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Feasibility of a portable X-ray fluorescence device for bone lead measurements of condor bones

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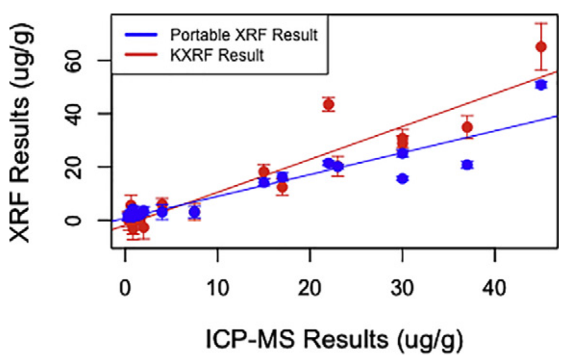
HIGHLIGHTS

- California condors have extensive chronic exposure to lead reflected in their bone.
- KXRF, portable XRF, and ICP-MS bone lead measurements shared strong correlations.
- Portable XRF is well-suited for field measurement of bone lead in avian species.

GRAPHICAL ABSTRACT



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ABSTRACT

Lead based ammunition is a primary source of lead exposure, especially for scavenging wildlife. Lead poisoning remains the leading cause of diagnosed death for the critically endangered California condors, which are annually monitored *via* blood tests for lead exposure. The results of these tests are helpful in determining recent exposure in condors and in defining the potential for exposure to other species including humans. Since condors are victim to acute and chronic lead exposure, being able to measure both would lend valuable information on the rates of exposure and accumulation through time. A commercial portable X-ray fluorescence (XRF) device has been optimized to measure bone lead *in vivo* in humans, but this device could also be valuable for field measurements of bone lead in avian species. In this study, we performed measurements of bone Pb in excised, bare condor bones using inductively coupled plasma mass spectrometry (ICP-MS), a cadmium 109 (Cd-109) K-shell X-ray fluorescence (KXRF) system, and a portable XRF system. Both KXRF and portable XRF bone Pb measurement techniques demonstrated good correlations with ICP-MS results ($r = 0.93$ and $r = 0.92$ respectively), even with increasing skin thickness ($r = 0.86$ between ICP-MS and portable XRF at 1.54 mm of soft tissue). In conclusion, our results suggest that a portable XRF could be a useful option for measurement of bone Pb in avian species in the field.

1. Introduction

The use of lead-based ammunition in hunting has drastically increased lead (Pb) exposure to a great number of wildlife and humans in the US (Hunt et al., 2009; Johansen et al., 2004). Lead-based

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ammunition in the form of bullets for center-fire and rim-fire ammunition is a primary source of exposure as weight loss, or fragmentation, of the projectile results in sometimes hundreds of ingestible particles, some so small they cannot be identified with the unaided eye (Hunt et al., 2009; Kollander et al., 2017). Scavenging wildlife, who might feed upon animals killed with Pb-based ammunition are most affected (Hunt et al., 2006; Stauber et al., 2010; Herring et al., 2016; Naidoo et al., 2017). California condors, a critically endangered species, undergo regular monitoring and testing and have demonstrated some of the ill-effects from lead exposure. Fifty-three percent of free-flying California condor deaths are attributed to Pb poisoning, the leading cause of diagnosed death in the wild-flock (Finkelstein et al., 2012; Rideout et al., 2012). The relationship between lead and condors is well understood because condors are monitored on an individual level, but it is highly probably that other species where calcium has a central role in bodily function are affected similarly by Pb, which primarily acts by mimicking calcium (Church et al., 2006; Ecke et al., 2017; Kerper and Hinkle, 1997). Currently, condors are primarily being monitored for Pb exposure by annual blood-lead analyses. The results from testing allow for a better understanding of recent exposure for the condors and of the potential exposure to other species including humans. Lead shot has been restricted nationally for use in hunting waterfowl within the United States and Canada, but lead-based ammunition is still widely used in many forms for other types of hunting and dispatch of domestic stock simply because of its mass, density, availability and cost relative to less dense metals (Johansen et al., 2004).

Since today's free-flying condors have been found to have both acute and chronic Pb exposure, measuring lead with a biomarker more reflective of the cumulative Pb stores in the body will add to our understanding of both short and long-term rates of exposure and accumulation. In human exposures, bone Pb has a half-life of years to decades, and over 95% of the Pb in the body is finally stored in the bones (Rabinowitz, 1991; Barry, 1975). It would make sense for the biokinetics to be similar in other species, thus, measuring bone Pb of condors would allow us to track the chronic, life-long exposure of Pb.

Traditionally, bone Pb is measured using a cadmium-109 based K-shell X-ray fluorescence (KXRF) system, which is restricted to measurement in labs due to its size, radioisotope restrictions, and 30-minute measurement time (Chettle et al., 1991). This device uses the higher K-shell energy for Pb quantification, and therefore has less dependence on soft tissue thickness due to less attenuation of the X-rays at this energy. Modern Cd-109 KXRF system (with a cloverleaf high-purity germanium detector setup) has a detection limit of 2–3 μg/g bone mineral.

Recently a portable X-ray fluorescence (XRF) device was validated for use in measuring bone Pb *in vivo* in humans (Specht et al., 2014; Specht et al., 2016). The portable XRF has the advantage of being handheld with only a 3-minute measurement time, which would be optimal for measuring in the field. This device uses the L-shell of Pb for quantification and has an X-ray tube source. Since the energies in this device are much lower, the attenuation of soft tissue can be significant. Thus, calibration approaches have been developed to correct for soft tissue thickness in the measurement. Nonetheless, the detection limit is still dependent upon the overlying soft tissue (1.8 μg/g and 11 μg/g at 1 mm and 5 mm of soft tissue respectively) (Specht et al., 2014).

XRF technology could be used to measure bone Pb *in vivo* in condors to help monitor their lifetime exposure levels. Portable XRF technology, being handheld and battery powered, has significant advantages specifically for these types of field measurements. Bone Pb monitoring will help guide intervention and policy to possibly interrupt a preventable pathway of Pb exposure to wildlife and humans. In this study, we validated the use of both KXRF and portable XRF to measure bone Pb in condor bone samples, and compared the values to those obtained using inductively coupled plasma mass spectrometry (ICP-MS).

2. Materials and methods

2.1. Condor bone samples

Seventeen condor bone samples were obtained from specimens held at the University of Arizona. They were bare bone samples taken from the avian equivalent of the tibia. The bones themselves were several centimeters in length and about one centimeter in width. Fig. 1 below displays a sample of one of the condor tibia bones measured in the study.

2.2. KXRF bone Pb measurement system

We used a KXRF bone Pb measurement system in this study to both further validate the portable XRF data and validate the use of XRF for condor bone measurements in comparison with ICP-MS measurements. The setup of the device is the same as used in previous studies (Specht et al., 2014; Specht et al., 2016; Nie et al., 2006). The system uses four 16 mm diameter high-purified germanium (HpGe) detectors with 10 mm thickness, four feedback resistance pre-amplifiers, four digital signal-processing systems, and a computer. A 135 mCi Cd-109 source is used to irradiate condor tibia bone or bone equivalent samples to produce the Pb K X-rays. The Cd-109 source requires site-specific licensing and is not easily transportable. The bone Pb measurements (one measurement per sample) were taken for 30 min with the HpGe detector. The spectra were analyzed using an in-house peak-fitting program and the final Pb concentrations were calculated (Somervaille et al., 1989; Bevington and Robinson, 2003). The whole body effective dose from this system was measured to be 0.26 μSv for human adults (Nie et al., n.d.).

The condor bone samples were placed 3–5 cm from the Cd-109 source. The condor tibia bones varied slightly in size, but the center of each sample (center of the diaphysis) was aligned with the source. If bone structure is similar to humans, this should also be the area with most cortical bone and least trabecular bone, which would reflect the longest cumulative exposure.

2.3. Portable XRF bone Pb measurement system

The portable XRF used for the bone Pb measurements in this study was the Niton XL3t GOLDD + model from Thermo Fischer Scientific Inc. (Billerica, MA). These and other similar systems typically cost between $30,000 and $50,000. Since the devices use an X-ray tube source, they typically need to be licensed for use, but the process is much

Fig. 1. One of the condor tibia bone samples.