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CONTAMINANTS IN LESSER SCAUP EGGS AND BLOOD FROM YUKON FLATS NATIONAL WILDLIFE REFUGE, ALASKA

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Abstract. Documented declines in Lesser Scaup (*Aythya affinis*) populations may be caused by several factors, including reduced reproductive success or survival from exposure to environmental contaminants during winter, migration, or breeding. We evaluated organochlorines and inorganic elements in Lesser Scaup blood ($n = 14$) and eggs ($n = 10$) from a breeding area in the relatively pristine Yukon Flats National Wildlife Refuge in interior Alaska. Most contaminants were not at concentrations of concern. Lead was detected in only four blood samples, with an average when detected (0.29 mg kg^{-1} wet weight [ww]) slightly above background levels (0.20 mg kg^{-1} ww). Our study area had little or no hunting, but since lead exposure is correlated with hunting pressure, lead should be evaluated in other Lesser Scaup breeding areas. Strontium in eggs (mean = 10.90 mg kg^{-1} dry weight [dw]) was significantly negatively correlated with eggshell thickness. Eggshell thickness was also 18% lower than in museum specimens, a percentage associated with population declines in other species, and was not correlated with other contaminants. Few comparative data in the literature exist, but productivity in this breeding area was low (mean nest success = 12%), so further research on the effects of strontium on productivity through the mechanism of eggshell thinning is needed. Most environmental contaminants are unlikely to be affecting Lesser Scaup populations breeding in interior Alaska, but lead and strontium should be studied further.

Key words: Aythya affinis*, contaminants, inorganic elements, lead, Lesser Scaup, persistent organic pollutants, strontium.*

Contaminantes en Huevos y Sangre de *Aythya affinis* en el Refugio Nacional de Vida Silvestre Yukón Flats, Alaska

Resumen. Las disminuciones documentadas de las poblaciones de *Aythya affinis* podrían estar siendo causadas por varios factores, incluyendo una reducción en el éxito reproductivo o en la supervivencia por la exposición a contaminantes ambientales durante el invierno, la migración y la época de cría. Evaluamos la presencia de elementos órganoclorados e inorgánicos en la sangre ($n = 14$) y en los huevos ($n = 10$) de *A. affinis* provenientes de un área de cría relativamente prístina del Refugio Nacional de Vida Silvestre Yukon Flats en el interior de Alaska. La mayoría de los contaminantes no se presentaron en concentraciones que fueran preocupantes. Se detectó plomo en sólo cuatro muestras de sangre, con un promedio detectado (0.29 mg kg^{-1} peso húmedo [ph]) ligeramente mayor al de los niveles basales (0.20 mg kg^{-1} ph). En nuestra área de estudio, la caza fue escasa o nula, pero debido a que la exposición al plomo está correlacionada con la presión de caza, el plomo debería ser evaluado en otras áreas de cría de *A. affinis*. El estroncio en los huevos (promedio = 10.90 mg kg^{-1} peso seco [ps]) estuvo significativamente y negativamente correlacionado con el espesor de la cáscara del huevo. El espesor de las cáscaras de huevo también fue un 18% más bajo que en los especimenes de museo, un porcentaje asociado con disminuciones poblacionales en otras especies, y no estuvo correlacionado con otros contaminantes. Existen pocos datos comparativos en la literatura, pero la productividad en esta área de cría fue baja (éxito promedio del nido = 12%), por lo que se requieren estudios adicionales sobre los efectos del estroncio sobre la productividad a través del mecanismo de adelgazamiento de la cáscara del huevo. La mayoría de los contaminantes ambientales probablemente no están afectando las poblaciones de *A. affinis* que crían en el interior de Alaska, pero el plomo y el estroncio deberían ser estudiados con mayor profundidad.

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INTRODUCTION

The Lesser Scaup (*Aythya affinis*) is the most abundant North American diving duck, but has become a species of concern following years of declining populations (Austin et al. 1998). Lesser Scaup breed predominantly in interior Alaska (Kessel et al. 2002), with the Yukon Flats wetlands containing the greatest density of nesting Lesser Scaup in North America (Austin et al. 1998). Population dynamics in the Yukon Flats National Wildlife Refuge (NWR) are therefore important indicators of species trends. Lesser Scaup in the Yukon Flats (Alaska-Yukon Waterfowl Breeding Population Survey Stratum 4) have declined approximately 30% from population highs in the late 1970s, in spite of recent short-term increases (B. Conant and D. Groves, U.S. Fish and Wildlife Service, unpubl. data). Low reproductive success, drought, habitat degradation, and environmental contamination have been hypothesized to have contributed to this decline (Austin et al. 2000). Here, we evaluate the potential impact of environmental contaminants, including persistent organic pollutants (organochlorine pesticides and polychlorinated biphenyls [PCBs]) and inorganic elements, on Lesser Scaup breeding in interior Alaska.

Avian exposure to persistent organic pollutants varies with life history characteristics such as migration pathways and status, trophic status, and local sources of contaminants. Lipid consumed in breeding areas may limit the number of Lesser Scaup eggs produced (Afton and Ankney 1991), suggesting that breeding area resources are used in egg production. Therefore, contaminants found in breeding areas may be transferred to eggs. Scaup are zoophagous, with potentially greater contaminant exposure than herbivorous waterfowl like geese. Persistent and lipophilic organic pollutants, including organochlorine pesticides and PCBs, are of particular concern in the Arctic and sub-Arctic (Arctic Monitoring and Assessment Programme 1998), including interior Alaska. DDT was used extensively in Alaska pre– and post–World War II and has a long half-life in cold climates (~35 years; Dimond and Owen 1996); the parent compound can still be found in biota at urban and military sites in Alaska (Mueller and Matz 2000). Effects of persistent organic pollutants on birds are numerous and varied, and include embryotoxicity, morbidity, mortality, and endocrine disruption (e.g., eggshell thinning) during reproduction and development (Blus 1995).

Inorganic elements including selenium (Se) are also of concern for waterfowl, with potential accumulation on the wintering grounds near industrialized areas (Custer and Custer 2000, Custer et al. 2003, Fox et al. 2005). However, persistence through migration, depuration rates into eggs, and subsequent reproductive effects are largely unknown. Selenium was elevated in livers of Lesser Scaup in wintering areas (Custer and Custer 2000), and elevated egg Se concentrations have been linked with impaired reproduction in a variety of avian species (Heinz 1996). However, Fox et al. (2005) found that despite consumption of bivalves with potentially toxic Se concentrations on staging areas, Se residues in Lesser Scaup eggs from across the breeding range were below embryotoxic levels. Additional analysis by Fox et al. (2005) suggested that depuration during migration was occurring, with the caveat that healthy birds (i.e., birds with nontoxic Se concentrations) were more likely to survive migration and produce eggs, and thus were more likely to be represented in a sample, than unhealthy birds.

Lesser Scaup may also be exposed to lead (Pb), a contaminant of concern in Alaska's wetlands. In Spectacled Eiders (*Somateria fischeri*) and other waterfowl, negative population effects from breeding-area Pb exposure were demonstrated in the Yukon-Kuskokwim Delta, including clinical poisoning, defined as blood concentrations $\geq$0.20 mg kg^{-1} wet weight (Franson et al. 1998), morbidity (Franson et al. 1995), mortality (Flint and Grand 1997, Flint et al. 2000), and reduced overwinter survival (Grand et al. 1998). Steller's Eiders (*Polysticta stelleri*) breeding near Barrow on the North Slope of Alaska had high Pb levels and rates of exposure (Stout et al. 2002), and, in 1980, 11% of captured Long-tailed Ducks (*Clangula hyemalis*) on the North Slope had Pb shot in their gizzards (Taylor 1986). Exposure and effects occurred both before and well after the 1991 U.S. ban on use of Pb shot for waterfowl hunting, probably because of slow sinking and upheaval of Pb shot into top layers of sediment through underlying ice action in permafrost areas (Flint 1998). Exposure to Pb depends on whether hunting has occurred in the breeding area, as well as diet and feeding strategy (Pain 1996). Therefore, Pb's relationship to breeding population morbidity and mortality differs by species and breeding location. Lead exposure data are lacking for Lesser Scaup and other birds in interior Alaska, despite demonstrated effects of Pb on waterfowl elsewhere in Alaska.

Strontium (Sr) is an alkaline earth metal found in low concentrations in the earth's crust and comprised of four naturally occurring stable isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr. High total Sr concentrations in biota can result from high environmental concentrations due to weathering of Sr-containing sediments, or from nuclear fission resulting in the release of the radioactive isotopes ^{89}Sr and ^{90}Sr (Irwin et al. 1997). Lesser Scaup could be exposed to radioactive Sr on the breeding grounds, as ^{90}Sr (which has a longer half-life than ^{89}Sr) was released into the atmosphere and deposited in arctic areas from northern nuclear weapons testing, the Chernobyl disaster, and storage and dumping of Russian and Norwegian spent nuclear fuel in the Arctic Ocean near Novaya Zemlya (Arctic Monitoring and Assessment Programme 1998). Lesser Scaup could also accumulate Sr, including radioactive Sr, during winter. Lesser Scaup that breed in interior Alaska migrate and winter in the Mississippi flyway (Bellrose 1980), where some forage on zebra mussels (*Dreissena polymorpha*) at nuclear power plants (Mitchell and Carlson 1993), and mussels accumulate radionuclides in nuclear power plant discharge waters (Mersch et al. 1992). In the Columbia River, ^{90}Sr concentrations in Canada Goose forage and eggshells were positively related to nearby reactor releases (Rickard and Price 1990), and scaup foraging at nuclear power plants have greater tissue Sr concentrations than those foraging elsewhere (Custer and Custer 2000).

Data on contaminant concentrations in Lesser Scaup breeding in Alaska are rare, with the exception of those collected by Fox et al. (2005), who reported organochlorine pesticides, PCBs, and inorganic elements in eggs and tissues from nesting females from one interior Alaska breeding site (Minto Flats) and other sites across the species' breeding range. We assessed similar organochlorines and PCBs as Fox et al. (2005), as well as additional inorganic elements (including Sr) in eggs and blood of adult Lesser Scaup from a remote lake with few anthropogenic influences in the Yukon Flats NWR in interior Alaska. Contaminant concentrations in blood are useful for examining acutely toxic exposure, which may affect populations through adult mortality. We collected these data to evaluate contaminants as factors in Lesser Scaup breeding population declines; to provide insight into the dynamics of contaminant mobilization during migration from wintering to breeding areas; and to provide reference data for this species and other boreal-nesting waterfowl.

METHODS

Eggs and blood were collected in 2001 in conjunction with a nesting ecology study (Corcoran 2005) in the Yukon Flats NWR (66°22′N, 144°15′W). One (in one case, two) unhatched, addled, or abandoned egg per clutch was collected, wrapped in foil, and cushioned for transport. Eggs were refrigerated or chilled as much as possible on site before transport to and refrigeration at the laboratory in Fairbanks, Alaska. Eggs were rinsed, dried, and weighed; contents were then removed and placed into chemically clean jars (I-Chem Series 200®, I-Chem Research, Hayward, California, or equivalent) by scoring the egg equator with stainless steel instruments rinsed with 15% nitric acid, followed by double-distilled water, reagent-grade acetone, and reagent-grade hexanes. Egg contents were frozen (−40°C), then shipped overnight on ice to the analytical laboratory. Eggshells were rinsed and air dried for at least 10 days. Eggshell thickness (without membrane) was measured to the nearest 0.01 mm with a micrometer at four locations along the equatorial edge of both shell halves and is reported as the eight-measurement average.

Prior to extracting contents, egg length and breadth were measured to the nearest 0.01 mm three times using dial calipers. The average length and breadth were used to calculate egg volume using $V = Kv \cdot lb^2$, where V = volume, Kv = 0.519, l = length, and b = breadth (Hoyt 1979). The constant Kv = 0.519 was calculated from water displacement of Greater Scaup (*Aythya marila*) eggs using the equation $Kv = v/lb^2$, where v = volume (Hoyt 1979). Because Greater and Lesser Scaup eggs are of a similar shape (Kessel et al. 2002), these equations were considered more accurate than equations derived from eggs of other species.

Blood was collected from prenesting males and females captured in a floating cage with decoy hens. Using sterile techniques, up to 2 ml whole blood was drawn from the brachial or jugular vein, then placed in a glass tube with sodium heparin additive. Blood samples were refrigerated or chilled as much as possible on site before transport to a storage freezer (−40°C) in Fairbanks, Alaska, then shipped overnight on ice to the analytical laboratory.

ANALYTICAL CHEMISTRY

Egg contents were analyzed by AXYS Analytical Laboratories, Ltd. (Sidney, British Columbia) for 18 organochlorine pesticides and metabolites, including α- and γ–benzene hexachloride (BHC), α- and γ-chlordanes, trans nonachlor, dieldrin, endrin, heptachlor epoxide, hexachlorobenzene (HCB), mirex, oxychlordane, *o,p′*-dichlorodiphenyldichloroethane (DDD), *o,p′*-dichlorodiphenyldichloroethylene (DDE), *o,p′*- dichlorodiphenyltrichloroethane (DDT), *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, and toxaphene; 119 polychlorinated biphenyl (PCB) congeners; and individual and summed PCB Aroclors 1242, 1248, 1254, and 1260. (Blood was not analyzed for organochlorines or PCBs due to cost constraints and because the primary concern for acute toxicity was lead.) Briefly, egg contents were thawed and then homogenized using a clean, solvent-rinsed homogenization apparatus. The sample was ground with anhydrous sodium sulphate, spiked with surrogate standards, and refluxed in a Soxhlet apparatus for 16–20 hr. The cooled extract was concentrated by rotary evaporation and loaded onto a calibrated gel permeation column (Biobeads SX-3, Bio-Rad Laboratories, Hercules, California) to remove high molecular weight interferences. The column was eluted with 1:1 dichloromethane and the second fraction collected. This fraction was concentrated by rotary evaporation prior to additional chromatographic cleanup procedures. The extract was loaded onto a Florisil column (2.1% deactivated), which was eluted with hexane followed by 15:85 dichloromethane:hexane. The eluates were collected together and contained chlorinated pesticides, toxaphene, and PCB congeners. The fraction was concentrated, an aliquot of recovery standard added, and the extract transferred to an auto-sampler vial in preparation for instrumental analysis. However, half the fraction was subject to additional cleanup on carbon-Celite to isolate the non-ortho-substituted PCB congeners. The Florisil column was then eluted with 1:1 dichloromethane:hexane and the eluate collected. This fraction contained polar chlorinated pesticides. The fraction was concentrated, an aliquot of recovery standard added, and the extract transferred to an auto-sampler vial in preparation for instrumental analysis.

Pesticides, PCBs (Aroclors and congeners), and toxaphene were analyzed with a Finnigan INCOS 50 mass spectrometer with a Varian 3400 GC, a CTC A200S auto-sampler, and a DG10 data system running Incos 50 (Rev 11) software (Thermo Fisher Scientific, Waltham, Massachusetts). The mass spectrometer was operated at unit mass resolution in the Multiple Ion detection mode. The most polar chlorinated pesticides were analyzed with a Hewlett Packard (Palo Alto, California) 5890A gas chromatograph with a 63Ni electron capture detector. Chromatographic separation for both analyses was achieved using a DB-5 capillary column (60 m, 0.25 mm internal diameter, 0.10 m film thickness). For both analyses, splitless-split injection sequences were used, a calibration solution was run every 12 hr, and response factors were determined. Analytes were quantified using the internal standard method, which compared the analyte peak area to that of the corresponding surrogate standard with correction for response factors.

Egg contents and blood were analyzed for 19 inorganic elements including aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), selenium (Se), strontium (Sr), vanadium (V), and zinc (Zn) by the Geochemical and Environmental Research Group, College Station, Texas. Samples were digested in heavy-walled, screw-cap Teflon bombs with concentrated high-purity nitric acid. These were heated (2–8 hr at 129°C) and opened three times to release CO_2 build-up, resulting in total digestion and solubilization of all inorganic elements present. Most inorganic elements in the digestate were determined by graphite furnace atomic absorption spectrometry (AAS), while some elements were typically in high enough concentration (e.g., Zn) to be analyzed by flame AAS. Mercury was determined by cold vapor AAS, with Sn^{2+} reduction of HgO.

Percent moisture was determined using a weighed subsample dried for at least 16 hr at 105°C, then reweighed. Percent moisture was calculated as the percent difference between the dry weight and the wet weight. Percent lipid was calculated as the percent lipid of wet sample weight, from two weighed subsamples of extract dried at 105°C for 30 min, then reweighed.

No analytes were rejected on the basis of quality assurance or quality control screening criteria of blanks, duplicates, spikes, mass spectrometry confirmations (performed on 10% of samples), and standard reference materials. All blanks were below the limit of detection. Duplicate samples were between 80% and 120% in relative percent difference (RPD) as defined by: $RPD = ((D_1 - D_2)/(D_1 + D_2/2)) \times 100$, where D_1 and D_2 are the duplicate samples. All mean percent recoveries of spiked samples were between 80% and 120%. Method detection limits for organochlorines and PCBs (Aroclors) were 0.01 and 0.05 mg kg^{-1} wet weight (ww), respectively. Method detection limits for PCB congeners were 0.01 μg kg^{-1} ww. Method detection limits for inorganic elements were 0.10 (Be, Cd), 0.20 (Hg), 0.50 (As, Se, Cr, Cu, Ni, Pb, Sr, Va), 1.0 (Ba, Mn, Zn), 2.0 (B, Mo), and 5.0 (Al, Fe, Mg) mg kg^{-1} dry weight (dw), respectively. Instrument detection limits varied by sample volume and analyte and are given for analytes with ≥50% detections.

STATISTICAL ANALYSES

Since all data were from the same site and year, no hypothesis tests were performed on contaminant concentrations. Instead, we computed measures of central tendency and variation to compare to published values. We substituted a value of half the limit of detection for values below the limit of detection (since a small number of such substitutions are unlikely to affect data distribution and therefore calculation of a mean; Helsel 1990), then calculated geometric means and SD (back-calculated on the transformed data) for all analytes with >90% (an arbitrary but reasonable threshold) of data above the limit of detection. To avoid distributional bias, we calculated medians and ranges for analytes with 50%–90% of data above the limit of detection, and did not calculate measures of central tendency for analytes with <50% of data above the limit of detection (Helsel 1990). We also compared eggshell thickness to contaminants that may have affected it using Pearson's correlation coefficient and Bonferroni-corrected *P*-values, with significance determined by $P \leq 0.05$. SYSTAT 11 (SYSTAT Software, Inc., Richmond, California) was used for all analyses.

Egg organochlorine data were not adjusted for lipid content because there were no significant associations with percent lipid ($P > 0.05$ for all organochlorines), but they were adjusted for moisture content (Stickel et al. 1973) and are reported as mg kg^{-1} adjusted ww. Inorganic element data were not adjusted and are reported as mg kg^{-1} dw for eggs (except for Se, which was also reported in adjusted ww to compare to published values) and mg kg^{-1} ww for blood. No data were corrected for percent recoveries.

RESULTS

Most persistent organic pollutants were detected in few or no eggs ($n = 10$), although dieldrin, *p,p′*-DDE, *p,p′*-DDT, HCB, and mirex were detected at relatively low concentrations in >50% of eggs (Table 1). Although the parent compound *p,p′*-DDT was detected in 60% of sampled eggs, DDT:DDE ratios were <1:10, indicative of exposure to metabolized, rather than parent, DDT (Hunt et al. 1986, Dimond and Owen 1996). When total PCBs were detected, they were at low concentrations (Table 1). Many PCB congeners were not detected in any eggs, while others were detected in >50% of samples, but at relatively low concentrations (Table 2).

The essential elements Ba, Cr, Cu, Fe, Mg, Mn, Se, Sr, and Zn were detected in >50% of eggs ($n = 10$; Table 3), and Ba, Cu, Fe, Hg, Mg, Se, Sr, and Zn were detected in >50% of blood samples ($n = 14$; Table 4). Cadmium was not detected in eggs or blood. Lead was not detected in eggs, but it was detected in four of 14 blood samples, with a mean concentration when detected of 0.29 mg kg^{-1} ww. Mercury was detected in 86% of blood samples, but at low concentrations (Table 4), with the excep-

TABLE 1. Summary statistics for organochlorine contaminants (mg kg^{-1} wet weight) detected in >50% of Lesser Scaup (*Aythya affinis*) eggs (n = 10) from the Yukon Flats National Wildlife Refuge, Alaska, 2001. Geometric means ± SD were calculated for analytes detected in ≥90% of samples; medians and ranges were calculated for analytes detected in 50%–90% of samples.

Contaminant	Mean ± SD	Median (range)	Detection limit	Detections (%)
Dieldrin		0.001 (nd[a]–0.001)	5.92×10^{-4}	70
p,p′-DDE	0.040 ± 0.165		1.40×10^{-4}	100
p,p′-DDT		4.0×10^{-4} (nd–0.002)	1.61×10^{-4}	60
HCB	0.003 ± 0.422		1.75×10^{-4}	100
Mirex		3.0×10^{-4} (nd–0.001)	4.19×10^{-4}	60
Aroclor 1254	0.010 ± 0.032		15.3×10^{-4}	100
Aroclor 1260	0.019 ± 0.074		12.8×10^{-4}	100
Total PCBs (Aroclor sum)	0.031 ± 0.108		14.9×10^{-4}	100

[a] Not detected.

tion of one sample at 0.55 mg kg^{-1} ww. Only one egg had an Hg concentration (0.67 mg kg^{-1} dw, 0.21 mg kg^{-1} ww) above the detection limit. Although detected in 80% of eggs and 86% of blood samples, Se concentrations were low (Table 3, 4). Strontium was detected in 50% of blood samples (Table 4) and in all eggs (Table 3), with a range of 3.4–32.3 mg kg^{-1} dw.

Mean eggshell thickness was 0.26 ± 0.02 mm SD (range = 0.22–0.29 mm; n = 10). No significant correlations between thickness and organochlorine concentrations in egg contents were found (*p,p′*-DDE, $r = -0.05$, $P = 0.88$; *p,p′*-DDT, $r = 0.09$, $P = 0.78$; all other $P > 0.05$). However, eggshell thickness was significantly negatively correlated with Sr concentrations in egg contents ($r = -0.81$, $P = 0.01$, n = 10; Fig. 1).

DISCUSSION

Our results are largely in agreement with those of Fox et al. (2005), who also concluded that

TABLE 2. Summary statistics for PCB congeners (µg kg^{-1} wet weight) detected[a] in >50% of Lesser Scaup eggs (n = 10) from the Yukon Flats National Wildlife Refuge, Alaska, 2001. Geometric means ± SD were calculated for congeners detected in ≥90% of samples; medians and ranges were calculated for congeners detected in 50%–90% of samples.

PCB Congener	Mean ± SD	Median (range)	Detection limit	Detections (%)
74/61[b]	0.414 ± 0.523		0.016	100
99	0.620 ± 0.569		0.010	100
105/127	0.434 ± 0.712		0.010	100
118/106	1.607 ± 2.924		0.010	100
128	0.239 ± 0.777		0.049	90
138/163/164	2.107 ± 6.566		0.014	100
146	0.600 ± 1.972		0.013	100
153	4.048 ± 12.409		0.014	100
156		0.124 (nd[c]–0.928)	0.049	70
167		0.088 (nd–1.085)	0.049	60
170/190		0.508 (nd–3.954)	0.085	70
180	1.582 ± 3.447		0.016	100
183	0.449 ± 1.756		0.016	90
187/182	1.471 ± 6.121		0.016	100
194		0.180 (nd–1.638)	0.100	80
196/203		0.285 (nd–2.249)	0.137	80

[a] Congeners analyzed but not detected included: 1, 3, 6, 15, 17, 18, 19, 22, 25, 26, 29, 30, 31, 37, 40, 44, 45, 46, 50, 53, 54, 55, 67, 72, 81, 82, 85, 91, 92, 103, 110, 129, 136, 141, 151, 166, 169, 173, 176, 179, 185, 188, 198, 200, and coeluting congeners 4/10, 7/9, 134/143, 144/135, 16/32, 174/181, 24/27, 33/20/21, 41/71/64/68, 42/59, 47/48/75, 49/43, 52/73, 70/76, 83/108, 88/121, 95/93, and 97/86.
[b] Coeluting congeners.
[c] Not detected.

TABLE 3. Summary statistics for inorganic elements (mg kg^{-1} dry weight) detected in >50% of Lesser Scaup eggs (n = 10) from the Yukon Flats National Wildlife Refuge, Alaska, 2001. Geometric means ± SD were calculated for analytes detected in ≥90% of samples; medians and ranges were calculated for analytes detected in 50%–90% of samples.

Element	Mean ± SD	Median (range)	Detection limit	Detections (%)
Ba	14.8 ± 13.8		1.0	100
Cr		0.55 (nd[a]–1.20)	0.50	60
Cu	3.45 ± 0.77		0.50	100
Fe	132 ± 31		5	100
Mg	422 ± 33		5	100
Mn	1.3 ± 0.4		1.0	100
Se		0.70 (nd–1.02)	0.50	80
Sr	10.88 ± 10.65		0.50	100
Zn	48.4 ± 6.6		1.0	100

[a] Not detected.

TABLE 4. Summary statistics for inorganic elements (mg kg^{-1} wet weight) detected in >50% of Lesser Scaup blood samples (n = 14) from the Yukon Flats National Wildlife Refuge, Alaska, 2001. Geometric means ± SD were calculated for analytes detected in ≥90% of samples; medians and ranges were calculated for analytes detected in 50%–90% of samples.

Element	Mean ± SD	Median (range)	Detection limit	Detections (%)
Ba	0.95 ± 1.02		0.25	100
Cu	0.43 ± 0.09		0.13	100
Fe	598 ± 94		1	100
Hg		0.08 (nd[a]–0.55)	0.05	86
Mg	95.9 ± 16.9		1.3	100
Se		0.66 (nd–2.76)	0.13	86
Sr		0.10 (nd–0.30)	0.13	50
Zn	6.63 ± 1.90		0.25	100

[a] Not detected.

concentrations of most contaminants found in nesting Lesser Scaup were unlikely to be a factor in population declines. However, we examined additional contaminants (particularly Sr and Pb) and an additional matrix (blood).

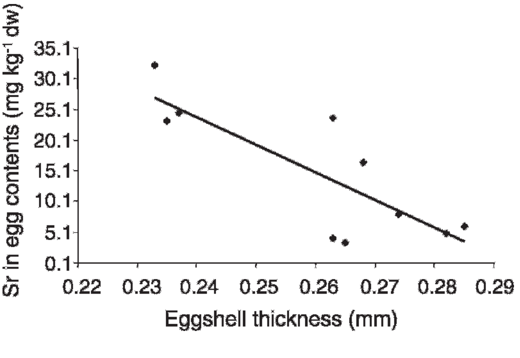

FIGURE 1. Eggshell thickness of Lesser Scaup eggs (n = 10) from the Yukon Flats National Wildlife Refuge, Alaska, was significantly negatively correlated with total strontium concentration of egg contents.

Concentrations of persistent organic pollutants were below those associated with embryotoxic or population-level effects for waterfowl or other birds. Concentrations of the DDT metabolite DDE, dieldrin, HCB, and mirex were well below concentrations of concern (Longcore et al. 1971, Peakall 1996, Weimeyer 1996). Aroclors, total PCBs (Aroclor sum), and toxic PCB congener concentrations were below those that had no effect on waterfowl hatching and survival (Hoffman et al. 1996).

Most detected inorganic elements were at or below levels considered background for bird eggs and blood (Eisler 1986, Osofsky et al. 2001, Burger 2002, Hui 2002). Blood Hg concentrations similar to those we found would result in low risk of reproductive effects in adult Common Loons (*Gavia immer*; D. Evers et al., Biodiversity Research Institute, unpubl. data). The one egg Hg concentration above the detection limit was lower than toxicity thresholds (approximately 2.5 mg kg^{-1} dw, 0.5 mg kg^{-1} ww; Thompson 1996). Selenium, an essential element that is nevertheless toxic at high concentrations, was detected in 80% of eggs, but at levels below those considered background (0.9 mg kg^{-1} dw; Heinz 1996), and comparable to the lower end of a range of Se concentrations in Lesser Scaup eggs throughout the breeding range (Fox et al. 2005). Median blood Se concentrations were also well below levels considered harmful (5–14 mg kg^{-1}; Heinz 1996). However, low concentrations of Se in both eggs and blood may indicate that Se accumulated on industrialized wintering grounds (Custer et al. 2003) is metabolized before or during migration (Fox et al. 2005).

Determining Pb concentrations in blood was the primary reason for blood collection, but the mean blood Pb concentration, when detected (n = 4), was indicative of only slight exposure above background levels of 0.2 mg kg^{-1} (Pain 1996). Some exposure may have occurred at wintering or staging areas along the Mississippi or Atlantic flyways, particularly in the Great Lakes (Pain 1996), and declined over the several weeks of migration and prenesting (Pain 1996, Austin et al. 1998).

The mean Sr concentration in eggs approached, and in many eggs exceeded, the 11.3 mg kg^{-1} associated with hepatic oxidative stress in pipping Black-crowned Night-Herons (*Nycticorax nycticorax*; Rattner et al. 2000). Some Sr concentrations in eggs were in the range of those potentially associated with decreased hatching success in passerines (Mora 2003). Mora (2003) postulated that elevated Sr concentrations may cause deformities in bills (or other keratinaceous tissues that require calcium deposition) such as those seen in Black-capped Chickadees (*Poecile atricapillus*) and other species in Alaska (Handel 2006), Willow Flycatchers (*Empidonax traillii*) and other passerines in the southwestern U.S. (Mora 2003), and other species elsewhere (Craves 1994). Zebra mussels ingested in winter have been implicated in transferring contaminants to Lesser Scaup (Custer and Custer 2000) and may be a source (Mersch et al. 1992) of the Sr we found in egg contents. Other possible sources include atmospheric transport from Asia or Russia (Kanayama et al. 2002) or local deposits (Ayuso et al. 2004).

We were most concerned with the effects of Sr on eggshells. Strontium has a strong biochemical similarity to calcium (Ca), which may result in enzymatic or structural substitutions during nutrient uptake (Graustein 1989, Blum et al. 2000) and other Ca-dependent processes (Irwin et al. 1997); inadequate Ca intake exacerbates Sr toxicity (Omdahl and DeLuca 1972). In birds, this may result in Sr replacement of Ca in eggshells, with subsequent altered gas exchange or other effects of weak or thin eggshells, or altered mobilization of eggshell calcium to the embryo through disruption of vitamin D metabolism resulting in strontium rickets or other embryotoxic effects (National Academy of Sciences 1980, Mora 2003). In this study, mean eggshell thickness was 18% thinner than the pre-DDT-era average of 0.32 mm (Austin et al. 1998), a percentage associated with population declines in raptors and other species, albeit due to DDE (Hickey and Anderson 1968), and was significantly negatively correlated with Sr concentrations in egg contents. There are few data in the literature with which to make comparisons; we need further research into the effects of Sr on eggshell quality and subsequent effects on embryo health, hatchability, and productivity.

Although most contaminants measured were not at levels of concern, we cannot categorically exclude contaminants from having an impact on declining Lesser Scaup populations. While Pb exposure was not an issue at our study site, it needs to be examined in other breeding areas with hunting pressure, given the evidence for exposure and effects on waterfowl elsewhere in Alaska. Strontium may be a factor in Lesser Scaup population declines, with plausible routes of exposure (zebra mussels in wintering areas or environmental exposure in breeding areas), a significant negative correlation of Sr (and not DDE) in egg contents and eggshell thickness, and demonstrated low productivity in this breeding area (mean nest success of 12%; Corcoran 2005). Further research on the effects of Sr on productivity through the mechanism of eggshell thinning is needed, as are additional analyses in avian species exhibiting elevated total Sr concentrations, eggshell thinning, or bill deformities.

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