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DEPARTMENT OF THE INTERIOR
U.S. FISH AND WILDLIFE SERVICE
REGION 7

ENVIRONMENTAL CONTAMINANTS PROGRAM
ON-REFUGE INVESTIGATIONS SUB-ACTIVITY

FINAL REPORT

Assessment of Lead Sources for Waterfowl in Alaska

FFS No: 7N22

by

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Fairbanks Fish and Wildlife Field Office
Fairbanks, AK
Aug. 1, 2004

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Introduction

Exposure to detrimental concentrations of lead has been documented in waterfowl in Alaska. In spectacled eiders (*Somateria fischeri*) and long-tailed ducks (*Clangula hyemalis*), lead exposure has been demonstrated on the Yukon-Kuskokwim Delta (Y-K Delta) at levels that have negative population effects (Franson et al. 1995, Flint et al. 1997, Flint and Grand 1997, Flint and Herzog 1999). Additionally, Steller's eiders (*Polysticta stelleri*) breeding near Barrow on the North Slope showed high levels and rates of exposure (Trust et al. 1997; A. Matz, U.S. Fish and Wildlife Service, unpubl. data), and 11 percent of long-tailed ducks captured northeast of Teshukpuk Lake on the North Slope in 1980 had lead shot in their gizzards (Taylor 1986).

Breeding populations of Steller's and spectacled eiders in Alaska have declined dramatically and both are listed as threatened species. King eiders (*S. spectabilis*), common eiders (*S. mollissima*) and long-tailed ducks are listed as species of concern by the Alaska Natural Heritage Program. Common eider population trend information is sparse, but a migration study at Barrow suggests a large (50 percent) decline from 1976 to 1994.

The presumed source for avian exposure above background is ingestion of lead shot, which waterfowl consume either intentionally or accidentally while feeding in wetlands where hunting has occurred. Lead shot settles slowly, with some shot potentially available more than three years after deposition (Flint 1998; P. Flint, unpubl. data). Alternatively, birds could be exposed to "background" lead associated with naturally occurring sediment concentrations or dispersed sources such as emissions from combustion of automotive gasoline or industrial processing. While use of leaded gasoline has declined overall in the Northern Hemisphere since the 1970s, combustion of leaded gasoline from Europe and Asia is still the major source of atmospheric lead in the Arctic (Dietz et al. 1998, Barrie et al. 1997). Baseline lead levels in the Arctic are typically low, however, except near point sources such as smelters, mining sites, and military installations such as Distant Early Warning (DEW) sites (e.g., Braune et al. 1999).

Avian exposure to lead from shot can be determined using radiographs or dissection, if shot are present within the bird. However, lead isotope analysis can identify sources even when no lead shot are found. Ratios of lead isotopes (e.g., $^{206}Pb/^{207}Pb$) can distinguish between different environmental sources, such as gasoline, natural deposits, or lead shot (Scheuhammer and Templeton 1998, Gelinas and Schmit 1997, Blais 1996). This technique has been used to identify lead shot as the major source of exposure for loons, waterfowl, and eagles in Canada (Scheuhammer and Templeton 1998). Our study goals were to identify the isotopic signatures of potential sources of lead exposure for nesting eiders and long-tailed ducks on the Y-K Delta and along the North Slope, and to examine variation in lead isotopic signatures over a range of blood lead concentrations in the same species.

We were also interested in determining if the standard clinical blood lead threshold of 0.2 ppm (Friend 1985) was applicable to eiders and other waterfowl in Alaska, because nesting Y-K Delta spectacled eider blood lead concentrations did not have an expected specific breakpoint at 0.2 ppm between background concentrations and elevated concentrations. Lack of a definitive breakpoint suggested that the level above which eiders should be considered "poisoned" by or even "exposed" to lead above background was unclear, based on standard blood lead residue analyses. We therefore compared blood isotopic signatures to those from reference matrices (sediments and shot) to define blood concentrations indicative of exposure to lead shot.

Methods

Data Collection

We minimized costs by partnering with a variety of research projects to obtain eider blood from throughout Alaska. In the Y-K Delta, spectacled eider, common eider, and long-tailed duck blood samples were obtained at Hock Slough on the lower Kashunuk River (KR; 61°20' N, 165°35' W) and Kigigak Island (KI; 60°50' N, 165°50' W). The KR study area was described in detail by Grand et al. (1997). The KI study area consisted of nearly the entire island which closely resembled the High Graminoid and Intermediate Sedge Meadows characterized in Grand et al. (1997). Both of these locations were long-term spectacled eider study sites (> 10 years) and historical data on lead exposure and effects (Flint et al. 2000, Franson et al. 1998, Grand et al. 1998, Flint and Grand 1997, Flint et al. 1997, Franson et al. 1995) were available.

Although a goal of the study was to measure Lead and Lead isotopes in Steller's eiders breeding near Barrow (71°17' N, 156°47' W), the years of this study (2001-2004) were non-breeding years – a phenomenon that may be related to predator-prey interactions (Quakenbush and Suydam 1996). Consequently, no Steller's eider blood samples were collected. However, we obtained king eider blood samples from Teshukpuk Lake (70°28' N, 153°14' W) and the Kuparuk oilfield (70°20' N, 149°30' W) on the North Slope. The North Slope landscape is lowland tundra with continuous permafrost, characterized by low relief, numerous shallow ponds and lakes, drained lake basins, and ice-wedge polygonal terrain. The landscape is shaped by the permafrost-driven thaw lake cycle (Britton 1957), involving the coalescence of small thaw ponds into a larger lake, subsequent thaw of ice-rich permafrost beneath the lake, eventual lake drainage, and re-freezing of lake sediments accompanied by reformation of polygonal features.

Up to 2 ml (but no more than 1.5 percent of body weight) blood was drawn from the brachial or jugular vein using sterile techniques, transferred immediately to sterile tubes with sodium or lithium heparin additive and refrigerated or placed in permafrost pits. Blood tubes were labeled with a unique identifier (U.S. Fish and Wildlife Service band number). Frozen samples were stored at the Fairbanks Fish and Wildlife office laboratory and shipped overnight on dry ice to the analytical facility. Additional data, referenced by the unique identifier, included species, sex, age, weight, and capture area, and specific location (lat/long or UTM).

Sediment reference samples were collected from sites with a minimum of organic material within waterfowl nesting ponds in the Y-K Delta and Barrow on the North Slope. The top five centimeters of sediment were collected with acid-washed polyethylene scoops into acid-washed polyethylene jars, stored refrigerated, and transferred to the analytical laboratory within two weeks. Samples were labeled using permanent ink with the date, time, general and specific location (lat/long or UTM) and collector's initials. We also analyzed sediment grab samples collected from the Bering Sea at the wintering location of spectacled eiders (62°30' N, 173°0' W) by the St. Lawrence Island Polynya Project and provided to us by J. Grebmeier at the University of Tennesse Knoxville. Lead shot references samples were obtained in Bethel and Barrow through purchase or confiscation by law enforcement officers during the last five years. All samples were analyzed for total lead and lead isotopes using thermal ionization mass spectrometry (TI-MS), after deproteinisation in an acid solution. Data were presented as isotope ratios of the lead isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. Analyses were performed at the U.S. Geological Survey's Central Mineral Resources Team laboratory in Denver, CO.

Data Analysis

We graphically compared lead isotope signatures from sediment, shot, and blood. We then developed a discriminant function classification criterion for the stable isotope signatures based on the reference samples of shot and sediment and applied the classification criterion to the blood samples. We ran a logistic regression using total blood lead concentrations as the independent variable and the discriminant function's classification of blood as "shot" or "sediment" as the categorical dependent variable, with bootstrap randomization procedures to examine probabilistic thresholds for lead exposure according to isotopic signature.

Results and Discussion

We analyzed lead isotopes in twenty-six shot samples of various sizes, loads, and manufacturers; three, five, and five duplicate sediment samples from Kigigak Island, Hock Slough, and near Barrow, respectively; and eight duplicate sediment samples from the Bering Sea. Sediment lead isotope patterns were distinct from those of shot (Fig. 1).

We analyzed 67 spectacled eider, common eider, king eider, and long-tailed duck blood samples from Hock Slough, 80 from Kigigak Island, and 24 king eider blood samples from the North Slope. For all species combined, blood samples with high concentrations of total lead (> 0.2 ppm) had isotope patterns similar to shot, while blood samples with low concentrations of total Lead (< 0.02 ppm) had isotope patterns similar to sediments (Fig. 2). Blood samples with intermediate total lead concentrations spanned the isotopic gradient between sediments and shot (Fig. 2).

Three of the seven isotope ratios showed clear separation between lead shot and sediments (Fig. 3), so these were used for the discriminant function classification. In the discriminant function analysis, there was complete separation of the isotopic signatures of sediments and shot.

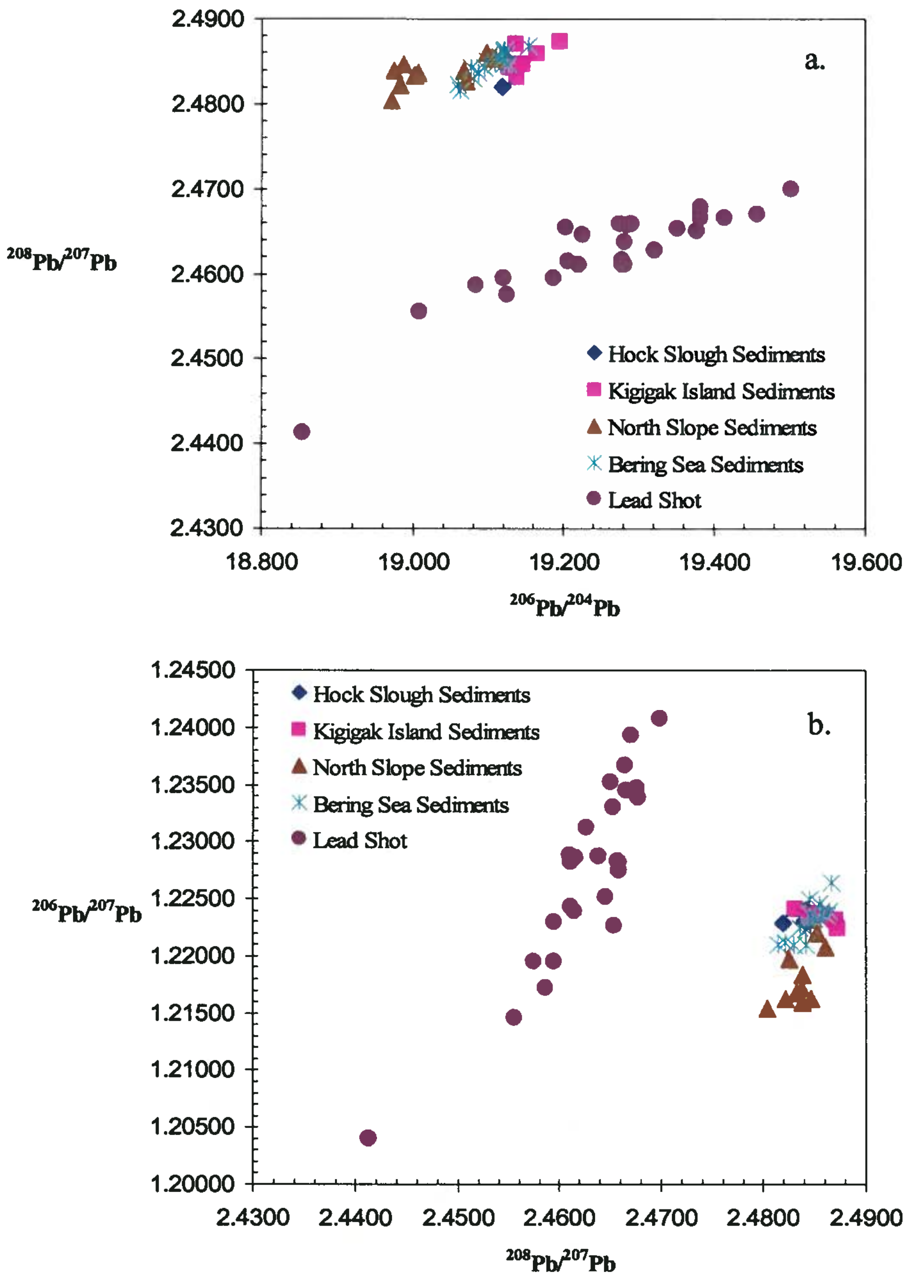

Fig. 1. Lead isotope ratios in lead shot and sediments collected from the Yukon-Kuskokwim Delta, the North Slope of Alaska, and the Bering Sea. Isotope signatures of shot are distinctly different from those of sediments.

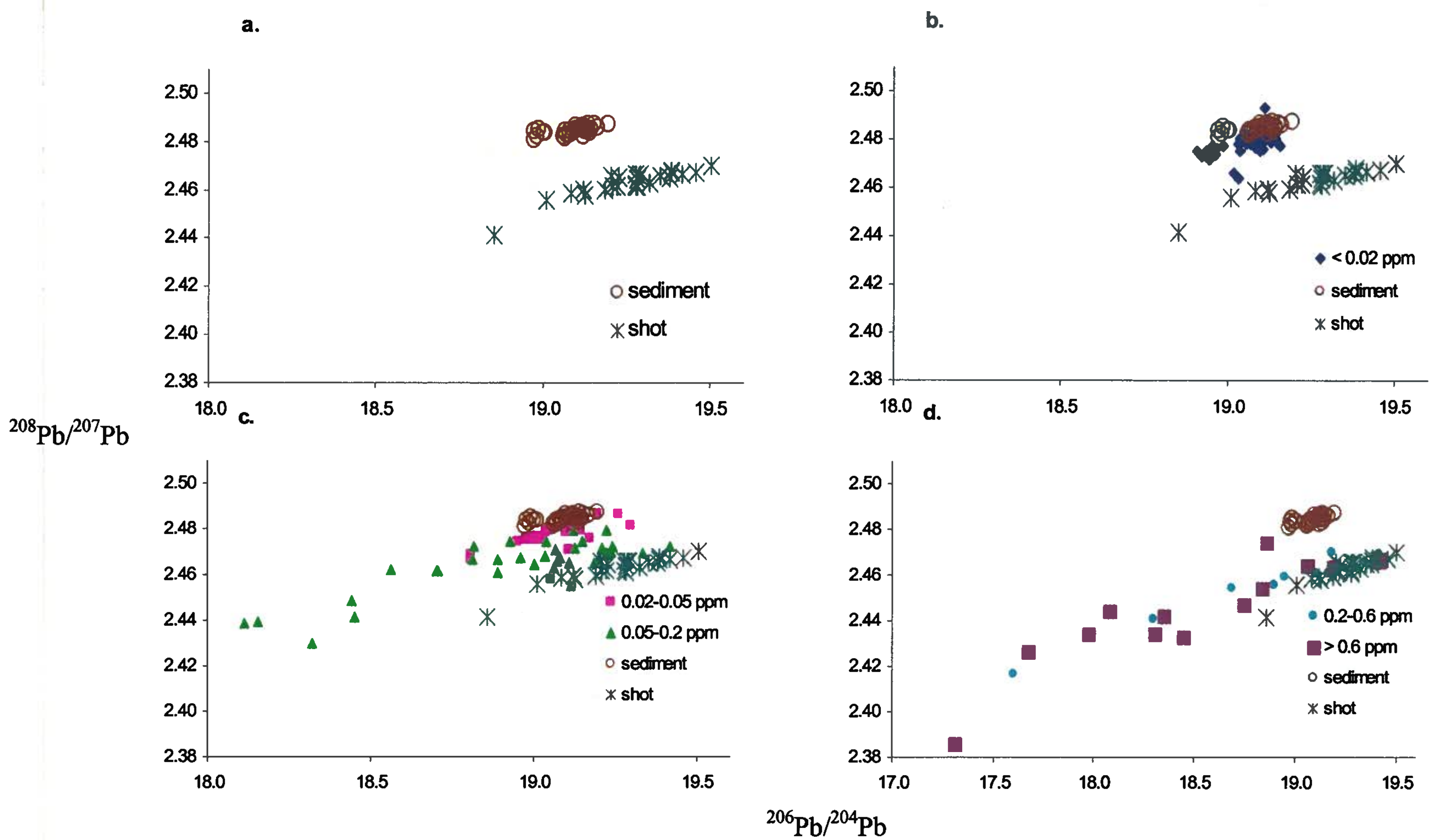

Fig. 2. Lead isotope (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) ratios in lead shot and sediments (a) collected from the Yukon-Kuskokwim Delta, the Bering Sea, and the North Slope of Alaska, compared to lead isotope ratios in spectacled, common, and king eider and long-tailed duck whole blood, grouped by total blood lead concentrations. Low blood lead concentrations (<0.02 ppm) matched sediment signatures (b); median blood lead concentrations (0.02 – 0.2 ppm) had signatures intermediate between sediments and lead shot (c); and greatest blood lead concentrations (> 0.2 ppm) matched the signature from lead shot (d – note the longer x-axis).

PCL XL error

Subsystem: KERNEL

Error: IllegalTag

Operator: 0x1b

Position: 25068

CWA ESA MOA Oversight Panel Meeting
October 6, 2004
9:00-11:00 a.m.
NOAA Bldg. SSMC3
Silver Spring, Room 1311-B

Draft Agenda

Directions to NOAA, Silver Spring

To get to our building from the Metro:
Take the Redline to Silver Spring. Exit the station (the east side of Colesville Road), and take a left once out of the station. Go under the Metro Bridge, stay left and go through the little courtyard towards East-West Highway. Take a left and head up the street (east on East West Highway). Continue east past the big hand sculpture in front of NOAA Bldg. SSMC3--just a few doors down from the hand, you will see our meeting room 1311-B (next to the dentist's office).

Driving from Areas West of Silver Spring:
Take the Capital Beltway Exit 31-B at MD 97 South (Georgia Ave)
Turn right on 16th Street (1.0 mi). Turn left on East-West Highway. Turn left into second entrance to NOAA/Public Parking garage (0.4 mi)

Driving from DC (Herbert C. Hoover Bldg.):
Head North on 14th St. NW. Turn left onto U St. NW (0.1 mi). Turn Right onto 16th St. NW (5.2 mi). Turn slight right onto Colesville Road (0.2 mi). Turn right onto East-West Highway. Turn left into the second entrance to NOAA/Public Parking garage (0.1 mi).

Draft Agenda -

1) **Update on the National Consultation**

   - Status of Methods Manual
   - Status of Batch 1 BE analysis
   - Comparison of literature search strategies

2) **National Consultation Batch 2 Pollutants**

   - Status of Batch 2 data call for nickel, cadmium, lead, arsenic, silver, and zinc
   - Update on proposed Batch 3 pollutants: TBT, nonylphenol, atrazine, and diazinon, specifically whether EPA wants to proceed with atrazine and diazinon in this batch. The copper BLM could be consulted on a separate but parallel track with Batch 3.

- Discussion of the need to form a workgroup to determine how to approach the consultation on the BLM.

3) **Planning future batches of pollutants for the national consultation**

   - Status of EPA's white paper outlining a risk-based process for identifying future batches of pollutants for consultation.

4) **National Consultation Biological Opinion methodology update**

   - Services met for two days September 28 and 29 to discuss BO methodology. Services share highlights of discussion and next steps.

5) **Research and Data Gathering Plan**

   - Discussion of workgroup "straw-plan" for research and data gathering. Next steps.

6) **MOA Training Update**

   - Next training and regional meeting in Seattle, October 20 and 21, NOAA Sand Point

7) **Update on EPA's Antidegradation Policy and ESA Consultation Memo**

8) **Communication Strategy for Outreach to Services and EPA Staff on MOA-Related Efforts**

   - What might be included
   - How to develop and implement

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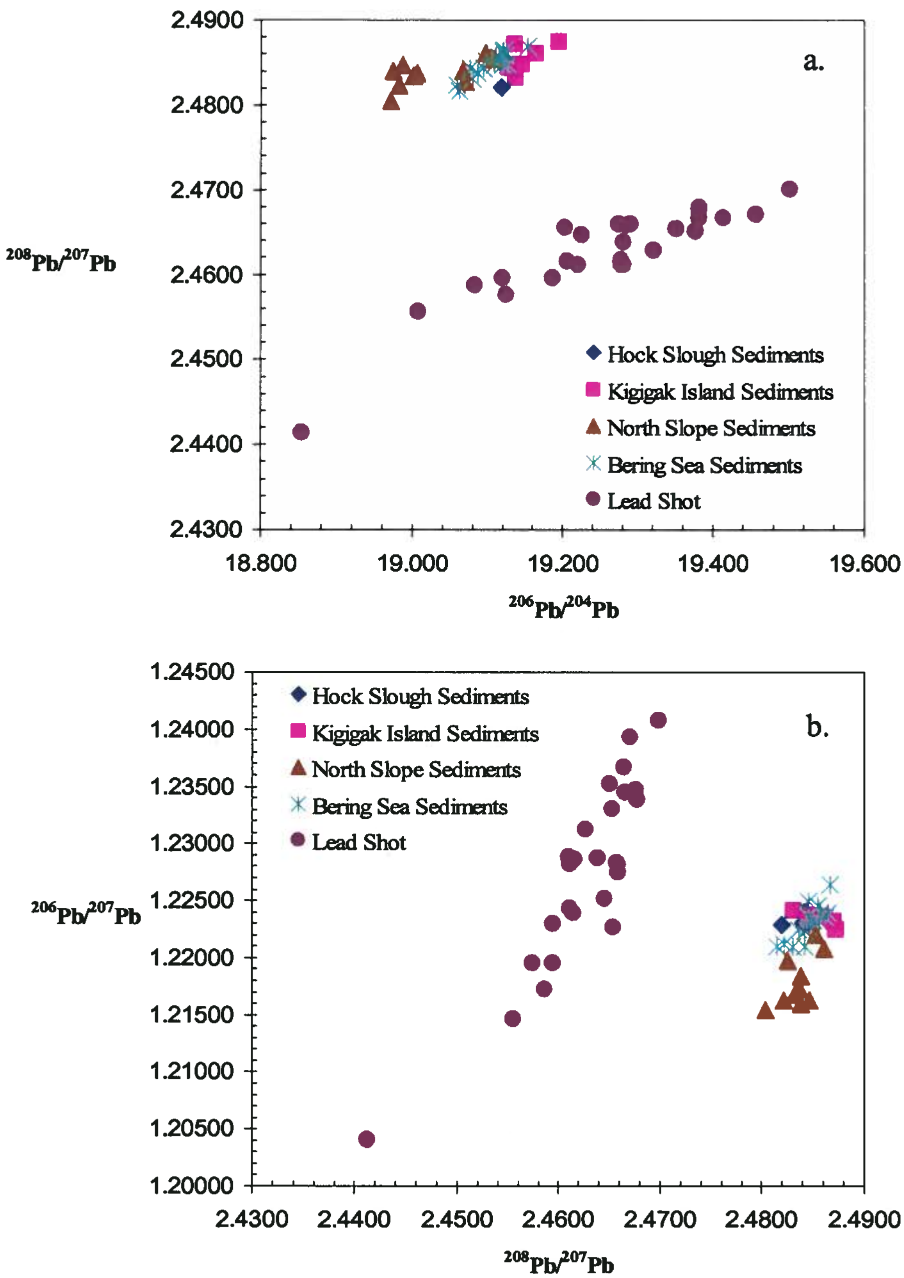

Fig. 1. Lead isotope ratios in lead shot and sediments collected from the Yukon-Kuskokwim Delta, the North Slope of Alaska, and the Bering Sea. Isotope signatures of shot are distinctly different from those of sediments.

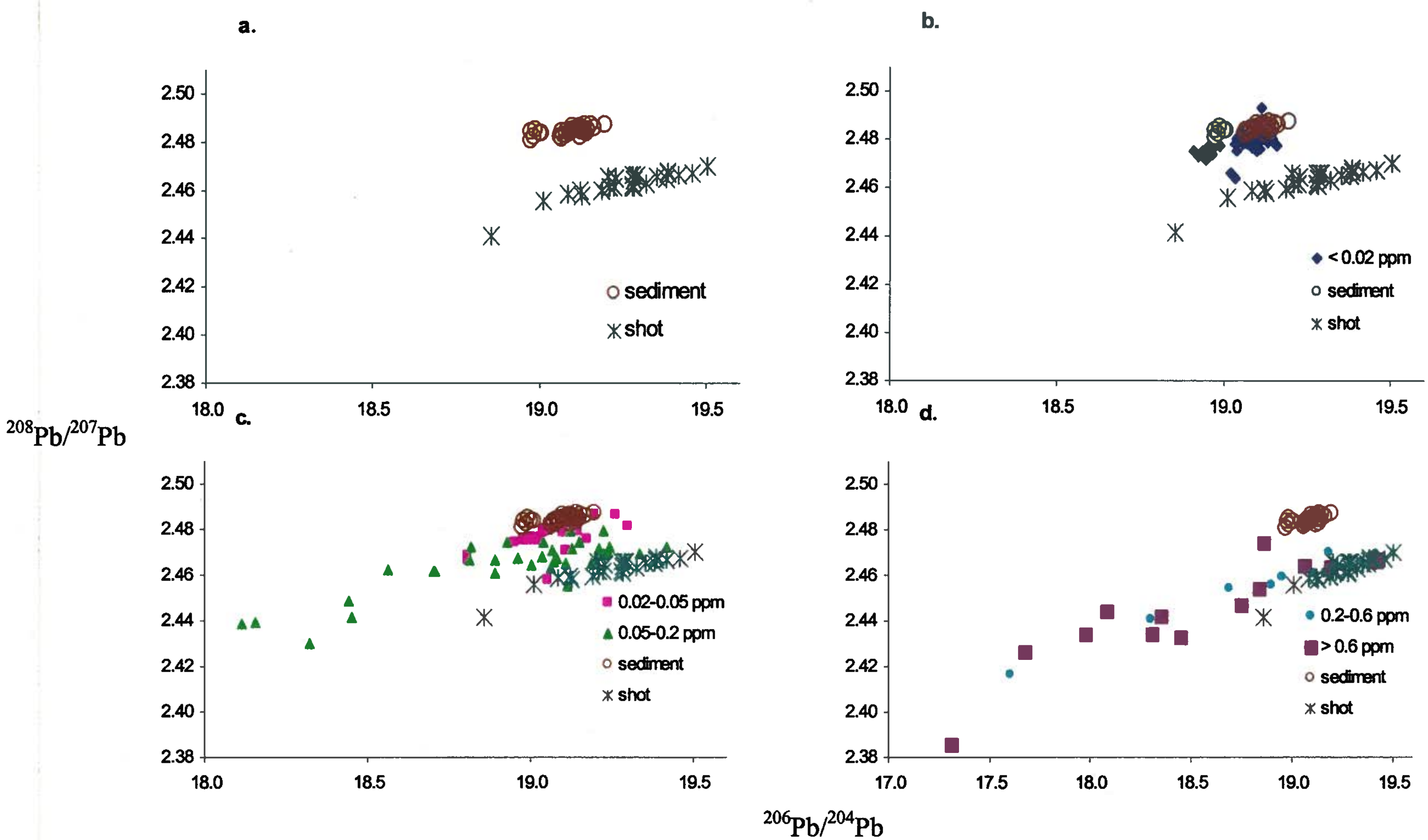

Fig. 2. Lead isotope (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) ratios in lead shot and sediments (a) collected from the Yukon-Kuskokwim Delta, the Bering Sea, and the North Slope of Alaska, compared to lead isotope ratios in spectacled, common, and king eider and long-tailed duck whole blood, grouped by total blood lead concentrations. Low blood lead concentrations (<0.02 ppm) matched sediment signatures (b); median blood lead concentrations (0.02 – 0.2 ppm) had signatures intermediate between sediments and lead shot (c); and greatest blood lead concentrations (> 0.2 ppm) matched the signature from lead shot (d – note the longer x-axis).

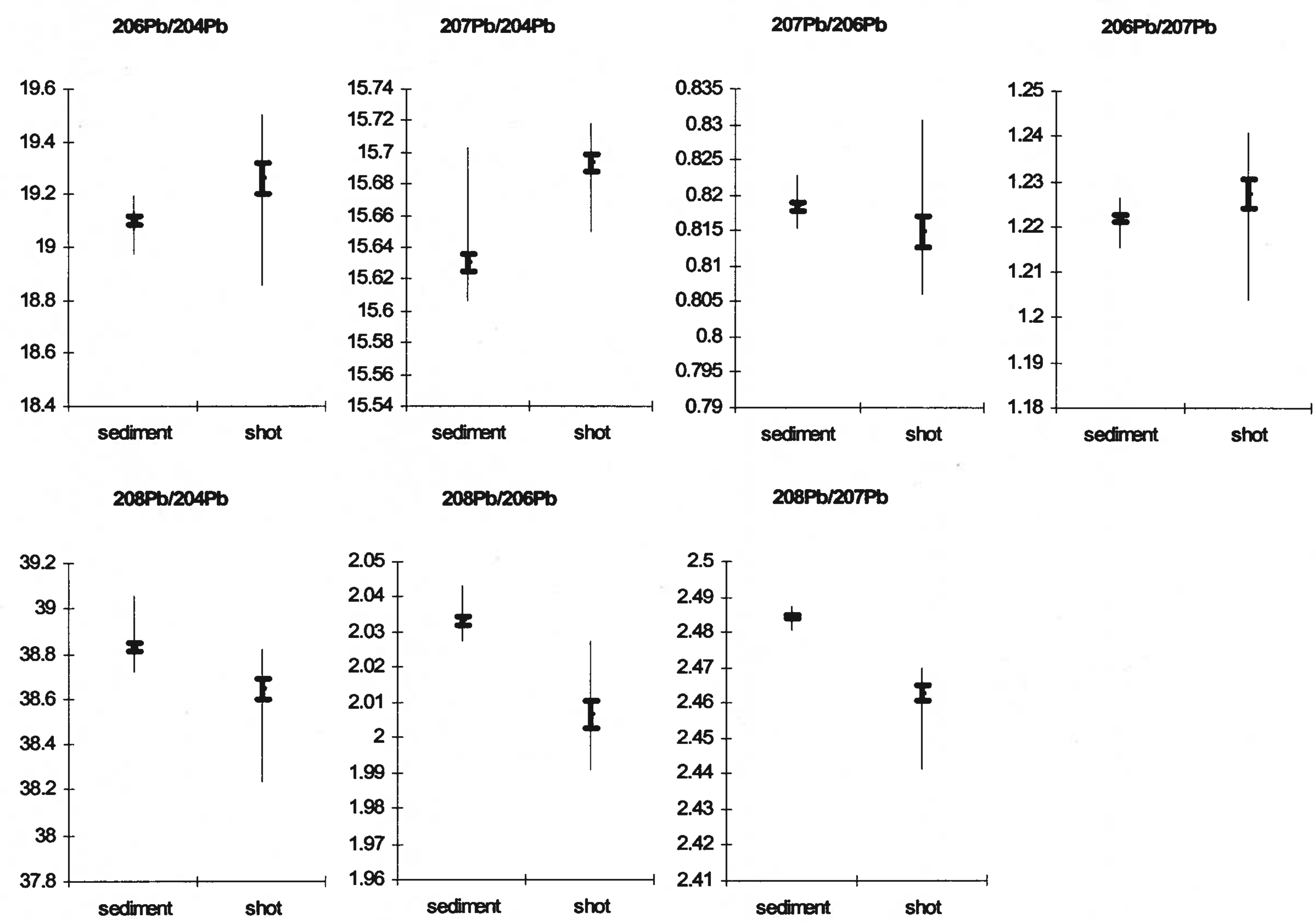

Fig. 3. Individual isotopic ratios measured in sediments and lead shot from Alaska. Bars represent two standard deviations from the mean and whiskers represent the range. The ratios $^{208}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$, and $^{208}Pb/^{204}Pb$ were distinctly different between sediments and shot.

The discriminant function classified samples from birds exposed to low (background) lead concentrations with sediments, and samples from birds exposed to high lead concentrations with our shot samples (or other lead ores which have been historically used to produce shot). Some samples' isotopic signatures were classified with neither sediments nor shot. Unclassified samples with high lead concentrations were probably derived from shot, as they fall within the isotopic signatures of known commercial ore deposits within North America (Fig. 4). Unclassified samples with lower blood lead levels may have actually had combined signatures from both sediments and shot, possibly from less initial ingested lead or from sampling before or after blood lead concentrations peaked (Fig. 5).

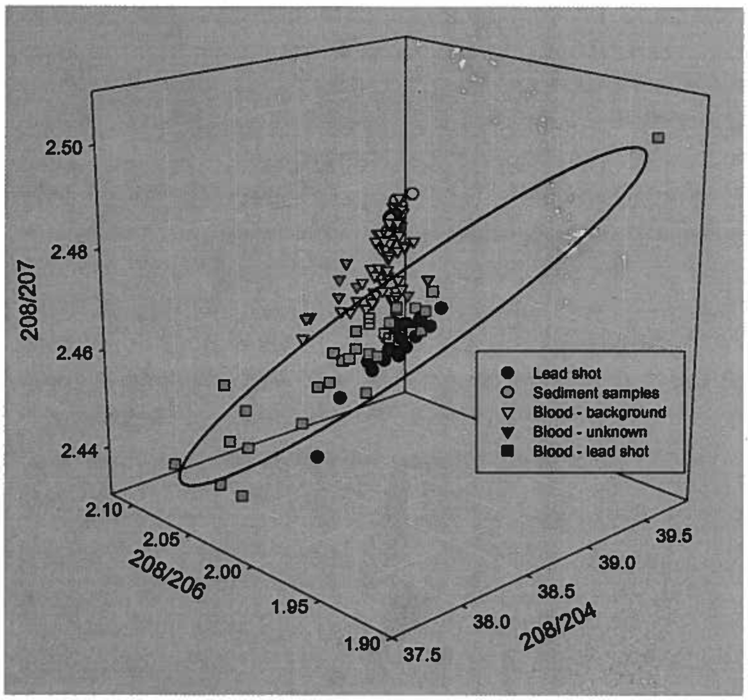

Fig. 4. Lead isotope ratios of reference lead shot, reference sediments, and duck blood classified by reference type. "Blood-background" most closely matched the isotope signature of sediment and "Blood-lead shot" most closely matched the isotope signature of shot. "Blood – unknown" had signatures intermediate between the two reference types but were probably lead-shot derived as they fell within the range of lead isotope signatures from commercial ore deposits (ellipse).

The logistic regression using total blood lead concentrations as the independent variable and the discriminant function's classification of blood into "shot" or "sediment" as the categorical dependent variable supported the clinical threshold for exposure above background (0.2 ppm) as a reasonable threshold for exposure above background and to lead shot for eiders and long-tailed ducks in Alaska. This clinical threshold was developed based on significant reduction in the lead-sensitive enzyme δ-aminolevulinic acid dehydratase (ALAD) after lead ingestion. In our

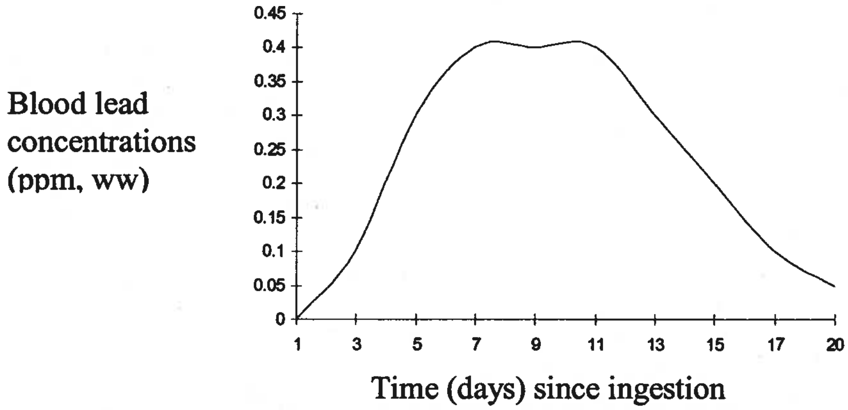

Fig. 5. Hypothetical blood lead concentrations after one-time ingestion of lead shot, illustrating how samples with intermediate lead levels may be obtained, depending on time elapsed since ingestion. After a single ingestion, blood lead concentrations would be expected to drop back to normal after several weeks.

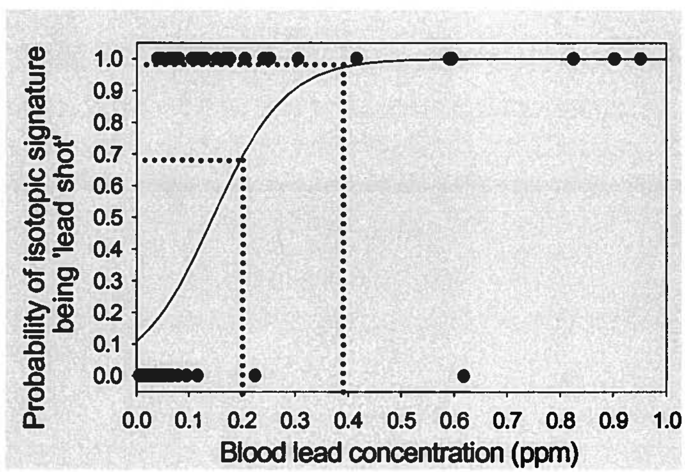

Fig. 6. Results of a bootstrapped logistic regression to estimate the probability of blood lead isotope signatures matching either background sediment or lead shot isotope signatures based on total blood lead concentrations in eiders from Alaska. The clinical threshold for above-background lead exposure (0.2 ppm) developed from studies of lead effects on enzyme levels is supported here, with an

diets are associated with lower lead toxicity. Chronic (long-term) lead exposure often leads to deterioration and death, while a bird can recover from an acute (short-term) exposure if the lead is passed from the body before too much has been ground and shunted into the blood stream. Because of these sources of variation, effects of lead shot ingestion will not be predictable for any one eider. However, lead has no biological purpose and is universally considered a toxicant; therefore, exposure above background can have only negative effects. These effects include reduced reproductive capability (physiological and behavioral), reduced immune functioning, anemia, and other effects leading to morbidity or mortality.

We have shown that nesting spectacled eiders, common eiders, king eiders, and long-tailed ducks in Alaska are exposed to lead at harmful concentrations, and the source of this exposure is lead shot. At the population level, negative effects of this exposure have been documented in spectacled eiders nesting on the Y-K Delta, including significantly reduced survival of nesting females with high blood lead levels (Grand et al. 1998), with mortality from lead poisoning equal to mortality from lead poisoning (Flint and Grand 1997), and greater probability of lead exposure in successful nesting females (who stay on the breeding grounds longer) (Franson et al. 1998, Flint et al. 1997). Lead poisoning was responsible for reductions in juvenile survival to fledging (Flint et al. 2000). Spectacled (and other) eider deaths due to lead poisoning were documented on the Y-K Delta as early as 1992 (Franson et al. 1995).

Elevated lead exposure also occurs on the North Slope of Alaska, although studies have not been as comprehensive as on the Y-K Delta. In 1995, two female and one juvenile spectacled eider captured between the Kuparuk and Sagavanirktok rivers had blood lead concentrations > 0.2 ppm (Wilson et al. 2004). In 1999-2000, eight of eight nesting Steller's eider hens near Barrow also exceeded this threshold (A. Matz, U.S. Fish and Wildlife Service, unpubl. data), and a Steller's eider found dead near Barrow had liver and kidney lead levels suggestive of poisoning (Trust et al. 1997). In the mid-1980's, lead pellets were found in 11% of long-tailed ducks collect from West Long Lake, just east of Teshukpuk Lake (Taylor 1986). Although we lack blood samples with both elevated blood lead concentrations and lead isotope signatures from the North Slope, we assume the same functional relationship between lead shot and elevated blood lead exists on the North Slope as on the Y-K Delta, especially since North Slope sediments are distinct from shot and similar to Y-K Delta sediments.

Management Implications

Spectacled and Steller's eiders breeding in Alaska are listed as threatened under the ESA, and other seaduck species are of concern. This project is one of several that have documented

Acknowledgments

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