

Articles

Trace Elements in Blood of Sea Ducks from Dutch Harbor and Izembek Lagoon, Alaska

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Abstract

In 2001, we collected whole blood from sea ducks—Steller's eider *Polysticta stelleri*, harlequin duck *Histrionicus histrionicus*, black scoter *Melanitta nigra*, and long-tailed duck *Clangula hyemalis*—wintering at Dutch Harbor, Alaska, and from Steller's eiders molting at Izembek Lagoon on the Alaska Peninsula. Analysis of blood samples was done for 19 trace elements, of which 17 were detected in one or more samples. In Steller's eiders, mean concentrations of six trace elements (As, B, Fe, Hg, Se, and Mo) were greater at Dutch Harbor and mean concentrations of four trace elements (Cr, Cu, Mg, and Zn) were greater at Izembek Lagoon. Among sea ducks at Dutch Harbor, mean concentrations of five trace elements (Cu, Hg, Se, Zn, and V) differed by species: Steller's eiders had greater concentrations of Cu, Zn, and V in their blood; black scoters had the highest concentration of Se; and harlequin ducks had the highest Hg level, with a mean concentration slightly above a threshold effect level. One Steller's eider and one harlequin duck from Dutch Harbor had blood Pb levels above background concentrations. We have no observations to indicate that concentrations of these trace elements were associated with adverse effects.

Keywords: Steller's eider; sea ducks; trace elements; Alaska

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Introduction

Large numbers of sea ducks use embayments along the western Alaska Peninsula and eastern Aleutian Islands during summer and winter (King and Dau 1981). These maritime habitats support populations of

mollusks and other invertebrates fed heavily upon by several species of sea ducks. Steller's eider *Polysticta stelleri* is a small sea duck that inhabits only northern latitudes, nesting near freshwater tundra ponds and moving to marine areas after the breeding season (Fredrickson 2020). In Alaska, small numbers of breeding



Steller's eiders have historically occurred near Utqiagvik (formerly Barrow), where 365 nests were found from 1995 to 2016, and on the Yukon-Kuskokwim Delta, where six nests were found during 1991–1998 (Flint and Herzog 1999; Safine et al. 2020). Once considered a common breeder in the Yakutsk Republic of Russia, Steller's eider was a rare species there in 1987, and in 1997 the U.S. Endangered Species Act (ESA 1973, as amended) listed the Alaska breeding population as threatened (Fredrickson 2020). On the Alaska Peninsula's Izembek Lagoon, a major molting area, counts of Steller's eiders declined by approximately 50% between 1975–1985 and 1986–1990 (Kertell 1991). Flint et al. (2000) studied annual survival of Steller's eiders molting on the Alaska Peninsula between 1975 and 1997 and calculated annual survival of 0.90 for females and 0.76 for males. They concluded that decreased adult survival may have initiated the population decline and suggested that lower survival rates of males vs. females may further limit reproductive potential. A later study reported that annual survival during 1993–2003 was 0.86 for females and 0.87 for males (Frost et al. 2013).

Although regional differences exist in populations of the other species in our study, black scoter *Melanitta nigra* and harlequin duck *Histrionicus histrionicus* are listed as species of least concern by the International Union for Conservation of Nature (IUCN 2021). The long-tailed duck *Clangula hyemalis*, however, is listed as vulnerable because overall the population is decreasing (IUCN 2021). In western North America, the breeding range of the harlequin duck extends from Alaska to the northwestern United States and wintering habitats include coastal Pacific regions from the Aleutian Islands to Washington and Oregon (Robertson and Goudie 2020). The western population of the black scoter in North America breeds mainly on coastal wetlands in Alaska, is less abundant in interior Alaska, and winters along the coast from the Aleutian Islands to Baja California (Bordage and Savard 2020). The long-tailed duck is a circumpolar breeder and, in Alaska, nests in arctic and subarctic regions, wintering in coastal areas from the Aleutian Islands to Oregon (Robertson and Savard 2020).

Marine birds have been used as bioindicators for a variety of environmental contaminants, including heavy metals and trace elements (Furness 1993; Burger and Gochfeld 2004). Some of these elements have no known biological function, and others are essential for life, but all can be toxic if exposure is excessive (Goldhaber 2003). Some of the most studied trace elements in sea ducks include lead, selenium, mercury, cadmium (Pb, Se, Hg, Cd) and, to a lesser extent, chromium, nickel, copper, and zinc (Cr, Ni, Cu, and Zn; Franson 2015). To evaluate the exposure of Steller's eiders to trace elements, we compared trace element concentrations in the blood of Steller's eiders sampled at the industrialized wintering area of Dutch Harbor with concentrations in Steller's eiders at our reference site, Izembek Lagoon, on the lower Alaska Peninsula. We also report our trace element findings in blood of harlequin ducks, black scoters, and one long-tailed duck sampled at Dutch Harbor.

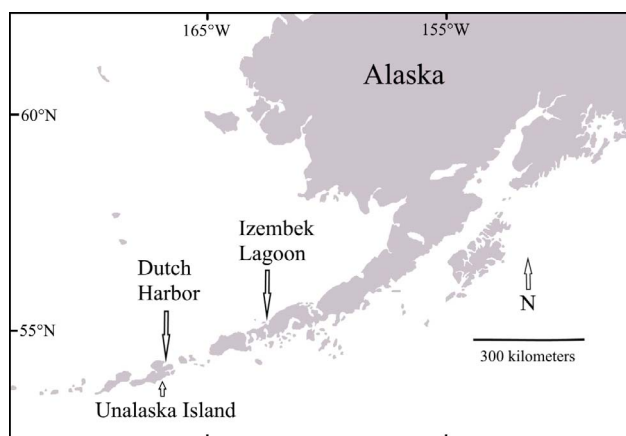


Figure 1. Map of southwestern Alaska showing locations of 2001 study at Dutch Harbor and Izembek Lagoon.

Study Sites

One wintering area used by all four of these sea duck species is Dutch Harbor, a nearshore embayment of Unalaska Island (Figure 1). In 1994, the Alaska Department of Environmental Conservation [ADEC] listed Dutch Harbor as impaired because of nonattainment of water quality standards for petroleum products (ADEC 2008). This designation was still in place as of 2008, with pollutant sources listed as industrial and urban runoff (ADEC 2008). Dutch Harbor was the top port in the United States for the total volume of seafood landed in 2018 for the 22nd consecutive year (National Marine Fisheries Service 2020). The city of Unalaska, southwest of Dutch Harbor, is a community of approximately 4,000 people that contributes wastewater from a municipal sewage treatment plant, stormwater runoff, and seafood processing plants to the local marine environment. Release of a variety of pollutants, including trace elements, in municipal wastewater may contaminate the local aquatic environment and sediments (Chambers et al. 1997). Potential sources of trace elements in wastewater include fossil fuel combustion, corroded pipes, stormwater runoff from roadways, seafood processing discards, paints, household cleaning agents, chemicals used for sewage treatment, and cookware (Chambers et al. 1997; Liaset et al. 2003; Pokomeda et al. 2018). Furthermore, metals may accumulate in aquatic invertebrates to concentrations that are greatly in excess of concentrations in the ambient environment (Rainbow and Luoma 2011). In their winter marine habitats, the four sea duck species in our study consume mussels and other invertebrates, potentially exposing them to elevated concentrations of trace elements. Reed and Flint (2007) reported that a large proportion of marked Steller's eiders frequented an area of Dutch Harbor receiving effluent both from the municipal sewage treatment plant and a seafood processing plant, indicating that they may have been attracted there by invertebrate populations enhanced by eutrophication. Hollmén et al. (2011) found the highest concentrations of *Escherichia coli* bacteria in water samples from the same

area of Dutch Harbor, referred to as the industrialized site, and reported a higher prevalence of *E. coli* in fecal samples from Steller's eiders there than in Steller's eiders at their reference site at Izembek National Wildlife Refuge on the Alaska Peninsula. They found evidence of avian pathogenic *E. coli* strains and serum biochemistry results indicative of intestinal disease, indicating harmful effects of the pathogenic strains to Steller's eiders. Miles et al. (2007) also reported evidence of environmental contamination in Dutch Harbor. They found elevated concentrations of polycyclic aromatic hydrocarbons in Steller's eider prey *Mytilus trossulus*.

Our other study location, Izembek Lagoon, is within the state of Alaska Izembek Game Refuge and surrounded by Izembek National Wildlife Refuge, on the north side of the lower Alaska Peninsula (Figure 1). In addition to being an important molting and wintering area for Steller's eiders, Izembek Lagoon is used by many other species of waterfowl and shorebirds and has been designated as a wetland of international importance under the Ramsar Convention (Ramsar 2011). We found no reports of any water quality issues in Izembek Lagoon. Steller's eiders exhibit high site fidelity (>95%) to molting areas on the Alaska Peninsula, and the small Alaska breeding population exhibits high fidelity (0.91) to nesting areas near Utqiagvik (Flint et al. 2000; Safine et al. 2020). However, little is known about site fidelity of sea ducks to the Dutch Harbor wintering area and what impact, if any, that it may have on overall contaminant loads throughout their life cycles.

Methods

In February 2001, we captured sea ducks (23 Steller's eiders, 8 harlequin ducks, 3 black scoters, and 1 long-tailed duck) wintering in Dutch Harbor (53°53'N, 166°33'W) with floating mist nets (Kaiser et al. 1995) and decoys. In September 2001, we captured flightless molting Steller's eiders ($n = 20$) in the northeastern part of Izembek Lagoon (55°25'N, 162°36'W), Alaska Peninsula, with corral traps (Flint et al. 2000). We collected 2–4 mL of whole blood by jugular venipuncture, transferred it to heparinized tubes, and stored it frozen at less than or equal to -20°C until analysis.

Analysis of trace elements

Analysis of blood samples was done for the following trace elements according to a list developed by the U.S. Fish and Wildlife Service (USFWS) Patuxent Analytical Control Facility (Laurel, Maryland): Al, As, B, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Se, Sr, V, and Zn (aluminum, arsenic, boron, barium, beryllium, cadmium, chromium, copper, iron, mercury, magnesium, manganese, molybdenum, nickel, lead, selenium, strontium, vanadium, and zinc). Analysis was performed at the Research Triangle Institute (Research Triangle Park, North Carolina). Analysis involved weighing each blood sample, freeze-drying it to determine moisture content, and then digesting it in nitric acid. Analysis of total mercury was via cold vapor atomic absorption; analyses of all other

trace elements in blood were by inductively coupled plasma mass spectroscopy or inductively coupled plasma emission spectroscopy. Lower limits of detection ranged from 0.01 $\mu\text{g/g}$ dry weight (dw) for Hg to 5.4 $\mu\text{g/g}$ dw for Al, Fe, and Mg. Recoveries from spiked heparinized samples averaged 98%. The average moisture content of blood of Steller's eiders was 77.8 and 74.7% in birds from Izembek Lagoon and Dutch Harbor, respectively; 75.0% for harlequin ducks; 76.3% for black scoters; and 75.9% for the long-tailed duck. We report results (Data S1, *Supplemental Material*) on a dw basis (Table 1) to account for variations in moisture content of blood among individuals; however, for comparisons with other studies reporting results on a wet weight (ww) basis (Table 2), we converted our results as follows:

$$\mu\text{g/g ww} = (\mu\text{g/g dw}) \left(\frac{100 - \% \text{ moisture}}{100} \right)$$

Data analysis

We determined age (hatch year vs. after hatch year) for 51 of the 55 sea ducks sampled, and all but 3 of the 51 sea ducks were after hatch year. Thus, we did not include age in statistical analysis of trace element concentrations. When detectable residues of an element were found in at least 50% of the samples, we substituted a value of one-half the lower limit of detection for nondetections (Clarke 1998). To evaluate variability in concentrations of trace elements in blood, we tested for differences due to sex and location for Steller's eiders, due to sex for harlequin ducks, and due to species among Steller's eiders, harlequin ducks, and black scoters at Dutch Harbor by using analysis of variance on rank-transformed data and the Mann-Whitney rank sum test. We used a significance level of 0.05 for all comparisons. Because there were no differences for any trace elements by sex for Steller's eiders at either location and for harlequin ducks at Dutch Harbor (all P values ≥ 0.05), we combined data for males and females. We did not test trace element data from black scoters for sex differences because of the small sample size.

Results

Steller's eiders, Dutch Harbor and Izembek Lagoon

Of 17 trace elements detected in blood of one or more Steller's eiders, mean concentrations of six trace elements (As, B, Fe, Hg, Se, and Mo) were greater in wintering ducks at Dutch Harbor than in those molting at Izembek Lagoon and mean concentrations of four trace elements (Cr, Cu, Mg, and Zn) were greater in ducks at Izembek Lagoon than at Dutch Harbor (Table 1). We detected 10 trace elements in 100% of the Steller's eider blood samples from both Dutch Harbor and Izembek Lagoon. We did not detect the trace elements Al, Be, Mn, and Sr in any samples from Izembek Lagoon, but we did detect them in 100% (Al), 43.5% (Be), 34.8% (Mn), and 8.6% (Sr) of Steller's eiders at Dutch Harbor. We detected Ba in 5.0 and 100%, Pb in 30.0 and 95.6%, and Mo in 85



Table 1. Trace elements in whole blood of Steller's eiders *Polysticta stelleri* (STEI) from Izembek Lagoon and Steller's eiders, harlequin ducks *Histrionicus histrionicus* (HADU), black scoters *Melanitta nigra* (BLSC), and a long-tailed duck *Clangula hyemalis* (LTDU) from Dutch Harbor, Alaska, 2001. Values are presented in micrograms per gram, dry weight (standard error [SE]; minimum–maximum [min.–max.]).

Element	Izembek Lagoon (molting), mean \pm SE (min.–max.)	Dutch Harbor (wintering), mean \pm SE (min.–max.)			
	STEI (n = 20)	STEI (n = 23)	HADU (n = 8)	BLSC (n = 3)	LTDU (n = 1)
As	1.01 \pm 0.06 (0.64–1.54) A ^a	2.23 \pm 0.20 (0.75–5.26) B	2.42 \pm 0.32 (1.20–4.01)	2.39 \pm 1.14 (0.99–4.66)	1.21
B	2.38 \pm 0.26 (0.96–5.63) A	3.44 \pm 0.15 (2.39–5.45) B	3.42 \pm 0.11 (3.06–3.93)	4.75 \pm 0.68 (3.54–5.88)	4.73
Cr	1.91 \pm 0.18 (1.75–2.05) A	1.86 \pm 0.07 (1.27–2.73) B	1.73 \pm 0.02 (1.58–1.83)	1.78 \pm 0.07 (1.66–1.90)	1.81
Cu	2.29 \pm 0.08 (1.71–2.98) A	0.79 \pm 0.09 (1.00–1.68) B a	0.29 \pm 0.07 (<0.10 ^b –0.57) b	0.26 \pm 0.11 (0.10–0.47) b	1.26
Fe	2072 \pm 21.7 (1846–2353) A	2244 \pm 26.8 (2008–2745) B	2194 \pm 51.0 (1965–2349)	2221 \pm 29.7 (2164–2264)	2195
Hg	0.28 \pm 0.02 (0.14–0.45) A	0.52 \pm 0.04 (0.30–1.06) B a	0.83 \pm 0.06 (0.59–1.06) b	0.59 \pm 0.11 (0.43–0.81) a	0.76
Mg	335 \pm 2.78 (303–367) A	303 \pm 3.64 (262–358) B	309 \pm 5.31 (286–332)	311 \pm 10.3 (297–331)	289
Se	18.5 \pm 2.02 (7.86–43.9) A	41.3 \pm 3.32 (18.2–85.0) B a	12.6 \pm 1.08 (6.09–14.9) b	71.2 \pm 13.6 (55.1–98.2) c	15.9
Zn	27.2 \pm 0.68 (23.3–34.8) A	19.8 \pm 0.78 (14.7–26.7) B a	15.1 \pm 0.35 (13.8–16.6) b	14.9 \pm 0.38 (14.3–15.6) b	18.0
V	0.47 \pm 0.04 (0.23–1.06)	0.43 \pm 0.08 (0.10–1.63) a	0.16 \pm 0.01 (0.09–0.21) b	0.16 \pm 0.02 (0.12–0.18) b	0.18
Mo	0.22 \pm 0.01 (<0.21–0.30) A	0.32 \pm 0.03 (<0.21–0.62) B	<0.21–0.24 ^c	0.21 \pm 0.05 (<0.21–0.28)	2.02
Al	<5.4	10.2 \pm 0.72 (6.05–17.5)	10.7 \pm 0.66 (6.65–13.0)	14.2 \pm 1.13 (12.3–16.2)	11.8
Ba	<0.11–0.17 ^c	0.30 \pm 0.02 (0.18–0.51)	0.30 \pm 0.01 (0.25–0.35)	0.38 \pm 0.02 (0.35–0.42)	0.33
Be	<0.05	<0.05–0.09 ^c	<0.05–0.06 ^c	0.07 \pm 0.01 (0.06–0.10)	0.08
Pb	<0.05–0.38 ^c	0.17 \pm 0.04 (<0.05–0.96)	0.38 \pm 0.28 (<0.05–2.37)	0.07 \pm 0.02 (0.05–0.11)	<0.05
Mn	<0.21	<0.21–0.37 ^c	<0.21	0.15 \pm 0.03 (0.11–0.21)	<0.21
Sr	<0.54	<0.54–0.56 ^c	<0.54–0.67 ^c	<0.54	<0.54

^a Uppercase letters (A, B) following data for Steller's eiders at Izembek Lagoon and Dutch Harbor indicate that means are significantly different (*P* values: As, Cu, Fe, Hg, Mg, Se, Zn < 0.0001; B = 0.0011; Mo = 0.0067; Cr = 0.0189). Lowercase letters (a, b, c) following data for Steller's eiders, harlequin ducks, and black scoters at Dutch Harbor signify species differences. Trace elements without lowercase letters in common have significantly different means (*P* values: Se, Zn < 0.0001; V = 0.0002; Cu = 0.0005; Hg = 0.0030).

^b Values preceded by less than symbol (<) are below the minimum detection limit.

^c Mean and SE not calculated because less than 50% of samples were above the minimum detection limit.

Table 2. Trace elements in whole blood of Steller's eiders *Polysticta stelleri* (STEI) from Izembek Lagoon and Steller's eiders, harlequin ducks *Histrionicus histrionicus* (HADU), black scoters *Melanitta nigra* (BLSC), and a long-tailed duck *Clangula hyemalis* (LTDU) from Dutch Harbor, Alaska, 2001. Values are presented in micrograms per gram, wet weight (standard error [SE]; minimum–maximum [min.–max.]).

Element	Izembek Lagoon (molting), mean \pm SE (min.–max.)	Dutch Harbor (wintering), mean \pm SE (min.–max.)			
	STEI (n=20)	STEI (n = 23)	HADU (n = 8)	BLSC (n = 3)	LTDU (n = 1)
As	0.23 \pm 0.01 (0.12–0.35)	0.56 \pm 0.05 (0.18–1.30)	0.60 \pm 0.07 (0.31–0.86)	0.55 \pm 0.25 (0.24–1.04)	0.29
B	0.53 \pm 0.06 (0.17–1.34)	0.87 \pm 0.04 (0.62–1.50)	0.86 \pm 0.04 (0.66–1.03)	1.13 \pm 0.16 (0.87–1.43)	1.14
Cr	0.42 \pm 0.01 (0.33–0.48)	0.47 \pm 0.02 (0.30–0.68)	0.43 \pm 0.01 (0.37–0.47)	0.42 \pm 0.03 (0.37–0.46)	0.44
Cu	0.51 \pm 0.02 (0.34–0.64)	0.20 \pm 0.02 (0.02–0.46)	0.07 \pm 0.02 (<0.02 ^a –0.13)	0.06 \pm 0.02 (0.02–0.10)	0.30
Fe	460 \pm 9.62 (361–525)	569 \pm 10.3 (520–758)	550 \pm 24.5 (428–610)	527 \pm 15.2 (498–550)	529
Hg	0.06 \pm 0.005 (0.03–0.10)	0.13 \pm 0.01 (0.07–0.26)	0.21 \pm 0.02 (0.13–0.26)	0.14 \pm 0.02 (0.10–0.18)	0.18
Mg	74.3 \pm 1.43 (57.4–83.8)	76.7 \pm 1.38 (67.9–98.9)	77.1 \pm 1.64 (71.0–83.7)	73.6 \pm 0.83 (72.1–74.9)	69.5
Se	4.12 \pm 0.44 (1.68–9.04)	10.4 \pm 0.81 (4.35–19.7)	3.18 \pm 0.31 (1.30–4.01)	17.0 \pm 3.51 (12.3–23.9)	3.83
Zn	6.00 \pm 0.14 (4.93–7.76)	5.00 \pm 0.20 (3.64–6.84)	3.79 \pm 0.16 (3.09–4.49)	3.54 \pm 0.15 (3.33–3.83)	4.33
V	0.10 \pm 0.009 (0.05–0.24)	0.11 \pm 0.02 (0.02–0.40)	0.04 \pm 0.004 (0.02–0.05)	0.04 \pm 0.004 (0.03–0.04)	0.04
Mo	0.05 \pm 0.004 (<0.05–0.07)	0.08 \pm 0.007 (<0.05–0.15)	<0.05–0.06 ^b	0.05 \pm 0.01 (<0.05–0.07)	0.49
Al	<1.30	2.59 \pm 0.19 (1.62–4.79)	2.69 \pm 0.19 (1.56–3.32)	3.38 \pm 0.35 (2.73–3.95)	2.84
Ba	<0.03–0.035 ^b	0.08 \pm 0.004 (0.05–0.12)	0.08 \pm 0.004 (0.06–0.09)	0.09 \pm 0.006 (0.08–0.10)	0.08
Be	<0.01	<0.01–0.022 ^b	<0.01–0.017 ^b	0.017 \pm 0.004 (0.01–0.02)	0.02
Pb	<0.01–0.08 ^b	0.04 \pm 0.009 (<0.01–0.23)	0.09 \pm 0.07 (<0.01–0.56)	0.017 \pm 0.004 (0.01–0.02)	<0.01
Mn	<0.05	<0.05–0.054 ^b	<0.05	<0.05–0.052 ^b	<0.05
Sr	<0.13	<0.13–0.15 ^b	<0.13–0.14 ^b	<0.13	<0.13

^a Values preceded by less than symbol (<) are below the minimum detection limit.

^b Mean and SE not calculated because less than 50% of samples were above the minimum detection limit.

and 56% of samples from Izembek Lagoon and Dutch Harbor, respectively. We did not detect Cd and Ni in any blood samples from Steller's eiders at either location.

Sea ducks, Dutch Harbor

Concentrations of Cu, Hg, Se, Zn, and V differed significantly among sea duck species at Dutch Harbor. Trace elements had the following patterns: Cu, Zn, and V: Steller's eiders greater than (harlequin ducks = black scoters); Hg: harlequin ducks greater than (Steller's eiders = black scoters); and Se: black scoters greater than Steller's eiders greater than harlequin ducks (Table 1). There were no differences among species for Al, As, B, Cr, Fe, Mg, Ba, and Pb; however, blood Pb concentrations in one Steller's eider and one harlequin duck (0.96 and 2.37 $\mu\text{g/g dw}$, respectively, or 0.23 and 0.56 $\mu\text{g/g ww}$) were greater than the normal background concentration of less than 0.2 $\mu\text{g/g ww}$ (Franson and Pain 2011). Strontium, Be, Mo, and Mn were not detected in enough samples to compare concentrations among species. Lead, Mn, and Sr were not detected in the long-tailed duck. Cadmium and Ni were not detected in any blood samples.

Discussion

Steller's eiders, Dutch Harbor and Izembek Lagoon

Several factors could be responsible for greater concentrations of As, B, Fe, Hg, Se, and Mo in blood of Steller's eiders wintering at Dutch Harbor compared with those molting at Izembek Lagoon. One factor is potential contamination of anthropogenic origin from municipal sewage, seafood processing wastewater, and stormwater runoff. Meador et al. (1998) analyzed sediment samples from Dutch Harbor and 10 other coastal Alaska sites for several trace elements reporting that, among the 11 sites, Dutch Harbor ranked in the top 5 sites for As, Cu, Hg, and Se. Of those four elements in our study, concentrations of As, Hg, and Se in Steller's eiders were greater at Dutch Harbor than at Izembek Lagoon. Another contributor could be differences in food habits between eiders at Dutch Harbor and Izembek Lagoon, because trace metal accumulations in aquatic invertebrates vary with the invertebrate group and species, as well as with relative bioavailabilities of the metals in water and diet (Rainbow and Luoma 2011). Furthermore, a more plentiful supply of invertebrates may be available at Dutch Harbor because of eutrophication (Reed and Flint 2007; Hollmén et al. 2011). Izembek Lagoon has extensive eelgrass *Zostera marina* meadows, and Steller's eiders molting there may feed on a more diverse range of invertebrates that are associated with eelgrass, including gastropods, bivalves such as *Macoma* sp., polychaetes, and crustaceans, compared with Dutch Harbor (Ward and Amundson 2019; Fredrickson 2020). Less is known about food habits of Steller's eiders at Dutch Harbor, but those wintering on Izembek Lagoon consumed more shell-free foods, such as crustaceans

and polychaetes, than food items with shells (Metzner 1993). The fact that we found greater concentrations of Cr, Cu, Mg, and Zn in blood of Steller's eiders at Izembek Lagoon than at Dutch Harbor is not attributable to contamination, because the anthropogenic inputs known at Dutch Harbor do not exist at Izembek Lagoon. These differences may be the result of varying concentrations in food items between the two locations, temporal variation, or a combination of temporal and life-cycle stage (molting vs. wintering) differences.

Selenium in Steller's eiders. In addition to the potential effects of anthropogenic inputs and food habits mentioned above, temporal changes may play a role in differences in trace element concentrations, particularly for Se, which was twice as high in Steller's eiders at Dutch Harbor than at Izembek Lagoon. Most Steller's eiders molting at Izembek Lagoon were probably recent arrivals from nesting areas in Siberia. Selenium concentrations decline in blood and tissues of spectacled eiders *Somateria fischeri*, common eiders *Somateria mollissima*, and other waterfowl after departure from wintering areas and with increasing time on inland breeding habitats (Franson et al. 2002; Grand et al. 2002; Wilson et al. 2004; Lovvorn et al. 2013). Thus, Steller's eiders sampled at Izembek Lagoon would have had less time to accumulate Se from the marine environment than those at Dutch Harbor. In an experimental study, when common eiders were fed 20 ppm Se it took approximately 60 d for concentrations of Se in blood to reach the maximum level (Franson et al. 2007).

Interpretive data for Se concentrations linked to adverse effects in freshwater and terrestrial birds have been summarized by Ohlendorf and Heinz (2011), with the caveat that concentrations in apparently normal individuals of some marine species may be considerably greater. Experimental and field studies have indicated that common eiders and perhaps other sea ducks have higher tissue thresholds for adverse effects of Se than do freshwater birds (Franson 2015). Although common eiders fed added Se in an experimental study showed responses similar to experimental mallards *Anas platyrhynchos*, the common eiders accumulated greater concentrations of Se in liver tissue, but not in blood (O'Toole and Raisbeck 1997; Franson et al. 2007). In the current study, Se concentrations in blood of Steller's eiders were within the range or less than levels reported in common eiders, king eiders *Somateria spectabilis*, and spectacled eiders sampled elsewhere in Alaska, Canada, the Baltic Sea, and Svalbard, but considerably greater than in Steller's eiders nesting in northern Alaska (Franson 2015; Fenstad et al. 2017; Miller et al. 2019). The mean blood Se concentration (41.3 $\mu\text{g/g dw}$ or 10.4 $\mu\text{g/g ww}$) in Steller's eiders from Dutch Harbor was similar to that of experimental common eiders fed 20 ppm Se, resulting in few Se-related lesions and no weight loss compared with controls (Franson et al. 2007).

Mercury in Steller's eiders. Although tissue concentrations of Hg associated with adverse effects have been



described for nonmarine birds (Shore et al. 2011), limited information is available about such relationships, specifically in sea ducks. However, birds living in saltwater habitats typically accumulate greater Hg concentrations than do birds living in freshwater and terrestrial environments, and such species have been used for years to monitor Hg in the environment (Provencher et al. 2014; Ackerman et al. 2016). Ackerman et al. (2016) proposed a blood-equivalent Hg concentration of 0.2 $\mu\text{g/g ww}$ as an upper threshold for background level exposure. The highest Hg concentration in blood of Steller's eiders from Dutch Harbor was 0.26 $\mu\text{g/g ww}$, but the mean concentration (0.13 $\mu\text{g/g ww}$) was well below 0.2 $\mu\text{g/g ww}$ (Table 2). The Hg concentrations that we found in blood of Steller's eiders were lower than those reported in Steller's eiders elsewhere in Alaska (Miller et al. 2019), in king eiders and spectacled eiders in Alaska (Franson 2015), and in common eiders from the Baltic Sea and Svalbard (Fenstad et al. 2017) as well as the east coast of the United States (Meatley et al. 2014).

Copper and Zn in Steller's eiders. Little information is available on concentrations of Cu in blood of sea ducks associated with adverse effects; however, high Cu concentrations have been reported in livers, along with much lower levels in kidney tissue of sea ducks, particularly eiders (Franson 2015). Steller's eiders at Izembek Lagoon had similar blood Cu concentrations to those found in nesting Steller's and common eiders in northern Alaska, but Steller's eiders at Dutch Harbor had approximately one-half that concentration (Franson et al. 2004; Miller et al. 2019). Zinc poisoning has been reported from several species of wild waterfowl from a Zn and Pb mining area (Franson 2015). Among sea ducks, captive king eiders, common mergansers *Mergus merganser*, and Barrow's goldeneyes *Bucephala islandica* have been reported poisoned by Zn from the ingestion of pennies (Zdziarski et al. 1994; Culver 2007). In an experimental study, game farm mallards dosed with Zn shot exhibited signs of toxicosis by 15 d postexposure (Levengood et al. 1999). Zinc was not measured in whole blood in that study, but from concentrations reported in plasma and erythrocytes, we estimate that the mean concentration of Zn in whole blood (males and females combined) was approximately 40 $\mu\text{g/g ww}$. That equates to approximately 160 $\mu\text{g/g dw}$, or 6–8 times greater than Zn concentrations in blood of Steller's eiders in our study.

Lead in Steller's eiders. In Anseriformes, blood Pb concentrations of 20–50 $\mu\text{g/dL}$ (~ 0.2 – $0.5 \mu\text{g/g ww}$) are typically considered background concentrations, and concentrations of 0.5–1.0 $\mu\text{g/g ww}$ and greater are interpreted as evidence of elevated exposure or poisoning (Franson and Pain 2011). For example, a spectacled eider in Alaska diagnosed with Pb poisoning had a blood Pb concentration of 8.5 ppm ww (Franson 2015). Brown et al. (2006) reported that 43% of wintering Steller's eiders at Kodiak Island, Alaska, had blood Pb less than 0.14 $\mu\text{g/g ww}$, 50% had 0.15–2.0 $\mu\text{g/g ww}$, and 6.7% had

greater than 2.0 $\mu\text{g/g ww}$. In our study, 98% of Steller's eiders had blood Pb less than 0.14 $\mu\text{g/g ww}$. Although we detected Pb in 95.6% of Steller's eiders at Dutch Harbor vs. 30.0% at Izembek Lagoon, only one Steller's eider (from Dutch Harbor) had a blood Pb concentration (0.23 $\mu\text{g/g ww}$) above the background level. Miller et al. (2019) reported a mean blood Pb concentration in nesting Steller's eiders of 0.065 $\mu\text{g/g ww}$, approximately 50% greater than the mean that we found in Steller's eiders wintering at Dutch Harbor.

Interspecific variation in trace elements, Dutch Harbor

Although the reason(s) for the differences that we found in concentrations of Cu, Hg, Se, Zn, and V in blood among species of sea ducks at Dutch Harbor are largely unknown, there may be several influences involved. Little is known about food habits of Steller's eider, harlequin duck, black scoter, and long-tailed duck wintering at Dutch Harbor, and even if trace element exposures were very similar, levels in blood may vary among species. Although all four sea duck species consume mostly invertebrate prey, there are differences among them with regard to specific foods and diversity of diets. Generally, wintering black scoters feed heavily on mollusks and crustaceans (Bordage and Savard 2020); harlequin ducks feed on crustaceans, gastropods, and mollusks (Robertson and Goudie 2020); Steller's eiders forage on diverse invertebrate taxa (Fredrickson 2020); and long-tailed ducks feed on a wide variety of prey including crustaceans, snails, mollusks, and fish (Robertson and Savard 2020). Thus, differing accumulations of trace elements among prey items, and among different size classes of bivalves, may influence the concentrations of specific elements ingested (Riget et al. 1996; Rainbow and Luoma 2011). Savoy et al. (2017) reported a correlation between blood Hg in harlequin ducks and Hg in blue mussels *Mytilus edulis* and that concentrations differed among bays surrounding Unalaska Island, indicating local variation as another factor in the differences that we found among trace element concentrations in sea ducks. Body size may be another source of interspecific variation in blood concentrations of several trace elements among sea ducks, as observed on breeding grounds by Miller et al. (2019).

Interspecific variation in trace elements, North America

Comparison of studies elsewhere in Alaska and in Canada indicates variation in trace element exposure among and within species according to seasonal and life-cycle changes. Heard et al. (2008) sampled wintering harlequin ducks in March in Prince William Sound, Alaska, measuring the same trace elements that we did. Of 13 trace elements with enough detectable values to calculate a mean, 5 (As, Fe, Zn, V, and Mo) had similar concentrations, 4 (Cu, Hg, Mg, and Se) had lower concentrations in Dutch Harbor than in Prince William



Sound, and 4 (B, Cr, Al, and Pb) had greater concentrations at Dutch Harbor (Heard et al. 2008).

Interspecific variation, Se. A wide range of Se concentrations in tissues has been reported in studies of sea ducks (Franson 2015). We found that blood Se concentrations exhibited high variability among species, ranging from a mean of 12.6 $\mu\text{g/g dw}$ (3.18 $\mu\text{g/g ww}$) in harlequin ducks to 71.2 $\mu\text{g/g dw}$ (17.0 $\mu\text{g/g ww}$) in black scoters, one of the highest concentrations reported in sea ducks (Franson 2015). By contrast, Wayland et al. (2008) reported 3.9 $\mu\text{g/g ww}$ Se in blood of nesting white-winged scoters *Melanitta fusca* in Canada. Comparison of these data indicates that scoters, and other sea ducks, accumulate Se on wintering areas, with a subsequent decrease on breeding grounds. In keeping with the idea that blood Se concentrations acquired in marine environments decline during and after arrival on breeding grounds, the mean concentration (41.3 $\mu\text{g/g dw}$ or 10.4 $\mu\text{g/g ww}$) that we found in wintering Steller's eiders was more than 10 times greater than that found (0.78 $\mu\text{g/g fresh mass}$) in nesting Steller's eiders (Miller et al. 2019). Despite this relatively high Se exposure, we observed no evidence of negative effects in wintering Steller's eiders. Blood Se in harlequin ducks at Dutch Harbor was less than the mean of 5.5 ppm ww reported by Heard et al. (2008) in harlequin ducks wintering in Prince William Sound.

Interspecific variation, Hg. A comparison of our Hg results in harlequin ducks with those of Savoy et al. (2017) supports the contention that Hg exposure varies at multiple scales (regional and local). Thus, the mean blood Hg concentration of 0.83 $\mu\text{g/g dw}$ (0.21 $\mu\text{g/g ww}$) that we found in harlequin ducks was similar to that reported from three other bays on Unalaska Island (Savoy et al. 2017). However, in harlequin ducks on a fourth bay, Savoy et al. (2017) found a maximum of 0.92 $\mu\text{g/g ww}$ Hg. The fact that the blood Hg concentrations that we found in harlequin ducks were most similar to those found in undeveloped bays on the north side of Unalaska Island indicates little anthropogenic input. The mean Hg concentration (0.21 $\mu\text{g/g ww}$) that we found in harlequin ducks was slightly greater than the proposed upper threshold (0.2 $\mu\text{g/g ww}$) for background level exposure (Ackerman et al. 2016) and considerably higher than the mean of 0.04 $\mu\text{g/g ww}$ found in harlequin ducks on Kodiak Island (Savoy et al. 2017). Mercury concentrations in blood of Steller's eiders wintering at Dutch Harbor were generally similar to or less than the means reported in nesting spectacled eiders, common eiders, and king eiders from elsewhere in Alaska, Maine, Canada, and Finland, but were one-half the concentration found in Steller's eiders nesting in northern Alaska (Franson 2015; Miller et al. 2019). The mean Hg concentration that we found in blood of black scoters was similar to the mean (0.19 $\mu\text{g/g ww}$) found in nesting white-winged scoters in Saskatchewan, Canada (Wayland et al. 2008).

High interspecific variation among trace elements. We found a lack of clear patterns among species for Cu, Zn, V, and Pb. The Cu level in blood of wintering Steller's eiders was more than twice as high as in harlequin ducks and black scoters, but approximately one-half that reported in nesting Steller's eiders and common eiders in northern Alaska (Franson et al. 2004; Miller et al. 2019). In harlequin ducks at Dutch Harbor, we found a lower blood Cu concentration than that reported for harlequin ducks (0.82 $\mu\text{g/g ww}$) in Prince William Sound (Heard et al. 2008). Concentrations of Zn and V in blood of Steller's eiders were greater than concentrations in harlequin ducks and black scoters. In Steller's eiders, levels of Zn were somewhat lower and levels of V somewhat greater than those in nesting common eiders (26.2 and 0.31 $\mu\text{g/g dw}$, respectively; Franson et al. 2004). One harlequin duck and one Steller's eider from Dutch Harbor had blood Pb concentrations (0.56 and 0.23 $\mu\text{g/g ww}$, respectively) indicative of elevated exposure, but all other samples were within the normal background range or not detected at all (Franson and Pain 2011). All three black scoters at Dutch Harbor had less than 0.14 $\mu\text{g/g ww}$ blood Pb. In black scoters nesting at Aropuk Lake and wintering at Nelson Lagoon, Alaska, Brown et al. (2006) reported that 85% had less than 0.14 $\mu\text{g/g ww}$ and 15% had 0.15–2.0 $\mu\text{g/g ww}$ blood Pb.

Conclusions

With the exception of Pb and Hg, limited information is available for toxicity thresholds of trace elements in the blood of birds in general and sea ducks in particular (Franson and Pain 2011; Ackerman et al. 2016). We found evidence of greater exposure to several trace elements in Steller's eiders at Dutch Harbor than at Izembek Lagoon. In general, we have no reason to suspect that the concentrations that we found might be associated with adverse effects. However, at Dutch Harbor, the mean concentration of Hg in blood of harlequin ducks (0.21 $\mu\text{g/g ww}$) was slightly above a published threshold effect level (0.2 $\mu\text{g/g ww}$) and one Steller's eider and one harlequin duck had blood Pb concentrations greater than 0.2 $\mu\text{g/g ww}$. Additional studies of trace element exposure in sea ducks at Dutch Harbor and the Alaska Peninsula would be beneficial to evaluate potential trends 20 y after this baseline study. Because concentrations of trace elements in blood tend to reflect recent and local exposure, a better understanding of where and when sea ducks acquire trace metals, as well as variation among species, would be gained by sampling at life-cycle stages that include breeding locations, as well as molting and wintering locations. It would be useful if such investigations included measurement of biomarkers associated with trace element exposure to evaluate potential effects on the health of sea ducks (Wayland et al. 2003). Determination of trace elements in sea duck foods, and correlation with levels in the blood, may elucidate point sources of exposure related to environmental contamination.



Supplemental Material

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Data S1. Microsoft Excel file of trace element data in whole blood collected in 2001 from Steller's eiders *Polysticta stelleri* at Izembek Lagoon and Steller's eiders, harlequin ducks *Histrionicus histrionicus*, black scoters *Melanitta nigra*, and a long-tailed duck *Clangula hyemalis* at Dutch Harbor, Alaska. Data include species, location, age, sex, percent moisture of blood sample, and trace element results in micrograms per gram, dry weight.

Available: <https://doi.org/10.3996/JFWM-21-065.S1> (18 KB XLSX)

Reference S1. [ADEC] Alaska Department of Environmental Conservation. 2008. Alaska's final 2008 integrated water quality monitoring and assessment report.

Available: <https://doi.org/10.3996/JFWM-21-065.S2> (1.744 MB PDF) and <https://dec.alaska.gov/media/16347/2008-final-integrated-report.pdf>

Reference S2. National Marine Fisheries Service. 2020. Fisheries of the United States 2018. Current fishery statistics no. 2018. Liddel M, Yencho M, editors. Silver Spring, Maryland: National Marine Fisheries Service.

Available: <https://doi.org/10.3996/JFWM-21-065.S3> (12.589 MB PDF) and https://media.fisheries.noaa.gov/dam-migration/fus_2018_report.pdf

Reference S3. [ESA] U.S. Endangered Species Act of 1973, as amended, Pub. L. No. 93-205, 87 Stat. 884 (Dec. 28, 1973).

Available: <https://doi.org/10.3996/JFWM-21-065.S4> (308 KB PDF) and <http://www.fws.gov/sites/default/files/documents/endangered-species-act-accessible.pdf>

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Available: <https://doi.org/10.3996/JFWM-21-065.S5> (510 KB PDF) and <https://pubs.usgs.gov/of/2019/1042/ofr20191042.pdf>

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