

Heavy Metal Concentrations in Mandibles of White-Tailed Deer Living in the Picher Mining District

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Cervids have received considerable attention as biological indicators of environmental heavy metal contamination over large geographic areas, particularly in Europe (Gamberg and Scheuhammer 1994; Kalas and Myklebust 1994; Kardell and Kallman 1986; Sawicka-Kapusta 1979; Tataruch 1995). Although the metal residues of several cervid tissues have been investigated, bone tissue is easily obtained and stored and is the ultimate storage site for bioaccumulated lead (Pb) in mammals (O'Flaherty 1998). Previous studies (Witkowski et al. 1982; Sileo and Beyer 1984; and Storm et al. 1994) have been contradictory with regards to the value of white-tailed deer (Odocoileus virginianus) mandible and/or bone as tissue-level monitors of heavy metal contamination. An advantage to using tissue from white-tailed deer is that tissue metal residues can be associated with a relatively small geographic area, for most are non-migratory and have small annual home ranges of approximately 1.6-1.8 km² (Larson et al. 1978; Progluske and Baskett 1958; Severinghaus and Cheatum 1959; VerCauteren and Hygnstrom 1998). Another advantage to mandible tissue is the ease of collection; in Oklahoma, the Oklahoma Department of Wildlife Conservation (ODWC) collects thousands of mandibles per year from deer harvested during the hunting season for use in population age structure analysis. The approximate location of the deer's home range is available because each hunter, upon registering his deer at a hunter check station, must identify the location of the kill on a map of Deer Kill Location Zones (DKLZs) superimposed over a state road map. Combining information on the deer kill location with large numbers of harvested deer and sufficient tissue mass for metals analysis, deer mandibles could provide a very cost-effective means of monitoring environmental heavy metal contamination in Oklahoma.

Heavy metal concentrations in various white-tailed deer tissues have been investigated in many studies (Kocan et al. 1980; Sileo and Beyer 1985; Storm et al. 1994; Witkowski et al. 1982; Woolf et al. 1982). In a small study (n = 22) Sileo and Beyer (1985) found no differences in Pb concentrations in the teeth of deer harvested from reference areas compared to deer harvested near (< 8 km) a Palmerton, PA zinc (Zn) smelter. Storm et al. (1994) investigating the same Zn smelter, examined cadmium (Cd),copper (Cu), Pb, and Zn concentrations in metacarpals of deer (n=24) and found higher Pb concentrations in deer from sites

near the smelter (< 10 km) compared to reference areas. The authors concluded that Cd, Cu, and Zn were not partitioning to bone tissue in deer because metacarpal concentrations did not exhibit the great differences found in metal concentrations in kidneys and/or livers of deer from the control and smelter sites.

The purpose of the current study was to investigate the Cd, Pb, and Zn concentrations in the mandibles of white-tailed deer living in the Picher Mining District of Oklahoma. A large number of mandibles (n=67) were analyzed in order to assess the value of white-tailed deer bone tissue in heavy metal biomonitoring. We hypothesized that metal levels in mandibles would be highest in deer harvested in the DKLZ containing the majority of the Picher Mining District as well as the core of mining operations (Picher, OK), intermediate in DKLZs adjacent to the Picher DKLZ, and low in other DKLZs.

MATERIALS AND METHODS

The Picher Mining District is located primarily in Ottawa County, Oklahoma, with a small portion in Cherokee County, Kansas. The district is one of the Pb-Zn mining subregions comprising the Tri-State Mining Region of northeast Oklahoma, southeast Kansas, and southwest Missouri. From 1904 to 1964, the Picher mining area was one of the most productive Pb-Zn mining districts in the country, having produced over 7 million tons of Zn and nearly 2 million tons of Pb (OWRB 1983). In 1983, the U.S. Environmental Protection Agency designated 104 km² of the district, known as "Tar Creek", to receive national priority listing under Superfund due to heavy metal contamination of ground and surface water from acid mine seepage. Remedial investigation of the area has also revealed extensive soil contamination by heavy metals (ODEQ 1996). Analysis of bioavailable metals estimated using water-extracted soil samples from Cherokee County, Kansas, just north of the Picher/Tar Creek area, revealed elevated levels of Cd, Pb, and Zn that could potentially threaten wildlife (Abdel-Saheb et al. 1994).

The DKLZs from which the deer mandibles originated lie in the very northeast corner of Oklahoma (Figure 1). The primary DKLZ of interest is zone 232, which contains the Oklahoma portion of the Picher Mining District, centered around the Pb-Zn smelter just outside of Picher, Oklahoma. Mandibles were also obtained from deer harvested in adjacent DKLZs (233, 234, 235). Mandibles obtained from deer harvested in DKLZs >50 km from any known significant sources of heavy metal contamination served as reference tissues (230, 243, 248).

White-tailed deer mandibles were collected by technicians employed by the ODWC at hunter check stations during one weekend of the 1996 Oklahoma deer gun season. Specimen sex, antler circumference (at 2.5 cm above the burr), weight, age, and DKLZ were recorded for each. After receiving the mandible samples from the ODWC, the ages of the samples were double checked using a mandible aging procedure developed by Severinghaus (1949). Prior to metals analysis, each mandible was scrubbed with a plastic brush under distilled water

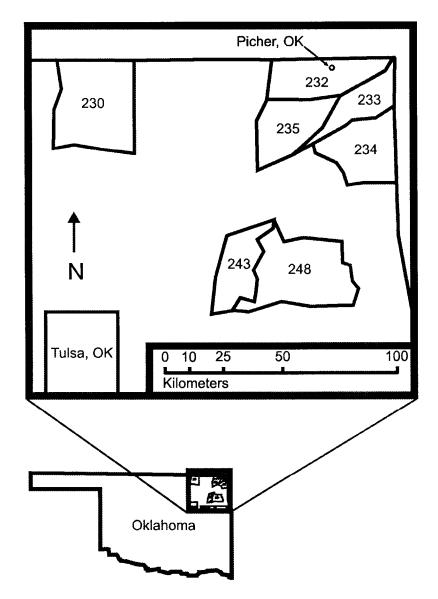


Figure 1. Map of the Deer Kill Location Zones (DKLZs) from which white-tailed deer mandibles were obtained.

and rinsed once in 0.2 N HNO_3 (Tracemetal grade, Fisher Scientific) and deionized water. To obtain a sample for metals analysis, the mandible was placed between two pieces of plastic and struck with a hammer. This produced small bone fragments without the risk of metal contamination associated with bone saws. To avoid possible heterogeneity in mandible metal levels, fragments were collected from the mandible ± 1 cm directly anterior to the first premolar. After oven-drying the fragments, approximately 1 g of bone was weighed and placed in 20 ml of concentrated HNO $_3$ and digested for 48 h at room temperature as

described by Zong et al. (1996). The samples were then diluted to 50 ml with deionized water and analyzed for Cd, Pb, and Zn using atomic absorption spectroscopy. Samples were below the graphite furnace detection limit for Cd (2.5 μ g/kg bone, dry weight). Blanks and spikes were used to correct for background contamination. Analyses of Pb and Zn concentrations of SRM 1486 Bone Meal (National Institute of Standards, US Department of Commerce) were within 5% of certified values. Mandible Pb and Zn concentrations were log transformed (Miliken and Johnson 1984) and analyzed using ANOVA, F-contrasts, and linear regression.

RESULTS AND DISCUSSION

the mandible could not be assessed.

A significant effect of DKLZ on the Pb concentration in white-tailed deer mandibles was observed (P = 0.0233. Table 1). F-contrasts showed elevated Pb levels between DKLZ 232 and all other zones pooled (P = 0.0047) and between DKLZ 232 and adjacent DKLZs (233, 234, 235) (P = 0.0137). Thus, elevated mandible Pb concentrations in white-tailed deer were only observed in deer harvested in DKLZ 232. The adjacent DKLZs may not be contaminated, possibly because the primary wind direction of the area is to the north. Within the mandibles obtained from DKLZ 232, there were no differences in Pb concentrations among ages 0.5-3.5 yr (P =0.5611). There were also no differences in Pb concentrations among ages 0.5-7.5 for the pooled DKLZs (P = 0.1787). Linear regression revealed no significant correlation between mandible Pb concentrations and body weight of deer harvested in DKLZ 232 ($r^2 = 0.1938$, P = 0.0675). Body weights of deer from DKLZ 232 do not differ from those of the other DKLZs investigated (2-way ANOVA: age*weight, P = 0.1484). Although deer antler data were available, there were only 5 mandibles originating from antlered deer analyzed in DKLZ 232, so relationships between this biomarker of health and Pb concentrations in

Cadmium levels in the samples are below the graphite furnace detection limit for (2.5 μ g/kg bone, dry weight). Although means appear to differ, there were no significant differences in mandible Zn concentrations among the DKLZs (P=0.35 18, Table 1). Since ANOVA suggested no significant differences between mean Zn levels, further means comparisons were not carried out in order to avoid Type I errors. There were also no significant differences in mandible Zn levels among the different age groups (P=0.0785). Mandible Zn concentrations were similar to those previously found in metacarpal tissue (Storm et al. 1994). Zinc is an essential element, with body burdens under physiological control even when Zn intake is fairly high (Melancon et al. 1992). When Zn accumulation occurs due to an inefficacy in physiological regulation, Zn may remain in the kidney and liver tissues instead of partitioning to bone (Storm et al. 1994).

Lead concentrations in the deer mandibles were lower than those found in white-tailed deer metacarpals (Storm et al. 1994) and teeth (Sileo and Beyer 1985) obtained from deer harvested both at reference and Palmer-ton Zn smelter sites.

Table 1. Zinc and lead in mandibles of white-tailed deer (*Odocoileus virginianus*) harvested from Deer Kill Location Zones (DKLZs) in northeastern Oklahoma.

DKLZ ¹	n	Zn (mg/kg, dry weight)	Pb (mg/kg, dry weight)
232	20 ²	77.1 (6.20) ³	1.43 (1.25)
Adjacent to 232:			
233	7	71.0 (4.70)	0.757 (1.22)
234	10	72.6 (6.50)	0.318 (0.079)
235	10	72.7 (7.60)	0.269 (0.114)
Reference:			
230	8	66.5 (6.70)	0.170 (0.054)
243	3	68.7 (12.2)	0.469 (1.12)
248	9	69.1 (9.40)	0.617 (0.565)

¹DKLZ 232 includes the Oklahoma portion of the Picher Mining District ²n=19 for Pb analysis of DKLZ 232 mandibles

Lead accumulates in the skeleton differentially (O'Flaherty 1998) and this may account for the observed difference in comparison with the metacarpals. Witkowski et al. (1982) however, found no differences between mandible and tooth Pb concentrations in white-tailed deer. The differences in Pb levels between teeth collected in the Palmerton study and mandibles collected during this study may indicate that even the reference sites in previous studies were contaminated. Surprisingly, one mandible contained 95 mg Pb/kg, dry weight, nearly 20 times the Pb concentration found in white-tailed deer teeth from Palmerton. It was hypothesized that this extremely high residue was the result of mobilization of lead shot from a hunting wound early in life, and not due to normal environmental exposure or bullet fragments within the analyzed mandible section. For this reason, that datum was excluded from statistical analyses.

The white-tailed deer of DKLZ 232, which includes the core and the majority of the Picher Mining District, have normal mandible Zn, but elevated mandible Pb concentrations. Analysis of body weights, a crude biomarker of health, and mandible Pb concentrations indicates no population-level impact of increased Pb exposure. However, if there is an area of contamination within the DKLZ posing a direct threat to smaller groups of deer, the lack of geographical resolution in the DKLZ approach would not necessarily depict a health-mandible Pb relationship, because only a few deer of the sample would originate from the contaminated area. This only causes an observed increase in the mean mandible Pb level; more mandibles from the specific contaminated area within the DKLZ would have to be obtained in order to assess effects on health. With the aid of specific harvest-locations, an investigation could focus within a particular DKLZ of interest. Due to ease of jaw extraction, accompanying data obtained from hunter check stations,

³mean ± 95% CI

and historical population data, monitoring the Pb levels in white-tailed deer mandibles may be an effective tool to investigate wide-scale Pb contamination in Oklahoma or other states with hunter check station programs.

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