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**ENVIRONMENTAL CONTAMINANTS PROGRAM
OFF-REFUGE INVESTIGATIONS SUB-ACTIVITY**

FINAL REPORT

**Contaminants in Steller's Eider (*Polysticta stelleri*) on Alaskan Breeding Grounds Near
Barrow, Alaska, 1999-2004.**

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by

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Introduction

Steller's eiders (*Polysticta stelleri*), the smallest of the four eider species, spend their entire life cycle in sub-arctic and arctic areas. The Pacific population historically bred in Arctic freshwater tundra ponds on the northern coastal plains of Alaska and Russia and the brackish marshes of the Yukon-Kuskokwim (Y-K) Delta, and wintered in shallow nearshore marine waters of the Alaska Peninsula. In 1997, Steller's eiders breeding in Alaska were listed as threatened (Federal Register 62(11):31748-31757) under the Endangered Species Act, based primarily on the disappearance of breeding Steller's eiders from the Y-K Delta. The area around Barrow, Alaska, on the northern coast of Alaska, now harbors the only known breeding concentration of Steller's eiders in the United States. Successful breeding occurs only in years when lemming populations are high; the exact mechanism of this relationship is unknown although hypothesized to be a predator-prey interaction (Quackenbush and Suydam 1996). Even in years when breeding is attempted, nest success and productivity are very low. The proximate cause is nest predation; predators have increased in Arctic areas with permanent human settlements and development (NRC 2003). However, exposure to contaminants on the breeding grounds, particularly lead, may also play a role.

Elevated blood and tissue lead levels, morbidity, and mortality from lead poisoning have been documented in spectacled eider (*Somateria fischeri*) (Franson et al. 1995, Flint et al. 1997), common eider (*Somateria mollissima*) (Franson et al. 1995), and possibly in Steller's eider (Flint and Herzog 1999) on breeding grounds in the Y-K Delta. Further, one Steller's eider found dead near Barrow had liver and kidney lead concentrations suggestive of lead poisoning (Trust et al. 1997). Median tissue lead concentrations in spectacled, common, and Steller's eiders were an order of magnitude greater in the Y-K Delta and in Barrow than in other areas of Alaska and Arctic Russia (Trust et al. 1997; see also Quackenbush and Snyder-Conn 1993). Lead levels were highest in birds that remain on the nesting grounds the longest (i.e., successful nesters), and low overwinter survival of these lead-exposed birds may have resulted in population declines (Flint et al. 1997).

Other contaminants may also affect Steller's eiders, including heavy metals, trace elements, and persistent organic pollutants such as organochlorine pesticides and polychlorinated biphenyls (PCBs). While overall levels of these contaminants are generally high in arctic biota (Jensen et al. 1997, AMAP 1998), concentrations in specific populations depend on trophic status, wintering areas, and local sources. Eiders eat molluscs, crustaceans, invertebrates, and vegetable matter; this relatively low trophic status results in generally lower concentrations of persistent organochlorines in eiders than other arctic seabirds (de March et al. 1998). However, there are few data on metals and persistent organochlorines in Steller's eiders. Trust et al. (1997) measured metals and organochlorines in common, spectacled, and Steller's eider carcasses, including seven Steller's eiders with three from Barrow. Elevated cadmium, selenium, and copper concentrations were found in spectacled and common eider carcasses from Alaska and Russia, and mercury concentrations were higher in Steller's eiders than the other eiders sampled. Finally, although organochlorine concentrations measured by Trust et al. (1997) in organs of common, spectacled, and Steller's eiders were low, these biomagnifying compounds may have

their greatest effects on reproduction, rather than through acute effects such as mortality. For this reason, I measured persistent organochlorine concentrations in eggs, which also filled a significant data gap for this threatened species.

The study objectives were to document and evaluate lead, other metal, and persistent organochlorine concentrations in Steller's eider blood, tissue, and addled eggs from the only known breeding concentration in the United States, at Barrow, Alaska.

Methods

Study Area

The terrain around Barrow, Alaska, is characterized by numerous thaw lakes in a poorly-drained, permafrost-underlain landscape. Wetlands include drained-lake basins, small ponds and lakes, beaded streams, and wet meadows (Ritchie and King 2004). Steller's eiders arrive in Barrow around the beginning of June, and congregate on large open water areas prior to pair formation and nesting, which begins around June 15 (Rojek and Martin 2003). Pairs and nests are found primarily on shallow ponds with emergent *Arctophila fulva* or *Carex aquatilis* (Obritschkewitsch et al. 2001).

Sample Collection

Sample collection was done in conjunction with ongoing Steller's eider research in a 182 km² area around Barrow, AK (Rojek and Martin 2003) conducted by the U.S. Fish and Wildlife Service, the North Slope Borough Dept. of Wildlife Management, and their cooperators. This research included annual location, nesting, and productivity surveys, telemetry studies, habitat use analysis, and outreach. Steller's eiders were present in the breeding area in early June 1999-2003 (pre-nesting) but nested only in 1999 and 2000.

Whole blood samples were collected from live birds. Adults were captured using decoyed mist nets during pre-nesting in June and incubating hens were trapped on nests in July using cautiously placed mist nets. Ducklings were captured with long-handled dip nets on brood-rearing ponds in August, when chicks were at least several weeks old. All birds were weighed, measured (wing chord, culmen, tarsus, and middle toe), banded with a U.S. Fish and Wildlife Service anodized aluminum band, and assessed for behavioral and physiological symptoms of lead poisoning (inability to fly, weakness, "roof-shaped" or drooping wings, emaciation, bile staining at vent). Up to 2 ml (but no more than 1% of body weight) was drawn from the brachial or jugular vein into sterile plastic syringes. Blood was immediately transferred to sterile tubes with sodium heparin additive, which were placed on ice in the field and stored frozen (-40° C) until overnight shipment on dry ice to the analytical laboratory.

Steller's eiders found dead were necropsied to determine cause of death, particularly for evidence of lead poisoning (e.g. bile staining of vent and breast muscle atrophy). Approximately 10 g of

liver and of kidney were removed using stainless steel instruments rinsed in 10% nitric acid, double-distilled water, acetone, and hexane, then placed in chemically clean jars and stored frozen (-40° C) until overnight shipment on dry ice to the analytical laboratory.

Addled (unhatched) eggs were collected from abandoned or old nests. They were wrapped in acetone-rinsed aluminum foil, transported in padded containers, and refrigerated after return from the field (< 8 hr). Egg contents were removed into chemically clean jars using stainless steel instruments rinsed in 10% nitric acid, double-distilled water, acetone, and hexane, then stored frozen (-40° C) until overnight shipment on dry ice to the analytical laboratory.

Analytical Chemistry

Whole blood, liver, kidney, and egg samples were analyzed for 19 elements (Al, As, B, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Se, Sr, V, Zn). Liver and egg samples were analyzed for organochlorine (OC) pesticides (α -BHC, α -chlordane, β -BHC, cis-nonachlor, dieldrin, endrin, δ -chlordane, HCB, heptachlor epoxide, mirex, *o,p'*-DDD, *o,p'*-DDE, *o,p'*-DDT, oxychlordane, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, toxaphene, trans-nonachlor) and total PCBs (Aroclor sum). All analyses were conducted at the Patuxent Analytical Control Facility (PACF) or a PACF contract laboratory using established methods (Appendix A). Quality Assurance/Quality Control (QA/QC) procedures followed PACF contract specifications, and included Standard Reference Materials (SRMs), duplicates, spikes, and blanks. The nominal lower limits of detection (detection limits) were 0.01 ppm for OC pesticides, 0.05 ppm for PCBs, and varied for metals depending upon analyte and sample volume. The nominal OC detection limits and the highest reasonable metal detection limits were used to determine data below the lower limit of detection (non-detects).

Data Analysis

Data were statistically summarized into measures of central tendency (mean, median) and estimates of variability (SD, range) depending upon the percent of non-detects (nds), by tissue. Means and SDs were estimated for analytes with $\leq 10\%$ nds (after nds were substituted with the arbitrary value of 0.5 times the detection limit; a small number of such substitutions are unlikely to bias the mean), and medians and ranges were estimated for analytes with $> 10\%$ nds.

Contaminant concentrations in blood, tissues, and eggs were compared to established toxicity thresholds, and statistical comparison of group means were made when data were sufficient using Analysis of Variance (ANOVA) or Kruskal-Wallis rank sum tests.

Results and Discussion

Because Steller's eiders are periodic breeders, and do not breed at high densities even during productive years, sample sizes were very small and not amenable to survival modeling as in Flint et al. (1997) or Grand et al. (1998). Steller's eiders bred at Barrow only in 1999 and 2000.

However, they arrived on the breeding grounds in each year from 1999-2003, so some samples were collected every year. During the study, whole blood was collected from eight incubating hens, 12 pre-breeding adults (five females and eight males), three wild fledglings, and serial samples from four nestlings hatched in captivity. Liver and kidney were collected from 11 dead adult Steller's eiders (three in Barrow, and one wintering female, and seven molting eiders) and three chicks that were hatched, raised, and died in captivity. Twenty-two unhatched eggs from eight nests were also collected. All analytes in all catalogs were within QA/QC criteria, except B in samples collected in 1999. These data were not reported or used.

Lead

Steller's eiders are probably exposed to lead on freshwater breeding grounds by consumption of spent lead shot. Consequently, greater lead concentrations were expected in breeding compared to pre-breeding, wintering, or molting adults as Franson et al. (2000) found for common eiders in Finland and Flint and Grand (1997) found for spectacled eiders on the Y-K Delta. Whole blood lead concentrations were significantly greater in incubating hens ($n=8$, $\bar{x} \pm SD= 2.148 \pm 1.877$) compared to pre-breeding, adults ($n=13$, $\bar{x} \pm SD= 0.165 \pm 0.144$) (Mann-Whitney $U = 101$, $n = 21$, $P < 0.0001$) (Fig. 1), and incubating hen concentrations were all above background (0.2 ppm), with most above toxic levels (0.4 ppm) (Friend 1985). Lead exposure at concentrations expected to cause toxic effects was therefore documented in Steller's eider females during the nesting season, specifically during incubation at Barrow.

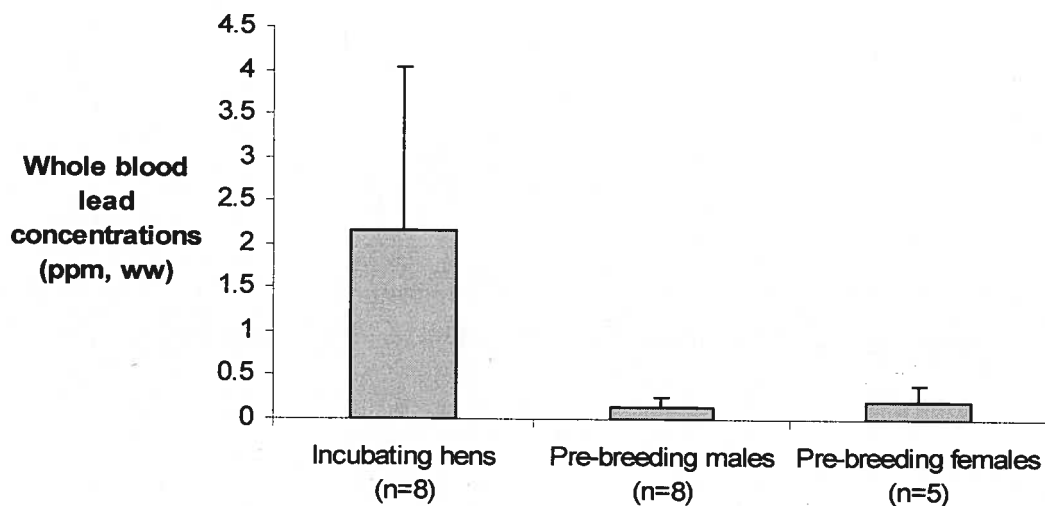


Fig. 1. Mean (\pm SD) lead concentrations (ppm, ww) in whole blood of adult Steller's eiders at Barrow, Alaska, 1999-2001. Pre-breeding males and pre-breeding females combined had significantly lower blood lead concentrations than did incubating females (although pre-breeders are separated by sex for illustrative purposes only).

Lead in livers of all non-breeding adults (a pre-breeding pair, a wintering female, seven molting adults, and a non-breeding female – no brood patch – collected during the breeding season) ranged from nd to 1.68 ppm ww, below the threshold associated with exposure above background (2 ppm), and far below the 76.5-187 ppm (dw; converted from fresh weight by Trust et al. 1997) in eiders that died of lead poisoning (Franson et al. 1995). Lead in kidneys of these birds ranged from nd to 2.07 ppm dw, below the 39-130 ppm (dw; converted from fresh weight by Trust et al. 1997) in eiders that died of lead poisoning (Franson et al. 1995). There were no significant differences in blood lead concentrations between captive-raised ducklings ($n=4$, $\bar{x} \pm SD = 0.114 \pm 0.038$) and wild ducklings ($n=3$, $\bar{x} \pm SD = 0.082 \pm 0.037$) ($t_{3,7} = 1.265$, $P = 0.281$), although the sample size was quite small and represented only two broods (one wild, one hatched in captivity).

Mercury and Selenium

Mercury and selenium are also of toxicological concern, and toxic effects are best characterized with organ and egg concentrations. Mercury and selenium are greater in marine animals, including seaducks, than in terrestrial counterparts because there are naturally greater mercury and selenium concentrations in the marine environment. Therefore, pre-breeding eiders captured in June were more likely than breeders captured in July to have greater concentrations of mercury and selenium in their tissues, since they were more recently arrived from marine areas. For example, blood selenium concentrations were substantially greater in pre-breeding adults ($\bar{x} \pm SD = 8.416 \pm 9.993$ ppm ww) compared to incubating hens ($\bar{x} \pm SD = 0.827 \pm 0.401$, calculated with 5 nds substituted with $\frac{1}{2}$ the detection limit), and mercury was detected only in pre-breeding adults, not incubating hens or juveniles. Further, although mallard ducks (*Anas platyrhynchos*) in a laboratory study died with 5-14 ppm ww Se in blood (Heinz 1996), these concentrations are not likely to be harmful to seaducks such as eiders because of their greater tolerance of relatively elevated selenium and other elemental contaminants (Trust et al. 2000).

Liver mercury concentrations of 30 ppm ww indicate intoxication in birds, far greater than our mean ($\pm SD$) liver concentration of 0.377 (± 0.202) ppm ww. Mercury in kidneys of a variety of birds that died of mercury poisoning ranged from 5.02 ppm dw in puffins to 125 ppm ww in kestrels (Thompson 1996), both far above adult mean kidney mercury concentrations ($n=11$, $\bar{x} \pm SD = 0.098 \pm 0.037$ ppm dw) from this study. Selenium in livers of non-breeding adults (including pre-breeding, molting, and wintering males and females) ($\bar{x} \pm SD = 4.80 \pm 1.75$ ppm ww) were less than a recommended toxicity threshold of 10 ppm ww (Heinz 1996), and adult liver:kidney ratios were all greater than 1, the threshold for exposure above background (Heinz 1996). Selenium and mercury concentrations in liver and kidneys were similar to those found in other eiders from Russia and Alaska (Stout et al. 2002). Mercury concentrations of up to 2.5 mg/kg dw (0.5 to 2.0 ppm ww) in avian eggs generally don't affect reproduction (Thompson 1996); this threshold was greater than egg concentrations in this study (range = 0.128 – 0.735 ppm dw; 18% nds, $n = 22$). Egg selenium concentrations in this study (82% nds, maximum value = 0.199 ppm ww) were below the > 3 ppm ww threshold that may impair reproduction (Heinz 1996).

Other Metals

Other metal concentrations in most tissues were low. In blood, other metals were at or below detection limits, except Cu, Fe, Mg, and Zn, trace elements that were not at toxic concentrations. Similarly, other metals were at or below detection limits in all or most eggs, except the trace elements Cu, Fe, Mg, Mn (detected in 95% of eggs), and Zn. The potentially toxic elements Ba, Cr (detected in 77% of eggs), and Pb (detected in 73% of eggs), and Sr were also detected in most or all eggs, but concentrations were of low and often of unknown toxicological significance. As, Cd, Cr, Cu, Fe, Mg, Mn, Sr, V, and Zn were detected in most or all adult kidneys and livers, but not at concentrations of concern. All other metals were detected in few or no organs.

Organochlorines

All OC pesticides and PCB data were below detection limits in most or all liver samples, and there were few detections of organochlorines in most eggs. The egg exceptions (with range, ppm wet weight, and percent of nds) were HCB (non-detect - 0.056, 23%), β -BHC (nd - 0.022, 68%), heptachlor epoxide (nd - 0.017, 68%), *o,p'*-DDE (nd - 0.048, 73%), oxychlorane (nd - 0.017, 68%), *p,p'*-DDE (nd - 0.061, 45%), and trans-nonachlor (nd - 0.015, 68%). The highest *p,p'*-DDE values do not exceed thresholds associated with eggshell thinning in mallards (46 ppm; Longcore et al. 1971). These results are consistent with OCs measured in other eiders (Stout et al. 2002).

Management Implications

Of the wide range of metal and organochlorine contaminants measured, only lead was at concentrations of concern, and then only in incubating females. Because of this and other studies documenting elevated blood and tissue lead levels, morbidity, and mortality from ingestion of lead shot, reducing exposure to lead is a high priority task in the Steller's Eider Recovery Plan (U.S. Fish and Wildlife Service 2002). The current study documented lead exposure in eiders nesting at Barrow, a populated area with waterfowl subsistence hunting and historical use of lead shot. Because 100% of sampled incubating hens (n=8) showed evidence of exposure to lead, and most were above clinical toxicity thresholds, lead exposure has the potential to impact Steller's eider reproduction, especially given that this threatened species does not nest every year. Once they do breed, nest success is low, proximally due to nest predation – but a lead-intoxicated female may exhibit behavioral abnormalities that make her or her nest more susceptible to predation, or she may abandon her nest or nesting attempt.

Management of spent lead shot that is dispersed over a large area is difficult and impractical. Spent lead shot are very difficult to find in and therefore remove from a wetland system, in spite of the relatively slow rate of settlement in Alaska (Flint 1998; P. Flint, U.S.G.S., pers. comm.). Seeding of areas with non-lead grit (gravel or ground oyster shells) may work if ducks are ingesting lead specifically for grit, but since the limited data on breeding Steller's eiders diet

shows a relatively soft diet of midge and caddisfly larvae (Quakenbush et al. 1995) and vegetation, they may be accidentally ingesting shot while feeding rather than deliberately ingesting it for grit (Locke and Thomas 1996). Further, seeding with calcium-carbonate shell grit may alter the acid-base balance of the freshwater ponds into which it is introduced. Developing a greater understanding of the management options for reducing lead shot ingestion is warranted.

The most practical management of lead shot is to reduce the amount of use with a combination of law enforcement and educational efforts, including steel shot clinics, lead-shot buy backs or exchanges, and education focusing on ecosystem and waterfowl health, and human health (e.g. high lead concentrations in subsistence foods prepared from birds shot with lead; Johansen et al. 2004, Johansen et al. 2001, Scheuhammer et al. 1998). The option to clinically manage individual birds with high lead levels should also be maintained in conjunction with ongoing Steller's eider research at Barrow.

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All data are available upon request from the author at the Fairbanks Fish and Wildlife Field Office, 101-12th Ave., Box 19, Room 110, Fairbanks, AK 99701.

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Appendix A: Analytical Chemistry Methods

Samples for metals analysis were freeze-dried (Labconco Freeze Dry System Model 7756). Then, an 0.5-1 g aliquot was digested in 10 ml ultrapure nitric acid and 4 ml of 30% hydrogen peroxide (OI Model 7301 Microwave Digestion System). Al, B, Ba, Be, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sr, V, and Zn were determined using a sequential Inductively Coupled Plasma (ICP) emission spectrometer (Perkin Elmer Plasma II), with an added post-digestion scandium internal standard. As and Se were determined by Stabilized Temperature Platform Graphite Furnace Atomic Absorption Spectroscopy (AAS) (Perkin Elmer Zeeman 3030 Atomic Absorption Spectrophotometer) using the methods described by Krynitsky (1987). Hg was determined by Cold Vapor AAS as described by Hatch and Ott modified for use with a Perkin Elmer Atomic Absorption Spectrophotometer 3100 equipped with a Perkin Elmer FIAS 200.

Samples for organochlorine analysis were prepared and extracted using methods described by Cromartie et al. 1975. Glass extraction thimbles were used. The silica gel separation of the pesticides from PCBs was different from the above reference in that four fractions were used instead of three to enable the separation of dieldrin and endrin from the rest of the pesticides. The pesticides in each fraction were quantified with a gas-liquid chromatograph (GLC), equipped with a ⁶³Ni electron capture detector. The GLC column used was a 30m MEGABORE coated with a 1.0 micron film of 7% cyanopropyl 7% phenyl polysiloxane. Residues in 10% of the samples were confirmed by gas chromatography/mass spectrometry (GC/MS). The nominal lower limit of detection was 0.01 ppm for pesticides and 0.05 ppm for PCBs based on a 10 g aliquot wet weight.

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