FAST, NONDESTRUCTIVE, AND COST-EFFECTIVE METHODS TO DETECT PESTICIDE RESIDUES: A CASE STUDY OF SEVERAL REPATRIATED KARUK TRIBE ARTIFACTS

Rosene Salmo,[1] Peter T. Palmer,[1] and Karuk Tribe[2]

[1] *Department of Chemistry and Biochemistry, San Francisco State University, 1600 Holloway Avenue, San Francisco, California 94132, USA*
rsalmo@bsugmail.net, palmer@sfsu.edu
[2] *Karuk Tribe, 64236 Second Avenue, Happy Camp, California 96039, USA*
btalley@karuk.us, lisahillman@karuk.us

Abstract.—This study describes the use of three different nondestructive methods to determine whether or not nine artifacts belonging to the Karuk Tribe had been treated with common inorganic and organic pesticide agents. A portable X-Ray Fluorescence analyzer was used to estimate the concentrations of arsenic, mercury, and lead at two different locations on each artifact. Black beads on a necklace were found to contain 2.1% lead and 0.23% arsenic, which can be attributed to the natural composition of the beads. Leather on a drum mallet was found to contain 0.49% lead and 0.10% arsenic, which were due to the pigments used to decorate this item. Microwave Plasma-Atomic Emission Spectrometry analysis of swab samples taken from the surfaces of an elk horn, bow, and musical drum showed nondetectable levels of arsenic and lead. Gas Chromatography/Mass Spectrometry analysis of a second set of swab samples taken from the surface of each artifact showed nondetectable levels of *p*-dichlorobenzene, naphthalene, dichlorodiphenyltrichloroethane, and other common organic pesticides. These results suggest that these artifacts were not treated with pesticides for preservation purposes, and hence they can be handled, worn, and used as intended.

Key words.—pesticides, artifacts, X-Ray Fluorescence, Gas Chromatography, Mass Spectrometry

Associate Editor.—Christine Johnson

Introduction

Since time immemorial, the Klamath River and its many tributaries and surrounding landscapes have shaped and, in fact, define the cultural units of its first peoples. This profound bond between people and land is apparent in endless ways, and the landscapes and associated waterways provide rich resources that the ancestral Karuk depended upon to maintain their elaborate and sustainable life style. By the time early ethnographers came to study the original inhabitants of the Klamath Basin, it was apparent that indigenous peoples had been utilizing area resources for many generations, not only for the seasonal harvest of plants, animals, and aquatic species to secure food and shelter, but also for religious and other cultural observances (Kroeber 1925).

The high art of basket weaving has been practiced in this region ever since the time of the Great Transformation, when the Spirit People were transformed into all of nature's creations, including the stars, the moon, the plants, and the people. Weaving plant materials into beautiful and practical baskets has been, and still is, a spiritual experience, and the resulting products are considered to be living things—the close relatives of indigenous peoples. Considering the immense value of these cultural heritage items, the Karuk people's desire to "bring them home" may be more widely understood. At the same time, there are concerns in repatriating items that ultimately affect their return.

Inorganic and organic pesticides have been widely used in the past to treat artifacts stored in natural history collections to preserve them from various types of pests. Many artifacts and Native American artifacts in particular represent a wide range of materials such as animal feathers, furs, nails, claws, and bone, as well as plant fiber, textile, and wood.

Collection Forum 2017; 31(1):23–33

These biological materials are a source of food for various pests. Pesticides were applied to artifacts for their preservation without considering long-term consequences. Anthropologists of the 19th and early 20th centuries could not have imagined that the artifacts might be repatriated to the tribe of origin at some point in the future and were likely unaware of the dangers pesticides can pose to human health (Eco-Hawk 2002).

A surprisingly wide variety of pesticides have been used for artifact preservation. Inorganic pesticides were most often in the form of mercury and arsenic salts, including mercuric chloride, arsenous acid, arsenic trioxide, and potassium arsenate (Hawks and Williams 1986; Goldberg 1996; Cross and Odegaard 2009). These pesticides were applied to the artifacts in the form of powder or paste, or by dipping artifacts in a bath of solutions of these compounds to saturate the exteriors with pesticides. In the mid-20th century, newer organic pesticides such as *p*-dichlorobenzene, naphthalene, and dichlorodiphenyltrichloroethane (DDT) were used (Goldberg 1996; Hawks 2001). These were often applied to the artifacts in a powder form or by placing naphthalene-based moth balls in a drawer or storage area containing the artifacts to serve as a fumigant (Hawks and Williams 1986). Most of these pesticides are resistant to biodegradation and can persist for years on these artifacts.

The passage of the Native American Graves Protection and Repatriation Act (NAGPRA) in 1990 has brought increased attention and concern to the issue of pesticide contamination on artifacts in the United States. NAGPRA established a process whereby federally recognized tribes can request the return of cultural items from institutions, agencies, and museums that receive federal funding (US Congress 1990). These cultural items include objects of cultural patrimony, human remains, funerary objects, and sacred objects. Given the wide use of pesticides to treat these artifacts and their resistance to degradation, contaminated artifacts represent a potential health hazard to people coming in contact with them (National Park Service 1998; Kearney 2001). Since many museums and collectors did not maintain complete records indicating the types of pesticides used to treat each artifact, chemical analysis represents the only reliable means for determining the types and levels of pesticide contamination on specific artifacts (Palmer et al. 2001; Sirois et al. 2008).

The most critical issue to assessing whether or not an artifact has been treated with pesticides is the sampling process. The selection of sampling location(s) on the artifact is an important consideration since many of these artifacts are made from more than one material and color. Different materials may or may not have been treated with pesticides, and different locations may contain widely varying concentrations. Tribal rules must be followed on who can handle the objects, and some tribal traditions prohibit non-native people and women from viewing or touching their artifacts. In rare cases, some museums or tribal members may allow destructive sampling through removal of a small piece of the artifact from a nonvisible location on the object. In most cases, only nondestructive sampling is allowed, which in turn has implications for the analytical methods used for pesticide determination. Most often, this type of sampling can be accomplished either by using a direct scanning or imaging-type analytical method, or by using a cotton swab or other applicator soaked in a suitable solvent to remove the contamination from a specific location on the surface of an artifact for subsequent lab-based analysis. It should be noted the results of any swab-based testing depends on the sampling location, and for practical reasons a compromise must be made in choosing this location because assessing contamination over the entire surface of an artifact is typically neither practical nor possible.

Several articles provide an excellent review of various analytical methods used to monitor inorganic and organic pesticides on artifacts (Palmer 2001; Sirois 2001; Sirois and Sansoucy

2001). Spot tests represent a simple and inexpensive means for nondestructive sampling and analysis of inorganic pesticides. These use a swab, reagents, and a colorimetric reaction to provide a visual estimate of the levels of arsenic and mercury on the surface of artifacts (Feigl and Anger 1972; Henry 1996; Osumex 2016). However, several studies have shown that spot tests can give false positives and consistently low results (Found and Helwig 1995; Constanzo 1999; Sirois 2001). A more common method to determine the presence of inorganic pesticides is by using portable or handheld X-Ray Fluorescence (XRF) analyzers. These provide nondestructive testing, analysis times on the order of a minute, detection limits down to low part per million (ppm) levels, and the ability to monitor multiple toxic elements (Janssens et al. 2000; Sirois 2001; Palmer et al. 2009). More conventional atomic spectrometry techniques such as Flame Atomic Absorption Spectrophotometry or inductively coupled Plasma Atomic Emission Spectrometry (ICP-AES) can be used to test samples that are in the form of either actual portions of the object (destructive testing) or swabs (nondestructive testing). These techniques are more costly, complex, and time consuming than spot tests or XRF (PerkinElmer n.d.). Microwave Plasma-Atomic Emission Spectrometry (MP-AES), a relatively new atomic spectrometry technique used in this work, is less expensive than ICP-AES and does not require the use of argon. Determining organic pesticides on artifacts is more challenging due to wide variety of these species that have been used to treat these artifacts, the lower levels found on artifacts as they slowly volatilize or degrade over time, and the cost and complexity of the methods used to measure them. Gas Chromatography (GC) coupled with Mass Spectrometry (MS) is the method of choice here due to its ability to separate complex mixtures and provide definitive identification of specific pesticides at trace levels (Palmer et al. 2003).

The goal of this study was to assess pesticide contamination on nine different artifacts that were recently repatriated from the Benton County Historical Society to the Karuk Tribe in northern California. Sampling and analysis of these artifacts was achieved nondestructively to protect the physical integrity of the artifacts, particularly since many of these artifacts are meant to be handled or worn during sacred ceremonies (Odegaard and Sadongei 2001). XRF analysis for inorganic pesticides was performed on site at the People's Center, the Karuk Tribe's museum and cultural center, located in Happy Camp, California. Swab samples were collected to assess surface contamination of the artifacts with inorganic and organic pesticides, with subsequent analysis performed using MP-AES and GC/MS at San Francisco State University. This work provides an example of how to effectively design and execute a study involving the use of nondestructive sampling and modern analytical methods to assess for pesticide contamination on NAGPRA-related artifacts.

Methods

Nine artifacts were tested for inorganic and organic pesticides. These artifacts represent a diverse range of samples and a wide variety of natural materials including wood, plant fibers, grass, feathers, shells, glass, bones, and leather. Table 1 provides a list of the repatriated artifacts, and Figure 1 depicts some of these artifacts. Sampling of artifacts was conducted at the People's Center via both direct testing using XRF and acquisition of swab samples from the surface of the artifacts for subsequent analysis by a graduate student at San Francisco State University.

Determination of arsenic, mercury, and lead contamination on the artifacts was conducted using an Olympus-Innov-X Delta premium model handheld XRF analyzer. Two different locations were monitored on each artifact. All testing was performed with the XRF analyzer in a test stand to minimize radiation exposure, with the exception of several

Table 1. Details of the nine artifacts repatriated to the Karuk Tribe.

Description	Materials
Cooking basket	Spruce root, hazel stick, five-fingered fern, and bear grass
Ceremonial cap	Hazel stick, dyed woodwardia, spruce root, five-fingered fern, and bear grass
Bow	Yew and sinew
Arrow	Wood, sinew, and feather
Wooden projectile	Wood
Necklace	Dentalium, glass black beads, and twine
Elk horn	Elk horn
Musical drum	Tanned leather and wood
Drum mallet	Tanned leather and wood

large objects including the musical drum, bow, and arrow, which would not fit inside the test stand. The analyzer was programmed to perform a 1-minute analysis in Soil Beam 2 mode, which provides the best detection limits for the toxic elements of interest.

Figures 2 and 3 show XRF spectra of certified reference materials (CRMs) containing 100 and 1,000 ppm arsenic and mercury, respectively. The presence of arsenic is indicated by K_α and K_β peaks at 10.54 and 11.73 keV, respectively, at the expected intensity ratio of 5:1. The presence of mercury is indicated by the presence of the L_α and L_β peaks at 9.99 and 11.82 keV, respectively, at the expected intensity ratio of 1:1. These same principles

Figure 1. Photographs of some of the objects. Clockwise from top left: ceremonial cooking basket, ceremonial cap with the *apxankuuykuuy* (no English translation) design, musical drum and wooden projectile.

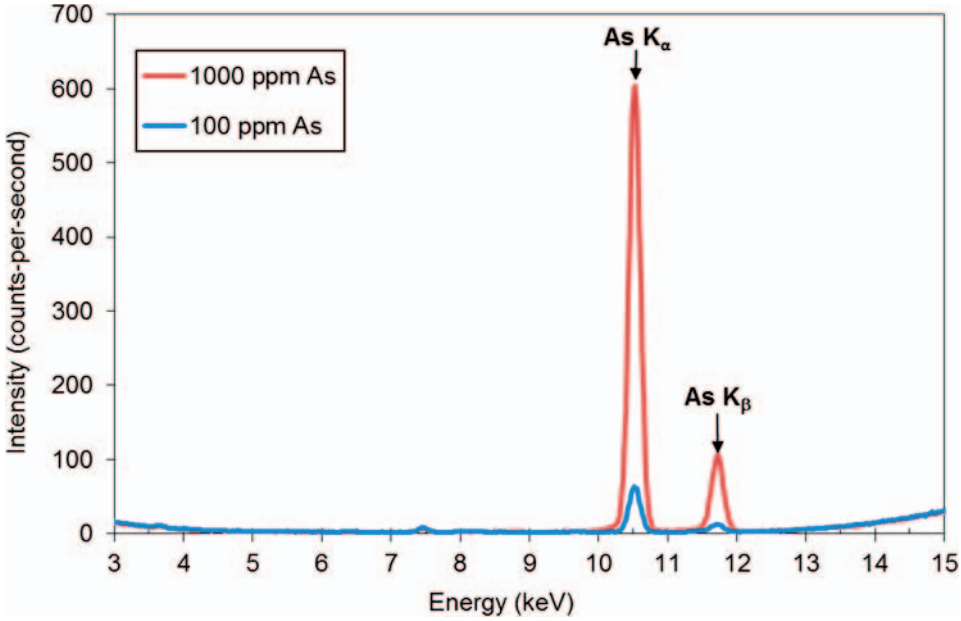

Figure 2. XRF spectra of CRMs containing 100 and 1,000 ppm arsenic.

were used to identify the presence of arsenic and mercury in the artifacts using visual inspection and interpretation of all sample spectra to ensure reliable identification, which is important as the onboard algorithms on handheld XRF analyzers can in some cases give false positives. A blank sample containing pure cellulose was also analyzed to ensure that

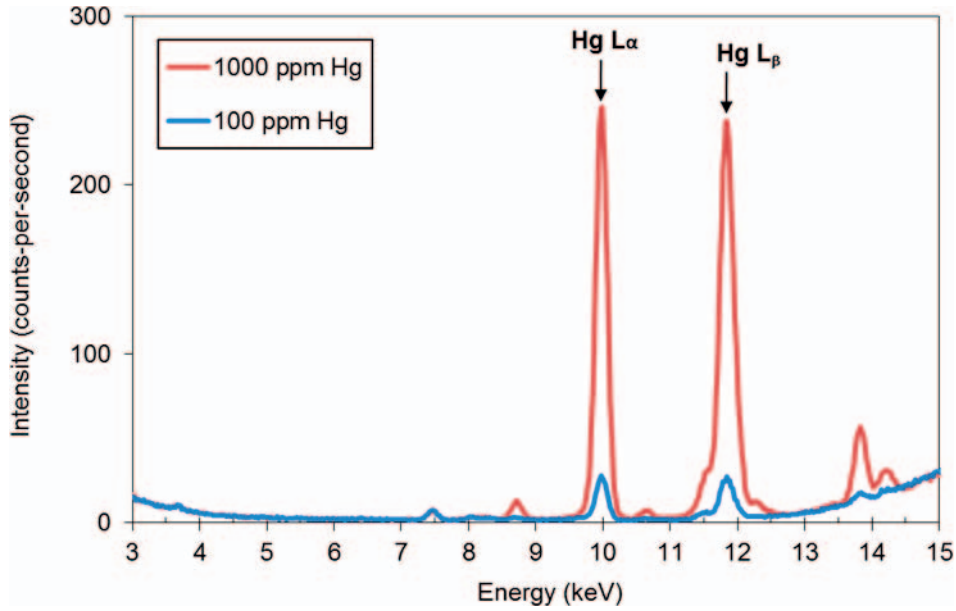

Figure 3. XRF spectra of CRMs containing 100 and 1,000 ppm mercury.

the XRF analyzer window was not cross-contaminated with the elements of interest. Concentrations of the toxic elements of interest are estimates obtained from the XRF analyzer software based on a factory calibration and Compton Normalization, with approximate limits of detection (LODs) in the 1–10 ppm range.

Swab samples and MP-AES were used to assess whether arsenic, lead, and mercury detected via XRF on the surface of some artifacts were either naturally occurring or the result of intentional pesticide usage. Swab samples were acquired from several artifacts at the People's Center using a cotton swab soaked in deionized water. An area the size of approximately 1 cm^2 was swabbed on several objects for which XRF testing indicated the presence of arsenic, lead, and/or mercury, with one swab obtained per sample. These swabs were stored in vials and transported to San Francisco State University for subsequent extraction and analysis. A trip blank made from a swab dipped in water was analyzed as well to demonstrate nondetectable levels of the target elements due to trace contaminants in the swab, vial, or transport process. Metals were extracted from swabs by adding 10 mL of deionized water and 2 mL of concentrated nitric acid to the swab vials. The three samples and the trip blank vials were agitated using an electric shaker for 3 hours at room temperature. The extract liquids were quantitatively transferred to 50-mL volumetric flasks and diluted to volume with deionized water. Certified 1,000-ppm aqueous stock solutions and 100-mL volumetric flasks were used to prepare three working standards for arsenic (0.1, 1, and 10 ppm) and four working standards for lead (0.1, 1, 10, and 100 ppm). Mercury was not measured because it cannot be detected on this particular model of the MP-AES instrument. All samples and standards contained the same proportion of nitric acid (2 mL of concentrated nitric acid per 100 mL volume).

An Agilent model 4100 MP-AES system was tuned to the optimal viewing positions, nebulizer pressures, and emission wavelengths for arsenic and lead (193.695 and 405.781 nm, respectively). Emission was monitored for 10 seconds using automatic background correction. Three readings were performed on each standard and sample to estimate reproducibility. Results from the analyses were imported into Microsoft Excel to generate calibration curves and compute sample concentrations. Linear least squares fits on the blanks and standards gave correlation coefficients (R^2 values) of 1.000 for both arsenic and lead. Where an element was detected, concentrations were converted from units of ppm in the sample extracts ($\mu g/mL$) to $\mu g/cm^2$ in the samples by factoring in the 50-mL extract volume and 1-cm^2 area sampled. The LODs in the sample extracts were estimated to be 0.04 ppm for arsenic and 0.004 ppm for lead, and the reproducibility was determined to be less than 5% (relative standard deviations) for both elements. Any sample concentrations found below the LODs were reported as not detected (ND).

For organic pesticide analysis via GC/MS, swab samples were collected from a 1-cm^2 area using a cotton swab dipped in acetone. These swabs were stored in vials and transported back to San Francisco State University for extraction and analysis. A trip blank made from a swab dipped in acetone was analyzed as well to demonstrate nondetectable levels of the organic pesticides due to trace contaminants in the swab, vial, or transport process. The organic pesticides were extracted from the cotton swabs using 5 mL of HPLC-grade methanol 0.1, added to the vials, followed by agitation on an electric shaker for 24 hours at room temperature. The extracts were transferred to 10-mL volumetric flasks and diluted to volume using methanol. A certified stock solution containing *p*-dichlorobenzene, naphthalene, and DDT was used to prepare 0.1, 0.5, and 1.0 $ng/\mu L$ standards. D_8-naphthalene was added to each sample extract and standard at a concentration of 10 $ng/\mu L$ in the 10-mL flasks, and

served as an internal standard to correct for drift in instrument response and provide more accurate quantitative results.

The GC/MS system used for analysis included a CTC A200S CombiPal autosampler, Varian 3900 GC, and Saturn 2100T ion trap MS system. 1.0-μL volumes of the blank, standards, and samples were injected into a 200°C injector operated in splitless mode. A 25-m, 0.25-mm ID, 0.1-μm thick J&W DB5-ms column was used to effect separation of the internal standard, target pesticides, and any other extractable organic species in the samples. The column oven was programmed to 60°C for 5 minutes, ramped at 25°C/min, then held at 280°C for 15 minutes for a total run time of 28.8 minutes. The transfer line was set to 200°C and the ion trap manifold to 100°C. The ion trap was operated in electron ionization mode using automatic gain control (AGC), a scan range of m/z 40 to 650, and auto setup-recommended values for filament emission, multiplier high voltage, and AGC target values. Three replicate analyses were performed on each standard and samples to assess reproducibility. Organic pesticides were identified on the basis of both a retention time match with an authentic standard and simultaneous maximization of the three major ions at that retention time, which is the same protocol used in most Environmental Protection Agency methods for organic pesticide analysis. Response of each pesticide and the internal standard were computed from the respective peak areas of the base peak (most intense ion) of each species (m/z 146 for *p*-dichlorobenzene, m/z 128 for naphthalene, m/z 136 for D_8-naphthalene, and m/z 235 for DDT). Peak area data were entered into Excel to generate calibration curves and compute pesticide concentrations. Calibration curves were created by plotting the relative response (peak area of pesticide divide that of the internal standard) as a function of the concentration of the blank and the standards. Linear least squares fits gave correlation coefficients (R^2 values) of 0.9914, 0.9921, and 0.8977 for *p*-dichlorobenzene, naphthalene, and DDT, respectively. Ten replicate analyses of the 0.5 ng/μL standard were performed to determine the LOD and assess reproducibility. The LODs were estimated to be 0.08, 0.1, and 0.2 ng, and the reproducibility was determined to be 5%, 8%, and 17% (relative standard deviations) for *p*-dichlorobenzene, naphthalene, and DDT, respectively.

Results and Discussion

XRF Analysis of Artifacts

Table 2 shows the results from XRF testing of two locations on each artifact. Most of the artifacts had either very low or nondetectable levels of arsenic, mercury, and lead, and the presence of such low levels of these elements suggests that they might be naturally occurring in the materials in the artifacts. It is also important to reiterate that this XRF testing provides semiquantitative results, and the results and conclusions are ultimately limited by the choice of the sampling location.

The necklace was found to have the highest levels of lead and arsenic at 21,000 (2.1%) and 2,300 ppm (0.23%), respectively. These high levels can be attributed to the presence of these elements in the glass beads, and not from their use as pesticide agents for artifact preservation, and hence do not represent a risk because these elements are immobilized in the glass. XRF spectra of the white and black beads are shown in Figure 4. The white beads were made from dentalium shells, and the corresponding XRF spectrum shows high levels of calcium and strontium and low levels of lead. The black beads were made from glass, and the corresponding XRF spectrum shows high levels of arsenic and lead and low levels of manganese and iron. Although the presence of arsenic is not obvious from this spectrum,

Table 2. Estimated concentrations of arsenic (As), mercury (Hg), and lead (Pb) on the artifacts as determined by XRF. The more remarkable findings representing higher concentrations are in boldface. ND denotes not detected.

Artifact description	As (ppm)	Hg (ppm)	Pb (ppm)
Ceremonial cooking basket (bottom)	9	ND	47
Ceremonial cooking basket (side)	6	ND	42
Ceremonial cap (top)	ND	ND	38
Ceremonial cap (side)	ND	ND	33
Bow (end)	ND	7	17
Bow (red paint)	ND	86	13
Arrow (feather)	6	ND	49
Arrow (stick end)	34	ND	97
Wooden projectile (painted wood)	ND	47	34
Wooden projectile (bare wood)	ND	ND	21
Necklace (white beads)	ND	ND	16
Necklace (black beads)	**2,300**	ND	**21,000**
Elk horn (front/side)	30	ND	74
Elk horn (end)	41	ND	53
Musical drum (bottom)	20	ND	**140**
Musical drum (red color)	72	ND	**330**
Drum mallet (round leather)	**1,000**	84	**4,900**
Drum mallet (end part)	ND	23	71

and its positive identification is complicated by a spectral interference (arsenic and lead give peaks at 10.54 and 10.55 keV, respectively), the XRF software also indicates it to be present, and an expanded view of this spectrum showed the presence of a low-intensity arsenic K_α peak at 11.73 keV.

The leather in the drum mallet was found to contain relatively high levels of lead (4,900 ppm or 0.49%) and arsenic (1,000 ppm or 0.1%), whereas the wooden stick portion

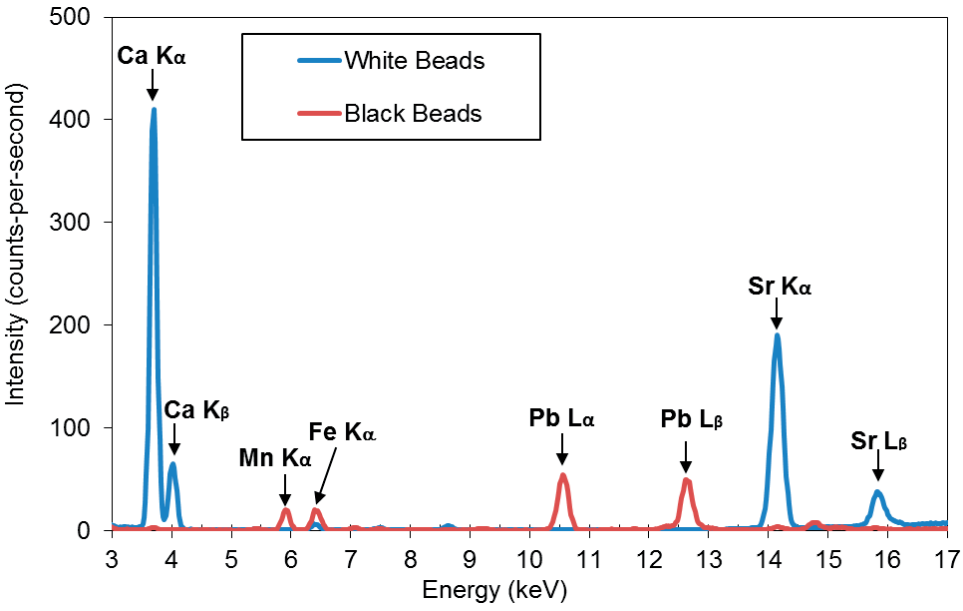

Figure 4. XRF spectra of white and black beads in the necklace. The white beads contain high levels of calcium (Ca) and strontium (Sr), and the black beads contain significant levels of lead (Pb).

contained low levels of lead (71 ppm) and nondetectable levels of arsenic. These results can be attributed to the process and chemicals used to treat, cure, and paint the leather material on this artifact. Low levels of mercury were detected in red-painted areas on the bow, wooden projectile, and drum, and are most likely due to the presence of this element in the cinnabar (mercuric sulfide) pigments used to decorate these artifacts (Cross and Odegaard 2009).

Previous case studies have shown that where arsenic and mercury-containing pesticide agents were used to treat artifacts, the concentrations were found to be higher than 10,000 ppm or 1% (Feigl and Anger 1972; Hawks and Williams 1986; Henry 1996; Palmer et al. 2006; Sirois et al. 2008). Other than the exceptions noted above (beads on the necklace, leather end of the drum mallet, and drum), none of the artifacts tested in this study showed the presence of arsenic, lead, or mercury above 100 ppm or 0.01%. These results indicate that these items were most likely not treated with arsenic, lead, or mercury-containing pesticide agents. It should be noted that cross-contamination can occur where artifacts are stored in areas were pesticides have been used. While it is difficult to rule out this possibility, the levels of arsenic, lead, and mercury found on these artifacts are low enough to suggest that this did not occur and can be attributed to trace levels of these elements in the native materials.

MP-AES Analysis of Swab Samples

MP-AES analyses of swab samples were conducted to test for the presence of toxic elements on the surface of some of the artifacts. The necklace and drum mallet were excluded from this testing for reasons described above, and this testing focused on the elk horn, bow, and drum, for which the pigments on the artifacts and/or XRF results indicated the possible presence of toxic elements. The results of this testing are shown in Table 3. None of these tests indicated the presence of arsenic on the surface of these artifacts. Although low levels of lead were found on each, these levels were comparable to that of the trip blank and indicate contamination of the swab or vials used for this sample. If indeed arsenic or lead based pesticide agents were used to treat these artifacts, this testing would indicate much higher levels of these elements (National Park Service 1998).

GC/MS Analysis of Swab Samples

Analysis of swab samples acquired from the surface of each artifact showed nondetectable levels of *p*-dichlorobenzene, naphthalene, and DDT. Additional manual evaluation of GC/MS data on each sample likewise indicated nondetectable levels of other common organic pesticides such as thymol, lindane, and dieldrin. Note that this method is quite sensitive and capable of detecting these species down to subnanogram levels. Given that artifacts treated with these pesticide agents have been found to contain levels as high as

Table 3. MP-AES results for arsenic and lead in swab samples.

Samples	Substance	
	Arsenic ($\mu g/cm^2$)	Lead ($\mu g/cm^2$)
Trip blank	ND	9
Elk horn (front side)	ND	9.5
Bow (red paint)	ND	8.7
Musical drum (red color)	ND	9.2

2,900 ppm or 0.29% (Palmer et al. 2006), these results suggest that these Karuk artifacts were not treated with these organic pesticides.

Conclusions

Over the past two decades, Native American tribes have increasingly used NAGPRA as a means to reclaim their cultural and religious heritage items from public art collections and museums. However, the possibility that these items may be contaminated with toxic chemicals has cast a shadow over tribes' aspirations. Moreover, tribes do not have the resources to conduct testing for such contamination, and there are relatively few published studies of the types and levels of inorganic and organic pesticides on Native American artifacts. The Sirois, Odegaard, and Palmer groups have frequently used XRF to monitor inorganic pesticides such as arsenic, mercury, and lead on artifacts (Sirois and Sansoucy 2001; Palmer et al. 2003; Odegaard et al. 2006; Cross and Palmer 2008). Although GC/MS has been used to assess for organic pesticides on artifacts, only a few studies are published in peer-reviewed journals (Glastrup 1987; Palmer et al. 2003; Palmer et al. 2006). Only one article provides a summary of results from a number of different case studies of this type to assess the frequency and levels of inorganic and organic pesticide contamination on Native American artifacts (Palmer et al. 2006).

This study will hopefully serve to renew tribal repatriation efforts, because it provides a model for how to conduct testing through the use of three different nondestructive methods to assess whether or not these particular artifacts had been treated with pesticide agents for preservation purposes. Other than high levels of arsenic in a necklace, lead in the beads, and mercury in the painted surfaces of the drum mallet from the use of a vermillion-based pigment used to decorate the artifacts, the levels of arsenic, mercury, and lead found on these nine artifacts were low enough to suggest that they were not treated with inorganic pesticide-based agents. Additional testing performed to assess for the presence of common organic pesticides showed nondetectable levels on the surface of the artifacts. Although there are caveats to this research due to the nature of limited testing (two samples per artifact, nondestructive surface sampling using swabs versus destructive extraction of a portion of the object), these results indicate that these artifacts have not been treated with the most common inorganic and organic pesticide agents, and hence can be handled and used without assuming significant risk to these toxic substances.

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