

PESTICIDE CONTAMINATION ON NATIVE AMERICAN ARTIFACTS—METHODS, RESULTS FROM SIX CASE STUDIES, AND NEXT STEPS

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Abstract.—This work describes several case studies involving the determination of pesticide contamination on objects from the Treganza Museum at San Francisco State University, the Phoebe Hearst Museum of Anthropology at the University of California at Berkeley, and the Elem Pomo, Hoopa, Karuk, and Yurok tribes of California. The focus of these studies was determination of arsenic and mercury via Flame Atomic Absorption Spectrophotometry and determination of six organic pesticides via Gas Chromatography/Mass Spectrometry. Mercury was detected in 31% of the samples at concentrations up to 16.6% by weight. Significant contamination was found in several different collections, with mercury and DDT concentrations at levels that may be of toxicological significance. DDT was detected in 44% of the samples with concentrations as high as 2,900 parts per million (ppm) or 0.29% by weight. Native Americans, museum professionals, and anyone handling potentially contaminated objects should continue to take appropriate measures to minimize exposure. In the future, it is hoped that government granting agencies will facilitate efforts to provide for free testing of pesticide contamination for tribes and museums, and that researchers will develop improved sampling techniques, analytical methods, and exposure and risk assessment data that more definitively address people's concerns about their safety.

INTRODUCTION

In the past, it was standard practice for museums to treat artifacts in their possession with arsenic, mercury, and other pesticides (Goldberg 1996, Hawks 2001). The purpose of this was to protect the objects from possible destruction by fungi, insects, and rodents. Museum staff working with these pesticides, handling contaminated objects, or breathing the air in rooms where they are stored may be exposed to these potentially toxic chemicals. Despite numerous symposia and publications on this issue, there is surprisingly little published work which shows the extent of this contamination within specific museums; only one study reported an evaluation of the potential health hazards of DDT exposure within a museum in the U.S. (Pryor 1982). To the best of the knowledge of the primary author, there are no published epidemiological studies that retrospectively evaluated the health of museum workers who may have been exposed to these pesticides.

Passage of the Native American Graves Protection and Repatriation Act (NAG-PRA) in 1990 allowed for repatriation of artifacts to federally recognized tribes. While tribes may be aware that these items could be contaminated, there is often little or no a priori information as to the types and levels of contamination that may be present. In most cases, no records were kept to document the types, quantities, and frequency of pesticide applications to each object within a collection. Hence, chemical analysis represents the only means for determining whether or not an item has been contaminated. Two publications provide a thorough review

of the various analytical methods that can be used for this purpose (Palmer 2001, Sirois and Sansoucy 2001).

Many tribes are actively pursuing repatriation of sacred artifacts, and the most common question encountered in this process is whether or not their items are contaminated. While some tribes and museums have resorted to the use of relatively inexpensive spot tests for this purpose, these tests often yield false positives (Found and Helwig, 1995) and spot tests for organic pesticides such as naphthalene or DDT are not available. Palmer and his students at San Francisco State University (SFSU) have been performing these analyses *gratis* or for a nominal charge to cover the cost of the supplies and standards. They have completed six case studies to date including analyses of items from the Treganza Museum at SFSU, the Phoebe Hearst Museum at the University of California at Berkeley, and the Hoopa, Elem Pomo, Karuk, and Yurok tribes of California. This manuscript describes the various methods used for sampling and analysis, summarizes the results from the six case studies, and concludes with some suggestions for future work.

METHODS

The artifacts of interest in this work included items such as baskets, headdresses, deerskin aprons, and baskets. In each case study, the issue of sampling has been an important consideration (Caldararo et al. 2001). From the standpoint of the tribes, an artifact is sacred and hence should be sampled in a manner consistent with their beliefs. For some tribes, this does not preclude the use of destructive sampling, in which a small amount of the artifact is removed for subsequent testing. For some case studies, nondestructive sampling methods using swabs and/or wipes were employed so as to minimize damage to the objects. While it should be understood that nondestructive sampling can underestimate the amount of contamination present, as it will neither remove 100% of the surface contamination nor be able to assess subsurface contamination, it may be an acceptable means for providing a sample that can answer the question as to whether or not the item is contaminated.

Another important consideration is where to sample the artifact. If possible, more than one sample from each artifact is desirable, as pesticides may not have been applied to the entire object. Ideally, a composite sample representing several locations on an object would be used as the most cost efficient means of determining whether or not an artifact was contaminated via a single analysis. Where both heavy metal and organic pesticide contamination were to be assessed, a separate sample was required for each of the two different types of analytical methods required.

In each case study, sampling was performed in accordance with the wishes of the tribes and/or museums. Where destructive sampling was used, a small piece of an artifact was removed from an inconspicuous area with typical sample sizes of a few square millimeters and sample masses on the order of a few milligrams. Where nondestructive sampling was used, several swabs wetted with an appropriate solvent (water for arsenic and mercury analysis and acetone for organic pesticide analysis) were rubbed over a 10-cm² sized area of the artifact. Once acquired, the sample was placed into a clean vial, which was sealed and sent to SFSU for subsequent analysis.

The analytical methods used in this work are described in more detail elsewhere (Palmer 2001, Palmer et al. 2003). Briefly, Flame Atomic Absorption Spectrophotometry (FAAS) was used to measure arsenic and mercury, and Gas Chromatography/Mass Spectrometry (GC/MS) was used to measure organic pesticides. The scope of the GC/MS analyses was limited to no more than six organic pesticides, which included p-dichlorobenzene, naphthalene, thymol, dieldrin, lindane, and DDT. All of these analyses were performed by undergraduate students majoring in chemistry, biochemistry, or environmental studies at SFSU. A number of quality assurance and quality control (QA/QC) procedures were followed to ensure generation of reliable data. Standard operating procedures (SOPs) were developed for sampling and analysis. Each student was trained in the relevant analytical methods. Certified reagents were used to prepare the standards used as the basis for quantitation. Method, field, and trip blanks were analyzed to ensure negligible levels of contamination in the media used for sampling (i.e., vials, swabs, solvents). Precision was assessed via replicate measurements of samples and standards. Limits of quantitation (LOQs) and limits of detection (LODs) were computed to qualify results where sample concentrations fell below the limits of reliable quantitation and detection, respectively. In some cases, separate standards and spikes of sample extracts were performed to assess accuracy of quantitation. Finally, each and every analytical result was verified and validated by Palmer prior to documenting them in a report to the tribe or museum.

CASE STUDY RESULTS

The results from six case studies completed to date are shown in Tables 1 to 3, which provide summaries of mercury testing via FAAS, organic pesticide testing via GC/MS, and cumulative results from all six studies. In some of the case studies, only metal analyses or organic pesticide analyses were performed due to the limited number of samples available. Note that arsenic was not detected in any of the samples in these case studies. While this does not preclude the presence of arsenic in these samples at concentrations below the LODs, these results indicate that arsenic was not used for preservation of these particular objects. It should be noted that QA/QC procedures demonstrated both accurate detection and quantitation of arsenic. For confirmation of accurate detection, a “blind” check standard was analyzed and found to give positive detection for arsenic. For confirmation of accurate quantitation, either a blind check standard prepared by M. Fang was analyzed and found to give an experimentally determined concentration of arsenic within 5% of the true value, or a sample was spiked with a known concentration of arsenic, analyzed, and gave a percent recovery close to theoretically expected value of 100%.

The first case study involved the analysis of arsenic and mercury on five items in the Treganza Museum collection at SFSU in 1999, which included a musical instrument, a fossil, cotton packing, debris, and a bag from a drawer where these items were stored. Here, destructive sampling methods were employed and a total of nine samples were acquired from these items. The musical instrument showed the highest level of contamination with 2.7% mercury (on a weight-weight basis) detected in the sample. The presence of mercury on the other items demonstrates that mercury was either applied to the entire contents of the drawer and/or migrated to other items.

Table 1. Summary of mercury analyses. Where destructive sampling was used, concentrations are reported on weight/weight basis in units of percent; where swab sampling was used, concentrations are reported in units of $\mu\text{g}/\text{cm}^2$.

Case study	Pesticide agent	Number of samples	Frequency of detection	Range of concentrations
SFSU	mercury	9	100%	0.4%–2.7%
Hoopa	mercury	28	32%	ND–16.6%
Elem	mercury	25	0%	ND
Yurok	mercury	22	73%	ND–3.3%
UC Berkeley	mercury	25	4%	ND–47 $\mu\text{g}/\text{cm}^2$

Table 2. Summary of organic pesticide analyses. Where destructive sampling was used, concentrations are reported on weight/weight basis in units of ppm; where swab sampling was used, concentrations are reported in units of $\mu\text{g}/\text{cm}^2$.

Case study	Pesticide agent	Number of samples	Frequency of detection	Range of concentration
Hoopa	p-dichlorobenzene	29	17%	ND–130 ppm
Karuk	p-dichlorobenzene	20	0%	ND
Yurok	p-dichlorobenzene	22	5%	ND–3 $\mu\text{g}/\text{cm}^2$
Hoopa	naphthalene	29	77%	ND–1830 ppm
Karuk	naphthalene	20	0%	ND
Yurok	naphthalene	22	10%	ND–88 ppm
Hoopa	thymol	29	3%	ND–10 ppm
Karuk	thymol	20	0%	ND
Yurok	thymol	22	0%	ND
Hoopa	lindane	29	7%	ND–30 ppm
Karuk	lindane	20	0%	ND
Yurok	lindane	22	0%	ND
Hoopa	dieldrin	29	0%	ND
Karuk	dieldrin	20	0%	ND
Hoopa	DDT	29	40%	ND–130 ppm
Karuk	DDT	20	55%	ND–2900 ppm
Yurok	DDT	22	67%	ND–1698 ppm

Table 3. Summary of results from all six case studies.

Pesticide agent	Number of samples	Frequency of detection	Range of concentration
mercury	105	31%	ND–16.6%
arsenic	105	0%	ND
p-dichlorobenzene	71	8%	ND–130 ppm
naphthalene	71	34%	ND–1830 ppm
thymol	71	1%	ND–10 ppm
lindane	71	3%	ND–30 ppm
dieldrin	49	0%	ND
DDT	71	44%	ND–2900 ppm

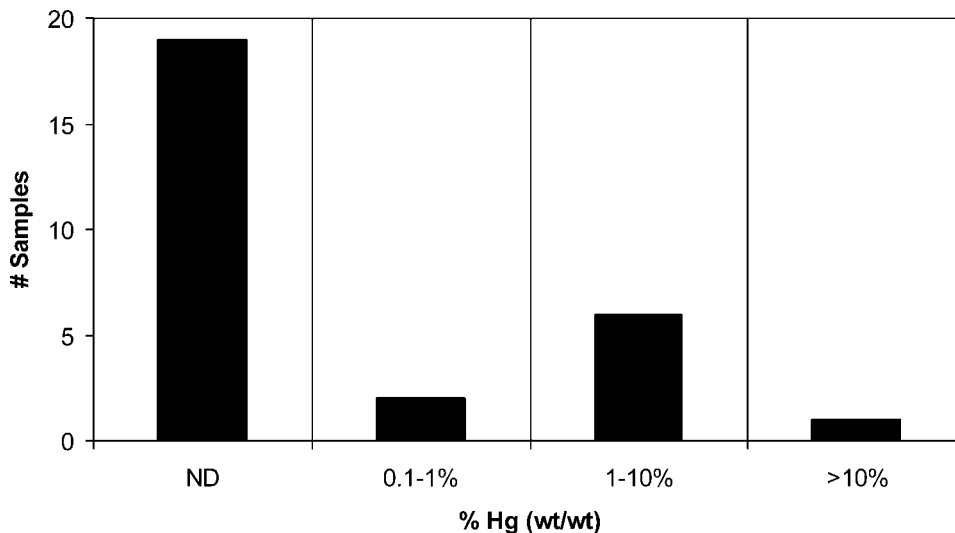


Figure 1. Results from Hoopa case study showing the frequency distribution of mercury in the samples. For the six samples where mercury was detected, the mean concentration was 4% with the standard deviation of 5%.

The second case study involved analysis of arsenic, mercury, and six organic pesticides on 17 items repatriated to the Hoopa tribe in 1999. Full details on this study including methods and results are provided elsewhere (Palmer et al. 2003). Here again, destructive sampling methods were used with the permission of the Hoopa curator responsible for repatriation of these objects (Caldararo et al. 2001). A total of 58 samples were acquired: 29 for arsenic and mercury analyses and 29 more for GC/MS analyses. Mercury was detected in nearly a third of the samples (32%) at concentrations as high as 16.6% for some of the smaller samples of feathers. Naphthalene was detected on nearly 80% of the samples with concentrations as high as 1800 parts per million (ppm) (equivalent to 0.18%). DDT was detected in 40% of the samples at concentrations as high as 130 ppm. Figures 1 and 2 show frequency distributions for mercury and naphthalene, and indicate the typical concentrations found and the variability in the data. For the nine samples where mercury was detected, the average concentration was 4% with a standard deviation of 5%. For the 23 samples where naphthalene was detected, the average concentration was 202 ppm with a standard deviation of 412 ppm. These results show wide variability in the concentrations detected, which is understandable given the heterogeneity of the pesticide application process and the different types of materials sampled.

The third case study focused on analysis of arsenic and mercury on 25 items from the Phoebe Hearst Museum at the University of California Berkeley (UC Berkeley). One sample from each object was acquired using *either* destructive or swab-based sampling for subsequent FAAS analyses at SFSU. Several additional swab samples were acquired from each object for subsequent spot tests by Fang. Mercury was not detected via FAAS, with the exception of one swab sample in which 47 $\mu\text{g}/\text{cm}^2$ of mercury was found. Of particular interest in this study was comparison of FAAS results with those from spot tests. FAAS results did not

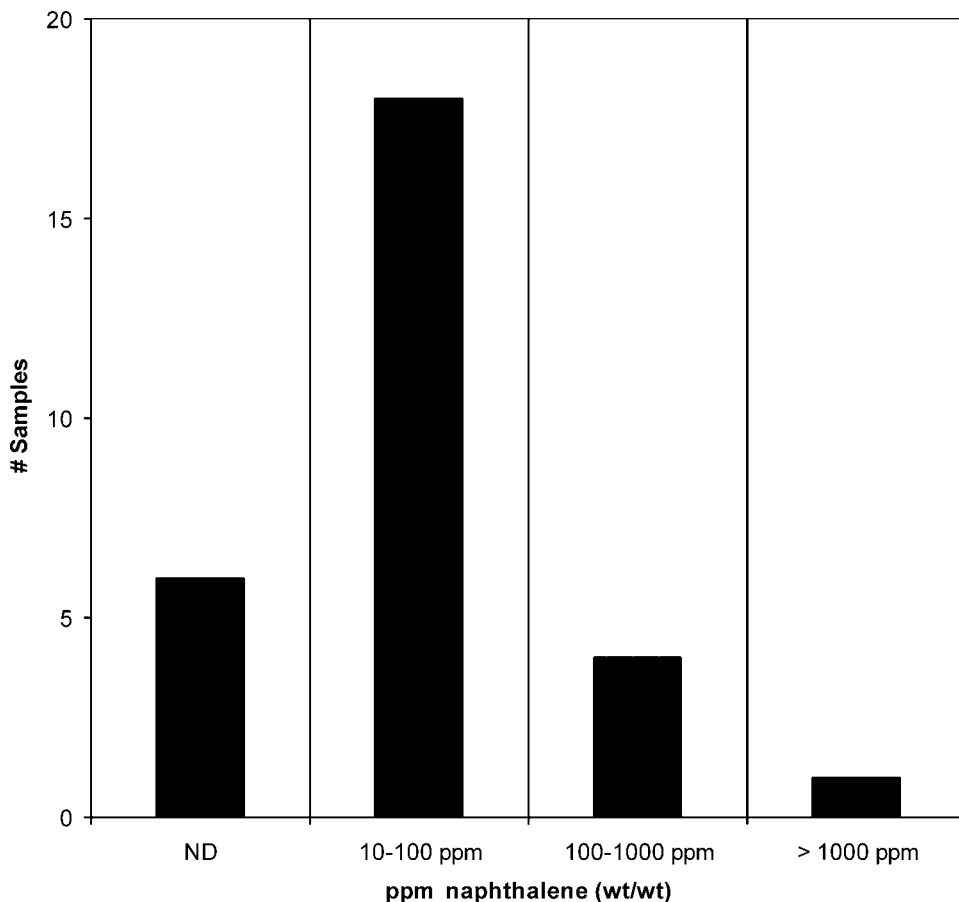


Figure 2. Results from Hoopa case study showing the frequency distribution of naphthalene in the samples.

show the detection of measurable levels of arsenic in any of these samples, whereas spot tests indicated the presence of arsenic in trace amounts in five samples (<0.025 mg/L in three samples and 0.1 mg/L in two samples). Assuming the arsenic spot test to be reliable (Found and Helwig 1995), these conflicting results may be due to the different LODs of the methods: typical LODs from FAAS were approximately 0.2 ppm whereas the LODs from spot tests were less than 0.1 ppm. FAAS and spot tests for mercury on four of these same samples agreed in that no mercury was detected on all but one of the objects. Here, FAAS indicated $47 \mu\text{g}/\text{cm}^2$ whereas the spot test showed no detection. The negative spot test result may well be the result of a desensitizing type of interference (Found and Helwig 1995). While it is possible that FAAS results may be incorrect, QA/QC data indicated accurate detection and quantitation of arsenic and mercury via FAAS in two blind unknowns prepared by Fang, and it is generally accepted that FAAS provides greater selectivity based on the use of a selective wavelength of absorption for detection and quantitation based on this method's greater selectivity. Clearly, the difficulties in correlating results from spot tests to those from FAAS

points out the need for a more rigorous intercomparison between these two methods.

The fourth case study involved determination of arsenic and mercury on 16 objects to be repatriated from the California Department of Parks and Recreation Museum in Sacramento to the Elem Pomo tribe. The tribe agreed to acquisition of 25 samples via destructive sampling. Neither arsenic nor mercury was detected in any of the samples. QA/QC data showed recoveries near 100% on samples spiked with known levels of arsenic and mercury, again indicating the reliability of quantitation, in this case within the sample matrix. While these results do not show arsenic or mercury contamination, this does not preclude the possible presence of organic pesticides on these objects.

The fifth study involved determination of six organic pesticides on 12 Karuk objects in the Hearst Museum at UC Berkeley at the request of the Karuk tribe. A total of 20 samples were acquired via either destructive or swab-based sampling. DDT was detected in 55% of the samples, with concentrations as high as 0.29% (2,900 ppm), which corresponds to the highest concentration found to date in these studies. Of particular interest here is comparison of GC/MS results with museum records that indicated the use of DDT via a small green dot on some of the objects. GC/MS results and historical data were in agreement on either detection or non-detection of DDT in 14 samples. In three samples, DDT was detected via GC/MS where historical data did not indicate its presence, suggesting that DDT has somehow migrated onto these objects or that the original marked tags may have been removed or detached. In the three remaining samples, DDT was not detected via GC/MS when historical data indicated its usage, suggesting that DDT was not applied to this particular sample location or that its concentration was reduced below the LOD via time, degradation, and/or volatilization.

The sixth case study involved determination of arsenic, mercury, and five organic pesticides on 12 objects repatriated to the Yurok tribe. A total of 48 samples were acquired via destructive sampling plus one more via swab-based sampling. Dieldrin was excluded from these analyses, as a standard was not available at the time these analyses were performed. Mercury was detected in 73% of the samples at concentrations ranging as high as 3.3%. DDT was detected in 67% of the samples at concentrations as high as 0.17% (1,698 ppm). P-dichlorobenzene and naphthalene were detected in only a few samples.

CONCLUSIONS AND NEXT STEPS

The results of these case studies spanning the period 1999 to 2004 have also been evaluated from the standpoint of developing recommendations for future work in this area. It should be noted that many Native American tribes do not have access to the expensive instrumentation required for this work and may not have the funds needed to use contract laboratories for these analyses. Although these labs certainly have the capability to do these analyses, they may be unaware of the special sampling considerations and typically charge approximately \$100 per sample for heavy metal analysis and \$500 per sample for pesticide analysis. University-based laboratories hopefully represent an unbiased third party that can provide objective and reliable data, in some cases free of charge or at costs well below that of contract labs.

In regards to sampling, nondestructive sampling is usually preferred from a

conservator's viewpoint but destructive sampling is preferred from an *analytical* standpoint given its near 100% extraction efficiency for either metals or organic pesticides. Nevertheless, nondestructive sampling methods based on the use of swabs give useful data showing whether or not an object has been contaminated. Very little work has been done comparing results from both destructive and non-destructive sampling methods, and such data will not be easy to obtain unless a uniform pesticide application process is employed. Assuming the goal of the study is to determine *if* an object has been contaminated, composite sampling is preferable as a sample taken from only one small area on an object may yield misleading results, as pesticide(s) may not have been applied to this particular location. Assuming the goal is to determine which *parts* of an object are contaminated (i.e., feathers, leather, etc.), replicate sampling is needed. Clearly, the issue of sampling is more complicated than it might seem, and the sampling strategies employed in a particular study will depend on a number of factors including cultural issues, conservator input, analytical data required, etc. Finally, some discussion of experimental error is appropriate in this context. While false positives and negatives can occur (especially when using spot tests) and errors can be attributed to a number of sources (i.e., analytical method, analyst, etc.), the major source of variability in the data results from the sampling process and the objects themselves. Once an object has been sampled using wipes or swabs, subsequent sampling at the same locations will result in lower concentrations of a given pesticide. More importantly, pesticides may not have been applied uniformly on an object, and this should be kept in mind when comparing data from replicate analyses of the same object.

FAAS appears to give good quality data and sufficient sensitivity to detect percent levels of arsenic and mercury contamination in samples. One concern for destructive sampling is acquiring a minimal sample weight to ensure sufficiently low LODs in the sample. For example, given an LOD of 3 mg/L for mercury *in solution*, a 50-ml extract volume, and a 10 mg sample weight, the corresponding LOD for mercury *in the sample* would be 1.5%. This suggests the use of sample masses greater than 10 mg in order to detect mercury concentrations above 1.5% in the samples. Although ICP-MS can provide much lower LODs and multi-element analysis capabilities, it requires very expensive instrumentation and hence this often precludes its use for this application. The major drawback to FAAS is the time and effort required to work up the samples. Typically, this process takes about 2 days for 25 samples; one day for digestion, filtration, and dilution; and another for instrument setup and analysis. XRF is far more efficient in terms of speed, and Sirois (2001) reported the analysis of more than 100 objects in an 8-hour time period. XRF should be the method of choice for future analysis of screening for heavy metal contamination on museum artifacts given that these instruments are portable, possess adequate sensitivity, and can be used for direct analysis of an object with results available in a timeframe on the order of a minute or less.

GC/MS appears to be the best method for identifying and quantifying the wide variety of volatile organic pesticide agents that have been employed in the past. The case studies discussed here have focused on six organic pesticides that were delineated from a prior study (Glastrup 1987). Historical data have shown that collections have been treated with other organic pesticides as well, and although

none have been tentatively identified in any published work to date, the scope of the target compounds should be expanded to include other likely substances as well as potential degradation products such as DDE. It should be noted that Solid Phase Micro-Extraction (SPME) can be used for nondestructive sampling of the headspace above an artifact. This simplifies the sample preparation versus destructive or swab based sampling (Ormsby et al. this volume), although correlating the resulting data to compute actual pesticide concentrations in the samples is difficult. Direct Sampling Mass Spectrometry represents an option for rapid screening of several pesticides within a sample. In this method, a small sample or swab is loaded onto a probe, introduced into the ion source region of a mass spectrometer, and heated to desorb the pesticides which are subsequently detected via selected ion monitoring and/or tandem mass spectrometry. This technique appears to be very promising for rapid screening of samples, and should give results in a few minutes per sample versus the typical 30–60 minute analysis times required for GC/MS.

The most important considerations in all these studies is providing data and information to Native Americans and museum professionals which can help them answer questions such as whether or not an item is contaminated, what is the extent of the contamination, what are the potential exposures and risks, and how to take appropriate measures to minimize these risks. Clearly, these case studies show significant contamination, especially with respect to mercury and DDT. One of the hardest questions to answer is evaluating the risks associated with handling or wearing the artifacts. Some work has been done to assess arsenic and mercury picked up on gloves after handling contaminated objects. Several studies have shown arsenic, mercury, and DDT in air at levels which are below appropriate workplace limits. Nevertheless, there is a need for more work in this area to more effectively answer these questions, particularly in assessing the risk from various activities, especially in light of the fact that children and elders may wear these objects during sacred dances. Finally, continued dissemination of data on contaminated collections is needed.

While several attempts have been made to secure major funding for development of new sampling and analysis methods, providing free testing of artifacts, and assessing potential exposures, these have not been successful to date. It is hoped that program managers and government funding agencies will understand that this problem affects not only Native Americans but is a public health issue that confronts a large number of museums.

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