1974; Thompson, 1996). Strontium concentrations in our study were similar to levels in the industrial portions of the Great Lakes (Custer and Custer, 2000) and not considered problematic, although little data exist for effects on birds. Strontium concentrations did vary among locations, however. Strontium was elevated in diving duck species that had a higher proportion of molluscs in their diet (Custer and Custer, 2000) and was higher in Manitoba than in Illinois or Minnesota. Strontium is a required element for embryonic shell development in molluscs (Nystrom et al., 1996). Perhaps lesser scaup increased their consumption of food rich in calcium, such as molluscs, in Manitoba in preparation for egg laying.

Essential trace elements

Our results indicate that the essential trace elements, copper, iron, magnesium, manganese, molybdenum, vanadium, and zinc, seemed to be within the normal range for waterfowl (Custer and Hohman, 1994; Puls, 1994; Franson et al., 1995; Henny et al., 1995; Hothem et al., 1998; Eisler, 2000; Trust et al., 2000; Stout et al., 2002; Takekawa et al., 2002) and were maintained there by normal homeostatic mechanisms. Additionally, concentrations of these essential trace elements were similar throughout the Mississippi Flyway including the industrial portions (Custer and

Custer, 2000; Custer et al., 2000). Although concentrations were within normal ranges, there were some minor differences among locations for copper, magnesium, vanadium, and zinc. These location differences could have a number of causes. For example, copper concentrations in bird tissues tend to increase in areas of human activity and intensive copper use (Eisler, 2000). Vanadium increases in liver tissue as concentrations in diet increase as well (White and Dieter, 1978). Takekawa et al. (2002) found a negative relationship between zinc and body mass in scaup sp. from California, however concentrations of zinc were far below the threshold for zinc toxicosis (1,200 μg/g, Gasaway and Buss, 1972). The effect of body condition on element concentrations will be addressed in a subsequent paper.

Concentrations of some essential trace elements were elevated. Chromium, which often is not detected in liver tissue of birds, was detected in >50% of samples at all four locations in the industrial portions of the Great Lakes (Custer and Custer, 2000), and in Arkansas. The average concentration in Arkansas (0.89 μg/g dw) was similar to or slightly higher than averages in the industrial portions of the Great Lakes, which ranged between 0.42 and 0.61 μg/g dw (Custer and Custer, 2000). The presence of chromium in lesser scaup from Arkansas, which were collected at bait-fish farms, may have resulted from fertilizers used in the fish ponds. Phosphate-based fertilizers can contain chromium (Eisler, 1986, 2000; Outridge and Scheuhammer, 1993). There are little data available on threshold effect levels of chromium on birds in field situations; however, chromium concentrations present in lesser scaup in Arkansas probably are not a cause for concern. Because chromium is an essential element, homeostatic mechanisms may prevent uptake beyond what is required unless concentrations in diet are high enough to overwhelm these control mechanisms; at that point accumulation in organs can occur (Outridge and Scheuhammer, 1993). Common terns (*Sterna hirundo*) nesting in Rhode Island did not have reduced reproductive success, nor reduced growth rates in nestlings, even though they were exposed to chromium in their diet (Custer et al., 1986). Nestling common tern livers had concentrations up to 18.3 μg/g dw in that study.

Selenium concentrations in lesser scaup livers from the non-industrial portions of the Mississippi Flyway (this study) were lower than those in the industrial portions of the Great Lakes (Custer and Custer, 2000, Custer et al., 2000). Twenty-eight percent of livers had selenium concentrations >10 μg/g dw in the present study compared to 88–95% in the industrial portions of the Great Lakes (Custer et al., 2000; Custer and Custer, 2000). Average selenium concentrations also were lower in the non-industrial portions (geometric mean = 4–11 μg/g dw) compared to the industrialized portions of the Great Lakes (22–41 μg/g dw, Custer and Custer, 2000).

A similar pattern of selenium exposure, between industrialized and non-industrialized areas, may be present in California. Morro Bay, which is on the coast between San Francisco and Los Angeles, potentially has more industrial influences than the area around Lake Earl in northern California. The geometric mean selenium concentration in lesser scaup livers from Morro Bay was 10.7 μg/g dw and ranged up to 19 μg/g dw (Hothem et al., 1998). In contrast, the mean concentration of selenium in lesser scaup livers from Lake Earl was 3.6 μg/g dw with a high of 4.2 μg/g dw. The difference between the two sites in California could be because one site was marine (Morro Bay) and the other was freshwater (Lake Earl), however, for scaup in the Mississippi Flyway the salinity of the water did not appear to be a factor in selenium concentrations; the coastal Louisiana site (marine) had the same selenium concentrations as freshwater sites (Illinois, Minnesota, and Wisconsin).

Selenium can vary according to body condition, but this seems to be more prevalent in studies where sick, dead or dying birds are included in the analysis (Esselink et al., 1995; Scheuhammer et al., 1998). This was not the case in the study reported here because only apparently healthy individuals were collected. Additionally, Takekawa et al. (2002) found that selenium concentrations in liver tissue of scaup sp. were not affected by four measures of body condition, although it was in canvasbacks (*Aythya valisneria*).

Although selenium concentrations in body tissues can drop rapidly when birds are removed from a selenium-contaminated diet (Heinz et al., 1990; Heinz and Fitzgerald, 1993) our findings that 20% of lesser scaup arrived at their breeding area in Manitoba with elevated selenium (>10 μg/g dw, Heinz et al., 1989; Heinz, 1996) may be cause for concern. It is unknown, however, if the threshold established in laboratory studies for reproductive problems in mallards is applicable to lesser scaup.

Based on our results and those published earlier (Custer and Custer, 2000; Custer et al., 2000), high selenium concentrations in lesser scaup livers in the Mississippi Flyway seem to be confined to the industrial portions of the flyway and are not normal for this species. This pattern is repeated in the Pacific Flyway, even though the selenium sources there may be a combination of industrial inputs as well as agricultural drain water (Hodson et al., 1984). A small percentage (20%) of lesser scaup at Erickson, Manitoba, a southern breeding area, may be at risk from elevated selenium based on laboratory studies of mallards. It is unknown whether lesser scaup that breed farther north in Canada or Alaska may be at lower risk because more time is required to migrate there from selenium-contaminated wintering and migration areas. The longer interval would enable scaup to depurate a greater amount of selenium prior to egg laying. Determination of selenium concentrations in eggs from major breeding areas in Canada and Alaska would answer that question. Additionally, it is unknown whether selenium and other trace elements may affect or be affected by female body condition and their ability to accumulate nutrient reserves. This should be further investigated.

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