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ELEMENTAL AND ORGANOCHLORINE RESIDUES IN BALD EAGLES FROM ADAK ISLAND, ALASKA

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ABSTRACT: Adak Island is a remote island in the Aleutian Island archipelago of Alaska (USA) and home to various military activities since World War II. To assess the contaminant burden of one of Adak Island's top predators, livers and kidneys were collected from 26 bald eagle ($Haliaeetus\ leucocephalus$) carcasses between 1993 and 1998 for elemental and organochlorine analyses. Mean cadmium, chromium, mercury, and selenium concentrations were consistent with levels observed in other avian studies and were below toxic thresholds. However, elevated concentrations of chromium and mercury in some individuals may warrant concern. Furthermore, although mean polychlorinated biphenyl and pp'-dichlorodiphenyldichloroethylene concentrations were below acute toxic thresholds, they were surprisingly high given Adak Island's remote location.

Key words: Adak Island, Alaska, Aleutian Islands, bald eagles, contaminants, Haliaeetus leucocephalus.

INTRODUCTION

Many environmental contaminants, including heavy metals and organochlorines, are associated with industrial emissions and large-scale agriculture, yet studies have demonstrated elevated levels of some contaminants far from known or suspected sources (Bacon et al., 1999; Bard, 1999). Top-level predators, such as bald eagles (Haliaeetus leucocephalus), are believed to be especially vulnerable to many contaminants and can be used as sentinel species for contaminated areas (Welch, 1994; Holl and Cairns, 1995). In Alaska's Aleutian Islands (USA), bald eagles prey primarily on fish and birds (Anthony et al., 1999), though community landfills may also represent an important food source, particularly during winter (Byrd et al., 1974; U.S. Department of Agriculture, 1990). Both natural and anthropogenic food sources are potential routes of contaminant exposure for these birds.

Adak Island (51°53′N, 176°39′W) is one of approximately 150 islands that comprise the Aleutian Island Archipelago of Alaska. It is located 1,850 km west-southwest of Anchorage, Alaska and has been within the National Wildlife Refuge system since 1913. The only notable development on

the island resulted from U.S. military activities during and since World War II. In 1994, the developed northern half of the island was placed on the U.S. Environmental Protection Agency's National Priorities List (59 FR 27989). At that time, various investigations had identified approximately 185 chemically-contaminated sites in this area (U.S. Navy et al., 1999).

Most contaminant studies of bald eagles have involved relatively non-invasive egg, blood, and feather collection techniques. Of those, only two studies reported exclusively on Alaskan eagle populations (Estes et al., 1997; Anthony et al., 1999). Tissue studies of contaminants in bald eagles are also available, but are of limited applicability to Alaskan eagles (Kaiser et al., 1980; Anthony et al., 1993; Welch, 1994). This report examines contaminant residues in bald eagle tissues from Adak Island, which supports a non-migratory and reproductively stable eagle population (U.S. Department of Agriculture, 1990; Estes et al., 1997). Because of its status as one the island's top predators and largest vertebrates, assessment of these bald eagles offers an opportunity for better understanding effects of contaminants within the Adak Island ecosystem. Our objectives

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were to 1) determine elemental and organochlorine concentrations in liver and kidneys of bald eagles from Adak Island, 2) compare these residues to those found in related species, and 3) identify contaminants of concern.

MATERIALS AND METHODS

Twenty-six bald eagle carcasses were collected by Alaska Maritime National Wildlife Refuge personnel between 21 October 1993 and 3 February 1998. Carcass collections were not random. All birds were found during winter and most appeared to have died by electrocution as a result of perching on utility poles. Five birds were collected during the winter of 1993-94, six during 1994–95, nine during 1996–97, and six during 1997-98. Carcasses were double-bagged in plastic and frozen at −15 C until tissues could be collected. At necropsy, age class (juvenile, sub-adult, and adult) was determined by plumage, iris, beak, and cere characteristics (McCollough, 1989); and sex and cause of death were determined, if possible, by visual examination of tissues and carcasses. Liver and kidney collections were performed using acid/acetone-washed dissection tools and sterile scalpel blades. Tissues were placed into glass jars (I-CHEM® 300-series, I-CHEM, Hayward, California, USA), frozen, and shipped for laboratory analyses. All samples underwent moisture and lipid content determinations.

Samples were screened for 19 elements at the Research Triangle Institute (Research Triangle Park, North Carolina, USA) using analytical procedures similar to those described by Trust et al. (2000). Arsenic and selenium levels were determined using graphite furnace atomic absorption spectrometry analysis; mercury levels were determined using cold vapor atomic absorption analysis, and all other elements were determined using inductively-coupled plasma emission spectroscopy. Elements and their maximum detection limits (parts per million [ppm] in parentheses) included Al (6.1 ppm), As (0.61 ppm), B (1.2 ppm), Ba (0.61 ppm), Be (0.12 ppm), Cd (0.12 ppm), Cr (0.61 ppm), Cu (0.61 ppm), Fe (12.3 ppm), Hg (0.12 ppm), Mg (12.3 ppm), Mn (0.49 ppm), Mo (0.61 ppm), Ni (0.61 ppm), Pb (1.2 ppm), Se (0.61 ppm), Sr (0.25 ppm), V (0.61 ppm), and $Zn (1.\overline{2} ppm).$

Sample aliquots from 26 liver and 11 kidney samples were sent to the Mississippi State Chemical Laboratory (Mississippi State University, Starkville, Mississippi, USA) to be screened for 22 organochlorine compounds by gas chromatography using a modified version of the Micro Method (U.S. Environmental Protection Agency, 1980). Organochlorine compounds included alpha, beta, gamma, and delta benzene hexachloride (BHC); alpha and gamma chlordanes; dieldrin; endrin; hexachlorobenzene (HCB); heptachlor epoxide; mirex; op'-dichlorodiphenyldichloroethane, dichlorodiphenyldichloroethylene, and dichlorodiphenyltrichloroethane (DDD, DDE, and DDT, respectively); oxychlordane; total polychlorinated biphenyls (PCBs; sum of Aroclors); pp'-DDD, DDE, and DDT; toxaphene; and cis- and trans-nonachlors. Maximum detection limits were 0.28 ppm for total PCBs and toxaphene and 0.06 ppm for all other organochlorines. All analytical results are expressed in mg/kg (ppm) on a dry-weight basis.

Where necessary for comparison purposes, values from the literature were converted to dry weight using mean tissue moisture content for Adak Island eagles, 73% and 77% moisture for liver and kidney tissues, respectively. The percent moisture values for Adak Island bald eagles tissues were similar to those reported by Ohlendorf (1993), and the conversion factors are similar to those reported by Di Giulio (1982).

Additional quality assurance analyses were also applied to approximately 5% of the samples. Recoveries from spiked samples and standard reference materials were acceptable if they were $\pm 20\%$ of the expected value. Duplicate analyses were acceptable if the relative percent difference between samples and their corresponding duplicate was $\leq 20\%$. Procedural blanks were acceptable if concentrations were less than the limit of detection or <10% of the analytical result of individual analytes.

Summary statistics (geometric means and ranges) were determined for all analytes detected in ≥50% of the samples (Tables 1 and 2), with non-detect values substituted with one half of the detection limit (Frenzel and Anthony, 1989; Anthony et al., 1999). Statistical comparisons among collection years, age classes, and between sexes were performed on analytes detected in 70-100% of the samples within the same tissue type. For those analytes with less than 100% detects (some organochlorines), non-parametric statistical tests (Kruskal-Wallis) were used, with all non-detect data tied at the lowest rank. For those analytes with 100% detects (all elements and some organochlorines), data were log-transformed and tested using general linear models (GLM), including one or two-way multivariate analysis of variance (MANOVA). Significant MANOVAs were then followed by univariate ANOVAs with Bonferroni-adjusted post hoc comparisons or t-tests to determine group differences. Correlations

Analyte	Liver			Kidney		
	Percent detected ^a	Geometric mean ^b (ppm)	Range	Percent detected ^a	Geometric mean (ppm)	Range
Arsenic	54%	0.48	< 0.6-1.81	62%	0.53	< 0.61-1.96
Cadmium	100%	2.43	0.45 - 7.15	100%	13.7	1.43-104
Chromium	50%	0.73	< 0.61-18.7	54%	0.93	< 0.61 – 58.9
Copper	100%	25.6	11.2-395	100%	15.8	8.76-68.0
Iron	100%	2,180	714-9,120	100%	888	408 - 1,770
Mercury	100%	7.10	1.70-17.5	100%	14.6	3.19-68.4
Magnesium	100%	540	304-806	100%	598	423-851
Manganese	100%	9.94	6.04 - 16.5	100%	5.57	2.86-9.85
Molybdenum	100%	1.97	0.90 - 4.42	100%	1.87	0.92 - 3.86
Selenium	100%	10.2	3.25 - 33.8	100%	13.1	5.19 - 32.5
Strontium	58%	0.22	< 0.25-1.18	100%	0.55	0.10 - 2.41
Vanadium	19%	NC^c	NC	50%	0.48	< 0.61 – 3.52
Zine	100%	127	52.1–503	100%	96.4	52.3 – 278

TABLE 1. Results of analyses for elements in tissues eagles from Adak Island. Concentrations are in mg/kg (ppm), dry weight. The elements shown were detected in at least 50% of the samples.

between PCBs and pp'-DDE residues were also assessed. No significant correlations were found between lipid content and organochlorine residues (Wilks' λ =0.64, P=0.41), so organochlorine residues were not lipid-normalized. All results were assessed using SYSTAT 9.0 statistical software (SPSS, Inc. Chicago, Illinois, USA), with α =0.05. All results were assessed for influential outliers.

RESULTS

Outlying values did not influence statistical conclusions. In livers, Cd, Cu, Fe, Hg, Mg, Mn, Mo, Se, and Zn were detected in all samples (Table 1). No significant differences for these analytes were detected among collection winters (P=0.347), age classes (P=0.999), or between sexes (P=0.689). In kidneys, Cd, Cu, Fe, Hg, Mg, Mn, Mo, Se, Sr, and Zn were detected in all samples. No significant difference for these analytes was detected among age classes (P=0.874) or between sexes (P=0.911). Although these analytes differed significantly among collection winters (Wilks' $\lambda = 0.005$, P = 0.005), no clear patterns emerged. For example, Fe and Mn appeared to decrease over time, while Cu, Mg, and Zn appeared to increase. None of these trends in individual metals was statistically significant.

In Adak Island eagles, few organochlorines were found in appreciable concentrations. However, total PCBs, oxychlordane, pp'-DDE, and trans-nonachlor were detected in most or all individuals (Table 2). Two of three spike recoveries for pp'-DDE were lower than acceptable (61.5) and 69.2%), suggesting that the concentrations listed in Table 2 may underestimate the actual concentrations. In livers, significant differences were detected among collection winters for oxychlordane (P=0.048), total PCBs (P=0.002), and pp'-DDE (P=0.020). However, this finding was deemed inconclusive because we had no intermediate data from the winter of 1995–96 and because no discernable trend was apparent for these compounds across all collection periods. No significant difference was detected among age classes (all $P \ge 0.204$) or between sexes (all $P \ge 0.712$) for any of the organochlorines. In kidneys, significant differences were detected among collection winters for transnonachlor only (P=0.002). This finding

^a Proportion of 26 eagles in which the analyte was detected.

^b Calculated using one half of the detection limit in lieu of non-detect values.

^c Not calculated.

Kidney Liver Geometric Geometric Percent Percent mean mean Analyte detected^b Range detected (ppm) (ppm) Range **HCB** 88% 0.025 50% 0.041 < 0.06 - 0.105 < 0.06 - 0.300 Total PCBs 100% 100% 1.46 0.02 - 52.04.83 1.08 - 42.6Alpha-chlordane 54% 0.014 < 0.06 - 0.240 NC^e 10% NC Beta-BHC 73% 0.024 < 0.06 - 0.420 80% 0.051 < 0.06 - 0.200 Cis-nonachlor 65% 0.020 < 0.06 - 0.320 60% 0.054 < 0.06-0.223 Dieldrin 54% 0.017 < 0.06-0.130 40% NC NC

< 0.06 - 0.130

< 0.06-0.560

< 0.06 - 0.410

< 0.06 - 0.560

0.01-10.0 <0.06-1.260 40%

40%

90%

90%

100%

100%

NC

NC

0.087

0.079

0.142

1.23

NC

NC

< 0.06 - 0.302

< 0.06 - 0.232

0.24-8.09

0.040 - 0.851

TABLE 2. Results of analyses for organochlorines in tissues of bald eagles from Adak Island. Concentrations are in mg/kg (ppm), dry weight. The organochlorines shown were detected in at least 50% of the samples.

54%

62%

92%

85%

100%

92%

0.014

0.022

0.046

0.035

0.63

0.094

Heptachlor epoxide

Oxychlordane

Trans-nonachlor

pp'-DDD

pp'-DDE

Mirex

was also deemed inconclusive. No significant differences were detected among age classes (all $P \ge 0.298$) or between sexes (all $P \ge 0.286$).

Oxychlordane and *trans*-nonachlor were found at levels near the analytical detection limit. Conversely, total PCBs and pp'-DDE levels were high in some individuals and may warrant concern. Moreover, as found by Wiemeyer et al. (1984), PCBs and pp'-DDE concentrations were strongly correlated (R^2 =0.91; P=0.000).

DISCUSSION

Cadmium, a non-essential element, may cause severe effects in microorganisms, higher plants, and animals, though mammals and birds seem more resistant than other vertebrates to its toxic effects (Eisler, 1985a). The cadmium concentrations for eagles from Adak Island were consistent with those observed in several studies of healthy marine birds cited in Eisler's (1985a) review. In addition, the highest cadmium concentrations observed in this study were well below those suggested by Furness (1996) as being lethal to birds.

Given Adak Island's active geology, pyroclastic soils and Furness's (1996) assertion that cadmium is typically higher in marine birds, the residues reported here may be naturally enriched but still within normal background levels for bald eagles on Adak Island and in similar areas.

Chromium is an essential element for many animals, though it can be mutagenic at high concentrations (Eisler, 1986a). There are few data on toxic chromium tissue concentrations though the mean concentrations observed in this study were similar to those from healthy birds throughout the world and well below the 4 ppm contamination threshold suggested by Eisler (1986a). The highest chromium concentrations found in Adak Island eagles were above Eisler's (1986a) threshold level, but only in the birds collected during the winter of 1993-94 (liver and kidney geometric means: 5.81 and 35.2 ppm, respectively). Mean concentrations were below 1 ppm in liver and kidneys during subsequent collection periods.

Mercury has no known biological value and biomagnifies at higher trophic levels

^a HCB = hexachlorobenzene, PCB = polyclorinated biphenyls, BHC = benzene hexachloride, DDD = dichlorodiphenyldichloroethane, DDE = dichlorodiphenyldichloroethylene.

^b Proportion of 26 eagles in which the analyte was detected.

^c Calculated using one half of the detection limit in lieu of non-detect values.

^d Proportion of 10 eagles in which the analyte was detected.

e Not calculated.

(Thompson, 1996). In birds, elevated concentrations of mercury may affect reproduction, chick survival, metabolism, and behavior (Thompson, 1996). The mercury concentrations in some eagles from Adak Island appeared elevated and may indicate anthropogenic inputs (Eisler, 1987). Mean mercury concentrations observed in this study were similar to those detected in bald eagle carcasses from Florida (Wood et al., 1996) where high mercury concentrations are a notable problem in wildlife. However, the highest mercury levels found in our study were below the sublethal effects level reported for birds of prey by Thompson (1996) and well below the high mercury concentrations found in dead white-tailed eagles (Haliaeetus albicilla) from Finland (Henriksson et al., 1966; Oehme, 1981).

Selenium is a ubiquitous element that is important for the health of many species. However, at high concentrations it can be severely toxic causing reproductive, congenital, and developmental anomalies (Eisler, 1985b). Selenium concentrations for eagles from Adak Island were within normal ranges (Heinz, 1996) and were within the range of healthy marine birds reported in Eisler's review (1985b).

Persistent organic compounds, such as PCBs and DDE are often found in piscivorous birds like eagles (Eisler, 1986b; Blus, 1996). Polychlorinated biphenyls may cause tremors in birds as well as muscular incoordination and developmental, reproductive, metabolic, and behavioral effects (Eisler, 1986b). Given the extensive use of PCBs in electrical equipment prior to its ban in the US, their environmental persistence and the increasing evidence of their long range transport to polar regions (Bard, 1999), it was not surprising to find measurable concentrations of these chemicals in bald eagles from Adak Island. Mean PCB concentrations in Adak Island eagles were similar to those observed in a peregrine falcon (Falco peregrinus) liver from Amchitka Island (White and Riseborough, 1977), another contaminated military installation in the Aleutians, but were lower than concentrations of PCBs reported for poisoned birds (Hoffman et al., 1996). Concentrations of PCBs were high in peregrine falcon (Crayton, 2000) and bald eagle eggs (Estes et al., 1997) from several Aleutian islands and in potential prey of eagles such as sea otters (*Enhydra lutris*) (Krog, 1953; Giger and Trust, 1997) and Aleutian green-winged teal (*Anas crecca nimia*) (Scharf, 1995).

Of the DDT metabolites, pp'-DDE is one of the most toxic and extensively studied (Blus, 1996). The pp'-DDE concentrations for eagles from Adak Island were particularly elevated in some individuals, but the mean liver concentrations were similar to those described in a peregrine falcon from Amchitka Island (White and Riseborough, 1977). Recent releases of DDT in the Aleutian Islands are unlikely since its ban in 1972, but contamination stemming from distant sources (Bard, 1999) or residual, local sources on Adak and the surrounding islands are possible.

Overall, contaminant concentrations in eagles from Adak Island appeared elevated in some individuals, but still within sublethal ranges for most birds. However, elevated concentrations of elements could affect some individuals. The landfill on Adak Island was at one time a major food source for bald eagles and may have contributed to metal loading in these birds. However, this theory was only supported by a decrease in chromium concentrations in the birds after 1994, when the Navy began covering garbage at the landfill with soil on a daily basis. Alternatively, Adak Island eagles may have naturally-elevated residues of some elements because they reside and feed in the mineral-rich, volcanic environment of the Aleutian Islands. If so, it is unclear if the higher concentrations of elements found in eagles from Adak Island coincide with an increased tolerance for the more toxic elements.

Mean total PCBs and pp'-DDE concentrations were below acute toxic levels but were high in some individuals. Sublethal

physiologic responses may occur at some of the concentrations observed in this study but applicable threshold values were lacking in the literature. Concentrations of PCBs and pp'-DDE reflect direct or indirect anthropogenic sources. Historic military sites and activities in the Aleutian Islands may be a major contributor to elevated PCB residues in Aleutian Island sea otter and eagle populations (Estes et al., 1997). In addition, birds migrating from Asia may contain DDT-related compounds and thus may provide a source of secondary poisoning in Aleutian Island eagle populations that prey on them (Anthony et al., 1999). Contaminant sampling in resident and transitory prey species from Adak and other Aleutian Islands will help to distinguish between local and distant sources.

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