A General Overview of Pesticides, Testing, Mitigation, and Removal

Nancy Odegaard, PhD, FAIC
Conservator and Professor

Arizona State Museum
University of Arizona
Biodeterioration

The process that involves the combination of:

- An organism (the **PEST**)
- a food source (the **MUSEUM OBJECT**)
- a suitable environment (a **QUIET, DARK, COMFORTABLE PLACE**)

Organisms that threaten museum objects include:

- People
- Bacteria
- Insects
- Fungi
- Rodents
Insects of concern usually like materials such as Proteins: hair, fur, horn, quill, baleen, hoof, claw, feather, ink binders, hide glues
Insects of concern also like materials such as Cellulose and Starch: paper and sizing, paste adhesives.
Unprotected Objects often become infested
Unprotected objects with no signs of infestation may have been poisoned
Insects are the most numerous, resilient, and persistent of all the agents of deterioration. Fortunately, there are relatively few species that are of concern in the museum context.
Complete Destruction by Clothes Moths
Varied Carpet Beetle
Carpet Beetle larva
Pesticides can be placed into categories but most are effective in more than one category:

- Dermal poisons penetrate the cuticle or body wall of the insect and are sometimes referred to as **Contact Poisons**.
- **Desiccants** can also be used to absorb part of the outer protective was coating of the insect, causing dehydration and death.

- Oral poisons enter the body through chewing and are known as **Stomach Poisons**.
- Inhalation poisons enter the insect through the body wall or respiratory openings and include **Fumigants**. **Residual poisons** contact the insect during or after application but require a period of time to react.
Common Pesticide Products
“Arsenic” Tag
White powder residue that tested positive for arsenic
Grey residue that tested positive for mercury
Old product instruction labels
Old containers or bags used to dispense pesticides
Current Museum Practices

- Regulatory and toxicological date is time sensitive
- Museums will have unique pesticide histories
- Donors often did not know or reveal to museums the use of pesticides on objects
- Testing techniques and refinements are ongoing
- Interpretation of testing results may vary
Remove contaminated objects from museum education programs
Wear personal protective equipment (PPE)
Creating a History
Compiling a history of museum pesticide use

Internal Information:
- Catalog cards, specimen treatment cards, loan records
- Receipts and purchase order for pesticides
- Contracts with pest control operators and exterminator companies
- Published archaeological filed notes
- Correspondence by staff members
- Monthly or annual reports done by staff

Information from existing and previous staff members:
- Interviews with present long-term and retired staff
- Interviews with pest control operator or extermination companies
Physical Evidence

- Tags, labels, marks on specimens
- Powder or crystalline residues on or around artifacts
- Well preserved Physical Evidence
- Tags but susceptible artifacts
- Persistent odors
- Old containers or bags used to hold or dispense pesticides
- Old application equipment
- Old stocks of chemicals/pesticides
- Old labels or copies of labels from containers
External Information:
- Early pest control handbooks
- Professional pest control trade magazines
- Chemistry literature
- Websites and searchable databases
- Entomology literature
- Taxidermy manuals and literature
- General museum literature
- Conservation literature
- Websites and university agricultural department databases
- Websites of government agency databases
- Websites of medical institutes toxicological databases
Isolate known or suspect objects into storage containers
NAGPRA and post museum dispositions

- Objects leave the museum they may:
- Return to cultural use and be worn
- They may be reburied in the earth
- They may be placed in caves or shelters
- They may be returned to water
- They may be burned
- They may be held in homes or cultural centers
Tribal storage
Testing
Testing for Pesticides

Protocols for spot testing pesticide residues

- Arsenic (compounds)
- Mercury (salts, vapors)
- Zinc, Copper, Lead
- Borates
- Carbamates and thiocarbamates
- Organophosphates
- Sulfur (compounds)
Recommendations for using Spot Tests to determine the presence of pesticides

- Wear appropriate personal protective equipment
- Read test kit or test paper instructions prior to running the test
- Use fresh reagent solutions
- Hold test papers with tweezers
- Work in well-ventilated areas
- Test samples along with known positive and negative controls
- Make written notes of procedures used and results observed
- Prepare for proper disposal of test reagents and test material
- Maintain material safety data sheets for all chemicals
XRF Instrument Advantages

- Analyzes 25 metals in materials
- Internal calibration
- Non destructive
- Portable for field use
- Downloadable data
Non Destructive XRF Testing

**Detection Limit** - Depends on the element and Analysis time

**Analysis Time** – Typically 30 to 90 seconds

**Sample size** – Approximately 1 cm by 0.5 cm

Bruker

Niton

Innov-X
Instrument Calibration Study

Arsenic Samples Standard Deviation

- Arsenic Feather
- Arsenic Cotton
- Arsenic Wool
- Arsenic Filter Paper
Working as a team
Some NAGPRA eligible objects have high levels of residual pesticides that pose a health risk.

NAGPRA eligible objects should be tested prior to repatriation.

Health risks of any exposure should be determined.

Personnel working with these objects should be properly trained and perhaps undergo periodic medical exposure screening.

Regulations should be enacted to ensure that individual and environmental exposures do not occur.
Mitigation

*Mitigation*: efforts to diminish the effects of pesticides
Important to any pesticide residue mediation treatment strategy are:

- The cultural appropriateness of the method if objects are considered living beings.

- The degree of pesticide residue removal necessary to achieve sufficient human detoxification may also depend on the type of cultural use that is expected.

- The degree of pesticide residue removal necessary to achieve sufficient environmental detoxification may also depend on the type of physical, symbolic, or life ending use that is expected.
Risk Assessment

- Prevention of exposure depends on
  - Recognition
  - Risk assessment
    - Identification of hazard(s)
    - Identification of people at risk
    - Evaluation of the extent of the risks taking past history into account
    - Evaluation of existing control measures
    - Carrying out a risk rating (severity of injury x likelihood)
    - Arrangement of additional/new control measures
    - Recording of findings
    - Informing affected parties (managers, employees, contractors etc)
  - Instigate training if required
  - Monitoring and evaluation

- Take appropriate actions
  - Environmental
  - Personal
Recommendations for Human Health
The human health hazards from pesticide residues are mitigated by the use of personal protective equipment and containment.
Personal Protective Equipment

Eyes: goggles
Hands: gloves
Mouth: respirator
Body: lab coat or suit
Safety Guidelines

- Assume that hazardous pesticides are present.
- Wear nitrile gloves (not cotton or latex) while handling artifacts.
- Remove gloves so that hands do not touch the exterior surface.
- Discard gloves and wash hands with soap and water after handling objects, and especially before eating or smoking.
- Wear a lab coat or other protective clothing to keep dust off clothing. Remove the lab coat when out of the areas or no longer handling contaminated material. Assess the work area. If there is visible surface dust, shoe and hair coverings should also be worn.
- Keep lab coats clean so as to avoid transferring dust and dirt.
- Work with materials in a well ventilated area, ideally with a fume hood.
- Obtain medical certification to wear a mask or respirator and have an up to date fit test. Choose appropriate respirators and cartridges for the environment.
- Do not eat or drink in work areas.
- Ensure that work surfaces are well cleaned after they have been in contact with artifacts. Sponge-clean or wet-mop floors with soap and water.
- If dust has gotten onto clothing, remove clothes as soon as possible, bag and launder separately from other clothing.
- If there are concerns about exposure, consult a board certified occupational medical doctor or toxicologist.

Based on a 2000 monograph by
Monona Rossol (Conservation Scientist, Arts, Crafts, and Theater Safety)
Jane Sirois (Conservation Scientist, Canadian Conservation Institute)
http://bss.sfsu.edu/calstudies/arttest
Removing Pesticides

Remediation: efforts to remove or counteract pesticides
The cultural appropriateness of the method if objects are considered living beings.

The degree of pesticide residue removal necessary to achieve sufficient human detoxification may also depend on the type of cultural use that is expected.

The degree of pesticide residue removal necessary to achieve sufficient environmental detoxification may also depend on the type of physical, symbolic, or life ending use that is expected.
Development of SERS active vapor sensors for detection of volatile museum contaminants

After completing pesticide identification studies with FTIR and detection studies with XRF Odile has moved her research topic to “Surface Enhanced Raman Spectroscopy”.

Using a dispersive Raman Spectrometer she is preparing a sample on a roughened metal substrate that results in an amplified Raman signal. The benefits are amplification of the Raman signal above the fluorescence signal for certain fluorescent samples, and to ability to get Raman spectra for very small samples.

Gas chromatography and FTIR will be used as supporting techniques.

Odile Madden, PhD student
Pre-doc Fellow, MCI, Smithsonian
Non Aqueous Mechanical Methods

• Scraping of old surfaces to re-sanctify objects. (Loma’omvaya 2001).

• Compressed Air cleaning (Glastrup 2001).


• Absorbent activated carbon cloth used with vacuum cleaning (Piening 2001). Also tested with a fluorocarbon solvent (Kaiser 2007).

• Wiping with acetone solvent (Caldwell 1995).

Dry Cleaning by solvent emersion (Cavello et al. 2000, di Nola et al. 2002).

• Carbon Dioxide (Snow) for cleaning small particles (Wolbers 2000, Püschner 2002, Silverman 2006). Adapting the technique has been proposed (Unger 1998, Zimmt et al 2007).
2003
Vacuum Study
RESULTS

Cheryl Podsiki, Kress Fellow
2009 Solvent Studies

In Collaboration with Dr. Robert Kaiser of Entropic Systems, Massachusetts

Activated carbon cloth is also being tested for use with a fluorocarbon based solvent (Entro-Kleen™ Diffusion Cleaning Kit) to remove organic pesticide contaminants on museum objects based on previous success in decontaminating military equipment (Kaiser 2007).

After studying the solubility of several organic pesticide residues we prepared substrate materials (paper, wool, cotton) with Diazinon pesticide residue. We propose to test the applicability of Kaiser’s method as a possible pesticide removal technique for artifacts.
Aqueous Mechanical Methods

- Laundering techniques with pre-rinsing, hot water and detergents (Laughlin 1993).

- Steaming to reshape felt (Wood and Haigh 1955, Martin and Kite 2003).


- Chelating compound, dimercaptosuccinic (DMSA) used for follow-up treatment (Hill and Reuben 2008).


- Liquid carbon dioxide (Unger and Tello 2008)
2003-2005 Study Using Supercritical CO$_2$ to Remove Organic Pesticide Residues

Dr. Anthony Muscat, Chemical & Environmental Engineering

Dr. Werner Zimmt, ASM and Agricultural & Biosystems Engineering

Teresa Moreno, ASM

Dr. Nancy Odegaard, ASM
Materials Science & Engineering, Anthropology

Dr. Mark Riley, Agricultural and Biosystems Engineering

Support from the UA Vice President for Research
The simulated artifacts were treated with scCO2 (temperatures of 50-60°C and pressure in the range 100-250 atm) for 2 minutes and the extent of the removal of diazinon determined. Dyed feathers were similarly extracted with scCO2 and the colors of the extracted samples compared favorably with the untreated samples.

Detection of diazinon was performed using a unique toxicological screen based on the impact of toxins on Rat Lung Epithelial (RLE) cell cultures.

Known quantities of diazinon solution were applied to small pieces of commercially tanned (mineral) leather.
After loading, the reactor was chilled to 8°C and fed with liquid $CO_2$ to approximately 60 atm. The cylinder was valved off and the reactor was heated using a heating jacket and set point controller until the desired steady-state conditions were reached. After processing the fluid was exhausted through a needle valve.
Rat lung epithelial cells (RLEC) for determination of toxicity

- Results from the initial work with scCO$_2$ extraction showed that these cells will react with many different materials.

Decrease in metabolism is due to presence of pesticide.
Decrease at a low concentration means pesticide has high toxicity.
Decrease that only occurs at high concentrations means low toxicity.
Effect of diazinon solution, initially at 4 mg/mL in acetone, on RLE cell metabolic activity. The TC$_{50}$ value is reached at a dilution of 1:2500, which represents the condition of full toxicity to which all extractions can be compared.
Conclusions Of Study:

- scCO₂ With an appropriate co-solvent, can be used to remove pesticides.
- The system does not cause a change in visible appearance in the materials tested.

Further studies are justified.

- Extraction parameters (temperature, pressure, time)
- Co solvents
- Other pesticides
- Other substrate materials
- Other evaluative/analytical measurements
Chemical Alteration Methods

- Lugol’s iodine solution to remove stains caused by mercuric chloride (Hawks and Bell 1999).

- Bacteria as a cleaning technique to remove mercuric compounds (Roane 2007). Bacteria have detoxified contaminated soils and water (Roane and Pepper 2000). She sampled objects at ASM for bacteria. Her search yielded a species from a genus of common soil bacteria (Arthrobacter) that can remove about 30% of mercury contamination. *Cupriavidus metallidurans*, a bacterium isolated from zinc mine tailings that removes 60-80% of the mercury. *C. metallidurans* is also less likely to damage organic material in artifacts because it is an autotrophic bacterium that can make its own food from inorganic sources. Damage to objects has yet to be determined.

- Aqueous α-Lipoic acid solutions as a chelating agent for removal of arsenic and mercury (Cross 2007).
Removal of 48.8 μg/cm² arsenic (III) from filter paper using reduced lipoic acid.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Number of Sample</th>
<th>Average residual [μg/cm²]</th>
<th>Standard Deviation</th>
<th>% Arsenic Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>5</td>
<td>14.04</td>
<td>5.40</td>
<td>71%</td>
</tr>
<tr>
<td>Lipoic acid + alcohol</td>
<td>15</td>
<td>11.13</td>
<td>3.32</td>
<td>77%</td>
</tr>
<tr>
<td>Lipoic acid</td>
<td>15</td>
<td>5.32</td>
<td>1.39</td>
<td>89%</td>
</tr>
</tbody>
</table>

Percentage of mercury from various materials contaminated with mercuric chloride after one and two cleaning sequences.

<table>
<thead>
<tr>
<th>Material</th>
<th>Initial concentration</th>
<th>1 % Removed</th>
<th>2 % Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter paper</td>
<td>1548</td>
<td>93</td>
<td>99.3</td>
</tr>
<tr>
<td>Cotton</td>
<td>1496</td>
<td>65.1</td>
<td>93.2</td>
</tr>
<tr>
<td>Wool</td>
<td>2161</td>
<td>8.7</td>
<td>36.7</td>
</tr>
</tbody>
</table>

**Conclusions:** Reduced lipoic acid solutions can be used to remove high concentrations of arsenic and mercury from sulfur containing materials and arsenic from material containing sulfur but not mercury from materials which contain sulfur.
- Arsenic and Mercury Salts can be removed from non-sulfur materials (paper, cotton) using activated lipoic acid or DI water.

- Arsenic can be removed from sulfur containing materials (wool, feathers) using activated lipoic acid or DI water solutions.

- Mercury cannot be removed from sulfur materials (wool, feathers) using the chemicals tested.
External Energy Methods

- **Microwaves** to vaporize with carbon filters and suction (Tello 2006).

- **Freeze-drying** (Zabik and Dugan 1971).

- **Ultrasonic sound waves** with aeration and vaporization (Gustafsson 1993).


- **Ultraviolet light** from sunlight on clothing of agricultural workers (O'Rourke 2000). Pulsed ultraviolet flash lamp on painted surfaces (Asmus 2001).

- **Hydrolytic and photolytic decomposition** by UV light, conventional X-rays, and other sources (referenced in many journals of radiation, biochemical, analytical chemistry, and agriculture).
Conclusions

- The detection and removal of pesticide residues remains a problem for museum collections.

- Numerous factors affect the breakdown and potential removal of pesticides. There is no single solution for all pesticides or all objects.

- Most of the research currently underway includes:
  1. collaborative teamwork
  2. scientific methodology and measurements of effectiveness
  3. respect the cultural values associated with the objects.
Acknowledgements

- NCPTT Grant Program
- NAGPRA Grant Program
- Samuel H. Kress Foundation
- University of Arizona Faculty Small Grant Program
- University of Arizona Provost Award
- The Hopi Tribe
- Colleagues and students of the Arizona State Museum and Conservation Laboratory

Dept. of Chemical Engineering
Dept. of Agricultural and Biosystems Engineering
Dept. of Chemistry
Arizona Poison Center and Dept. of Medicine