Article: Research on identifying organic pesticide residues at the National Museum of the American Indian
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RESEARCH ON IDENTIFYING ORGANIC PESTICIDE RESIDUES AT THE NATIONAL MUSEUM OF THE AMERICAN INDIAN

Jenifer Bosworth, Jessica Johnson and Rolf Hahne

Introduction

Pesticides have long been used by museums and collectors to protect objects from insect infestation. The use of chemicals and substances lethal to insects may have preserved the physical manifestation of many objects, but it has also served to place those who handle contaminated objects at risk.

As part of its mission to protect, support, and enhance the development, maintenance, and perpetuation of Native culture and community, the National Museum of the American Indian (NMAI) has an inclusive program to repatriate sacred and ceremonial items and objects of cultural patrimony to their culturally identified lineal descendants throughout the Western Hemisphere.

NMAI acknowledges a responsibility to inform recipient communities about the possible presence of pesticides on repatriated objects (Fig. 1). The museum strives to provide as much information as possible to repatriating tribal communities and to museum staff in contact with NMAI collections about pesticides that may be present on objects.

Figure 1. Jessica Johnson discusses test procedures with NMAI Community Services staff.

In order to fulfill this responsibility NMAI has been conducting research to evaluate its pesticide use history, and to develop methods to test for the presence of pesticides. A recent historical review of the museum's documentation on pesticide use in its collections revealed that organic fumigants such as naphthalene, paradichlorobenzene and dichlorvos were widely used as pesticides (Fig.2; Pool 2001).

Figure 2. Label found on NMAI object during historical review.

The NMAI Conservation Lab has been conducting non-destructive in-house qualitative testing for inorganic substances (including arsenic and mercury) on objects and in storage areas for a number of years, but did not have a method for evaluating the presence of organic pesticides.

In May 2002, NMAI Conservators Jessica Johnson and Jenifer Bosworth collaborated with Dr. Rolf Hahne, Director of the Environmental Health Laboratory at the University of Washington, to test a protocol devised by Dr. Hahne for the non-destructive sampling and analysis of semi-volatile organic pesticides on museum objects (Fig. 3).

Figure 3. Rolf Hahne and Jenifer Bosworth test the sampling procedure.

What are organic pesticides?

Organic pesticides are carbon-based compounds that include chemicals and products such as naphthalene and paradichlorobenzene (mothballs), dichlorvos (No Pest Strip®, Vapona, DDVP), and pyrethrins.

These pesticides are applied as solids (dusts, flakes, mothballs) and as liquids (sprays, dips) which sublime into a gaseous state, acting as a fumigant. The vapors from these materials kill insects and work best in tightly closed spaces (Fig. 4).

Figure 4. Commercial organic pesticides.

In order to combat infestations at NMAI, pesticides were applied directly to specific objects at the Research Branch, the collections storage site in New York City. Mothballs or flakes were added to the storage container, or objects put into fumigation chambers. No Pest Strips® were hung in some storage areas and, at times, entire storage vaults were sealed off and fumigated (Fig. 5).

Figure 5. A storage vault at the NMAI Research Branch facility.

Most organic pesticide residues are expected to volatilize over time, if the container holding a treated object is not airtight. Despite this expectation, conservators at NMAI have noticed a 'pesticide smell' coming from many objects, especially during humidification treatments.

Health hazards associated with organic pesticides commonly used at the NMAI

Figure 6. Museums finally realized that pesticides on objects can be as big a problem as the insects.

Sensitivity to organic pesticides used at the NMAI can vary greatly depending on the individual, the exposure time and the level of exposure.

Naphthalene

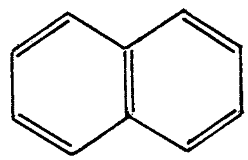

Figure 7. Naphthalene molecule.

Acute (short-term) exposure of humans to naphthalene by inhalation, ingestion, and dermal contact is associated with hemolytic anemia, damage to the liver, and neurological damage. Cataracts have also been reported in workers acutely exposed to naphthalene by inhalation and ingestion. Chronic (long-term) exposure of workers and rodents to naphthalene has been reported to cause cataracts and damage to the retina. Available data are inadequate to establish a causal relationship between exposure to naphthalene and cancer in humans. The EPA has classified naphthalene as a Group C, possible human carcinogen. (Environmental Protection Agency 2003)

Paradichlorobenzene

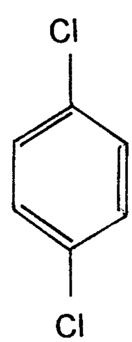

Figure 8. Paradichlorobenzene molecule.

Acute exposure to the vapors of this chemical can cause redness, irritation, and burning of the eyes with tearing, runny nose, and irritation of the throat. Excessive inhalation of vapors can be weakly anesthetic, causing depression of the central nervous system with symptoms of dizziness, headache, nausea, vomiting, anorexia, tremors, and increased deep tendon reflexes. Contact with the skin can cause irritation and blistering, and occasionally sensitization. Chronic exposure may cause liver and kidney damage, jaundice, abdominal tenderness, and blood disorders, including leukemia and hemolytic anemia. Repeated exposure of the skin of paradichlorobenzene can cause eczema with drying and cracking of the skin. (Occupational Safety and Health Administration 1999)

Dichlorvos

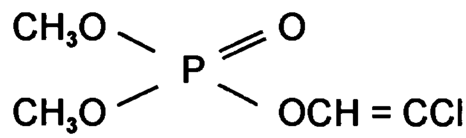

Figure 9. Dichlorvos molecule.

Acute (short-term) and chronic (long-term) exposures of humans to dichlorvos results in the inhibition of the enzyme acetylcholinesterase, with neurotoxic effects including perspiration, vomiting, diarrhea, drowsiness, fatigue, headache, and at high concentrations, convulsions, and coma. No information is available on the reproductive, developmental or carcinogenic effects of dichlorvos on humans. A study by the National Toxicology Program (NTP) reported an increased incidence of tumors of the pancreas, mammary glands, and forestomach in animals. EPA has classified dichlorvos as a Group B2, probable human carcinogen. (Environmental Protection Agency 2003)

Pyrethrins

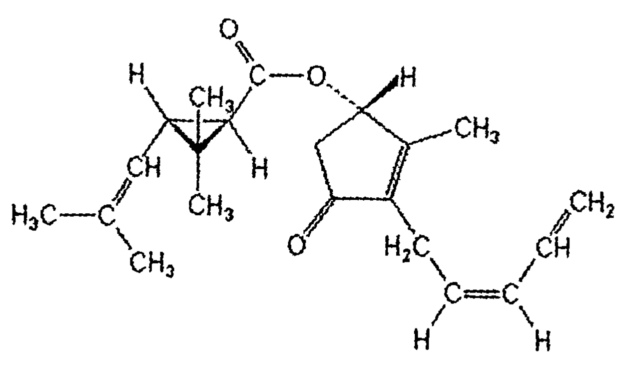

Figure 10. Pyrethrin molecule.

The most common effect of skin exposure to pyrethrum is a rash, which may be associated with intense itching and blister formation. Hay fever-like symptoms, wheezing and breathing difficulties may occur from exposure to pyrethrum by inhalation. An allergic reaction causing weakness and collapse may occur in sensitive individuals. Pyrethrum may irritate the eyes. (Occupational Safety and Health Administration 1999).

Testing for semi-volatile organic pesticides

Representatives from tribal communities requesting the repatriation of artifacts are advised of the tests for pesticides on objects that the NMAI is able to provide. The representatives are informed of testing procedures, including wipe and swab sampling, the newly available hand-held Niton XRF analyzer and the following organic pesticide protocol. It is also made clear that all the tests are only able to identify the *presence* but not the *amount* of contaminants on an object. Tests for pesticides on objects considered for repatriation are only performed with the approval of the tribal communities.

Materials for semi-volatile organic testing protocol:

- Tedlar T film (TR20SG4) [1]
- Heat sealer
- Valve for filling and evacuating fabricated Tedlar bag
- Wrenches: micro-allen, adjustable head
- Teflon tubing to fit attachments
- Stop watch
- Source of high purity nitrogen (or oxygen)
- Elf pump
- DC – Lite flow meter
- Tenax TA thermal desorption tubes for Perkin-Elmer Automatic Thermal Desorber (ATD)
- Thermal chamber/oven for heating objects to ~ 50° C/ 120 °F

Sampling Method

Step 1: Seal object inside a custom-made Tedlar bag.

The object to be sampled is sealed inside a bag made of a non-absorptive plastic (Tedlar), constructed in-house using a heat sealer. A sampling valve is attached to the bag to allow for passage of air and nitrogen (Fig. 11).

Figure 11. The object is put into a bag and the bag is sealed.

Step 2: Replace air in bag with nitrogen.

Air is pumped out of the bag and replaced with six liters of high purity nitrogen gas.
The evacuation of air and the addition of nitrogen are regulated using a small sampling pump and a flow meter (Fig. 12).

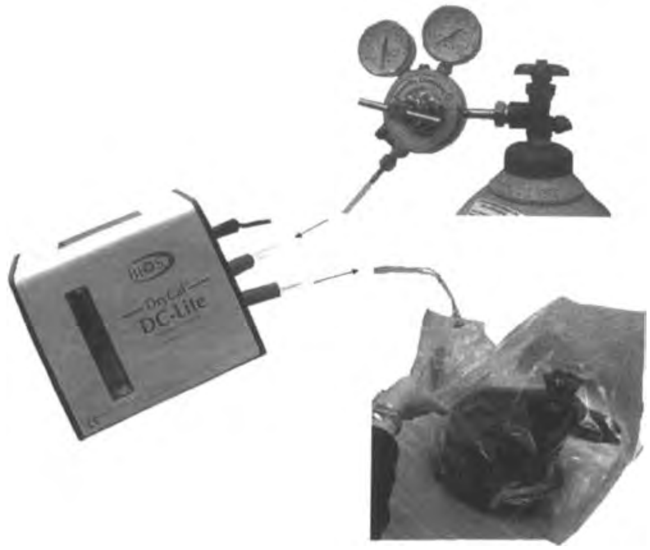

Figure 12. Air in the bag is replaced with nitrogen.

Step 3: Heat Object.

The bagged object is placed into an oven warmed to approximately 50°C (122°F). The closed sampling valve is attached to Teflon tubing which is threaded through an opening on the top of the oven. The object is allowed to warm for 30 minutes. Raising the temperature above room temperature causes residual organic pesticide within the object to evaporate into the bag (Fig. 13).

Figure 13. The bagged object is slightly warmed in an oven.

Step 4: Collect Sample.

After 30 minutes, the six liters of nitrogen in the bag are pumped out and collected in a thermal desorption tube. A thermal desorption tube has multiple layers of different materials that trap organic compounds when the nitrogen atmosphere from the bag is pumped through the tube (Fig. 14).

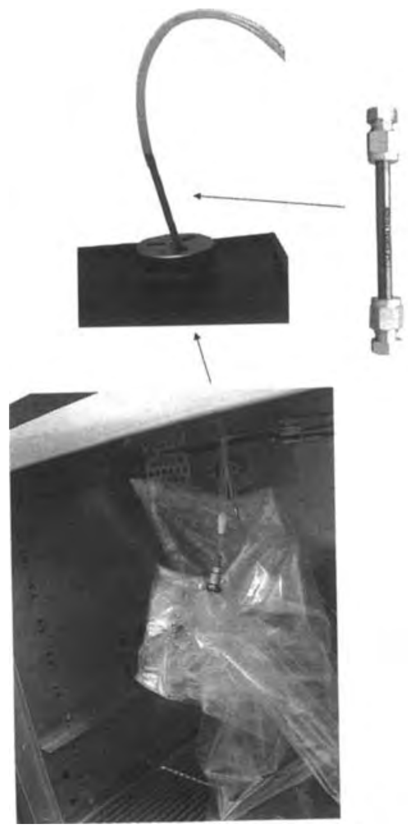

Figure 14. A sample of nitrogen is collected in the thermal desorption tube.

Step 5: Send Sample for Analysis.

After sampling, taking care to ensure that none of the volatile material was deposited on the transfer line from the bag by heating the line with a hair dryer, the object is removed from the oven and from the bag.

Samples collected by NMAI in desorption tubes were sent, along with a 'blank' tube as a control, to the Environmental Health Laboratory, Department of Environmental and Occupational Health Sciences at the University of Washington at Seattle to be analyzed for organic residues with gas chromatography/mass spectrometry (GC/MS).

Results and Observations

The initial testing trials of this procedure identified the presence of specific organic pesticide residues still present on objects known to have been fumigated, including dichlorobenzene, dichlorvos and naphthalene.

The experience of the first tests, as well as subsequent tests undertaken on five objects that are candidates for repatriation, has highlighted both positive and negative aspects of the protocol, demonstrating the need for further research. An instruction manual was created for the protocol after it had been tried a number of times and refined.

Positive Aspects

- This method of identification is very sensitive (detection limit ~ 5 – 10 mg/sample), as nearly every organic pesticide has some volatility and will be seen if there is even a small residue.
- The method tests for residues from the entire object and not just from the random location chosen for a wipe sample.
- The method is non-destructive in that no material is removed from the object.

Negative Aspects

- The testing procedure can only identify the presence and not the amount of contaminants on an object, giving no indication of health risks.
- The method currently works better for small objects that fit into bags made from one piece of Tedlar that require fewer seals.
- The procedure may put an object through some stress due to the rise in temperature and close proximity of the bag when air is removed. This method is not recommended for fragile objects or objects with fragile attachments.
- The method is time intensive and thus costly. The expense of GC/MS analysis may be prohibitive for some institutions, although the expense is similar to some analyses done for inorganic pesticides.

It may be possible to overcome the difficulties of testing larger objects, and close contact of the Tedlar with the object, by constructing a box framework around which the Tedlar could be sealed after the object is placed inside. The Tedlar could be heat sealed, rolled and taped for better seals and the framework would keep the Tedlar from contact with the object.

Continuing Work

Investigation into a different sampling method using solid-phase micro extraction (SPME) is currently underway in conjunction with Mark Ormsby, a physicist at the National Archives. The SPME sampling technique alleviates the issues of temperature change and ease of use posed by steps 2, 3 and 4 described above.

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Endnote

1. Tedlar, a polyvinyl fluoride film made by DuPont, is inert in response to a wide variety of chemicals and solvents. The film is non-absorptive, containers no plasticizers and can be heat sealed to form a bag.

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