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Collateral Damage: Unintended consequences of vapor-phase organic pesticides, with emphasis on p-dichlorobenzene and naphthalene

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ABSTRACT

Post-collection organic pesticide applications pose adverse risks to object/specimen integrity and user safety. Organic chemicals penetrate and absorb into wooden storage furniture and paper-based storage supplies, and adsorb on metal, glass, and other non-absorptive materials. P-dichlorobenzene and naphthalene recrystallize on both collections and storage equipment, resulting in a continual vapor accumulation and equilibration within a cabinet causing exposure upon case opening. Absorption/adsorption by collections also results in lingering inhalation exposure for anyone handling or studying treated items. Use of the chemicals leaves a sticky layer of fats and oils from the insects that adheres carcasses to storage furniture surfaces, requiring post-treatment labor to remove, or expense to replace storage equipment. Infestation prevention, inspection and effective eradication measures such as freezing, heat treatments, and anoxia are key steps toward precluding the reliance on chemical pest control.

Keywords: pesticides, safety, risk, p-dichlorobenzene, naphthalene, pest eradication

INTRODUCTION

Collection-based hazards, acquired post-treatment from pesticide use, are well documented, as is their potential for adverse safety and health effects on object or specimen users (Hawks 2011). The public health control measures of remediation/substitution, engineering controls, safe work practices and personal protection are more easily applied to the removal or minimization of toxic (usually heavy metal) particulates, such as arsenicals or lead. Cross-contamination from particulate residues (either among objects or between objects and person) can be significantly minimized through rigorous, consistent and frequent decontamination of work surfaces, floors, telephones, and break rooms.

However, exposure control of residual organic chemicals existing as vapor at standard room temperature and pressure is both difficult and complicated. Organic chemicals penetrate and absorb into wooden storage furniture and paper-based storage supplies, and adsorb onto metal, glass, and other non-absorptive materials. Many are easily retained by specimen tissue and lipids (including lipids remaining in osteological preparations). Some vapor-phase pesticides, such as para (1,4-) dichlorobenzene (PDB) and naphthalene, sublime but recrystallize at room temperature on both collections and storage equipment.

Additionally, the collections themselves may suffer intrinsic damage to proteins from residual chlorinated organic chemicals. Research suggests that certain fumigants do not negatively impact DNA in the short-term (Kigawa 2011); however the long term ramifications of PDB and naphthalene on deterioration of many materials have not been fully explored. Removal of residual organics from specimens, and decontamination of storage containers with insect frass embedded in sticky residues, are significantly costly, labor-intensive, and not altogether effective measures.

These persistent chemicals result in a continual vapor accumulation and equilibration within a cabinet that cannot be minimized through diffusion, even through key locks or door frames. Exposure risks to anyone accessing treated cases are heightened by residual vapor, recrystallized residues, and pesticides retained by specimen lipids or other fats and tissues. These conditions also pose long-term inhalation exposure for anyone handling treated items outside of cases (e.g., study tables)..

Staff exposures might be controlled through respirators and safe work practices, presuming staff and their supervisors are aware of the risks and use these precautions. However, casual research visitors, short-term students/intern staff, and contractors, are not always apprised of the risks. Some workers cannot escape the risks because their offices are in or around collection storage areas.

The range of persistent organic chemicals from legacy treatments is daunting (Goldberg 1996). Fortunately, use of many pesticide chemicals has ceased in U.S. museums. However, use of PDB and naphthalene (both potential carcinogens) continues, largely because of their widespread availability in this country. The argument for the continued reduction of PDB and naphthalene use, and its permanent removal from specimens and collection furniture to prevent continual off-gassing, is based on the need to protect users from exposure to concentrations that must be controlled to as low as reasonably achievable.

ENVIRONMENTAL MONITORING STUDIES

Over the past 15 years, the National Museum of Natural History (NMNH) and the Office of Safety, Health and Environmental Management, Smithsonian Institution, conducted a variety of risk exposure and remediation surveys involving PDB and naphthalene, to determine:

a. Staff exposure during typical tasks such as pesticide application; post-treatment curation and cleaning; extensive decontamination of storage cabinets; and collection care inspections.
b. Effectiveness of post-treatment decontamination of case interiors, drawers and liners as evidenced by vapor concentrations detected at sites throughout collection storage areas, or at open case fronts, pre- and post cleaning.

ADVERSE HEALTH RISKS TO COLLECTION USERS

PDB and naphthalene toxicity

The National Toxicology Program 12th Report on Carcinogens 2011 classified both chemicals as "reasonably anticipated to be a carcinogen," based on sufficient evidence of carcinogenicity from studies in experimental animals (NTP 2011a, NTP 2011b). The International Agency for Research on Cancer lists both PDB (IARC 1999) and naphthalene (IARC 2002) as a Group 2B agent, "possibly carcinogenic to humans," concluding that there was sufficient evidence for carcinogenicity in experimental animals. The U.S. Environmental Protection Agency Integrated Risk Information System

(IRIS) notes in the 2003 Draft Summary for 1,4-Dichlorobenzene that it is to be considered *likely to be carcinogenic* in humans (USEPA 2003).

Other reported health effects from PDB include eye and skin irritation and renal toxicity (ACGIH 2001a). Other reported health effects from naphthalene include eye and respiratory tract irritation, ocular toxicity, headaches, and blood dyscrasia including hemolytic anemia and hemoglobinuria. Systemic poisoning can occur following dermal contact and absorption (ACGIH 2001b).

Occupational Exposure Levels
An Occupational Exposure Level (OEL) is a limit based on evaluation of an agent's reported toxicity and epidemiologic data, and represents conditions under which the typical worker may be exposed (over an 8-hour shift, 40-hour workweek) without adverse health effect. These are not fine lines between safe and unsafe levels, and their goal is to protect the health of the working population. OELs are not meant to apply to the general population, nor used as community-based standards, which typically are much more conservative to protect a wide range of ages, the infirm, the physically impaired and those with other medical conditions and susceptibilities. OELs are established by both regulatory agencies (c.f., Permissible Exposure Limits, U.S. Occupational Safety and Health Administration) and professional standard setting organizations (e.g., Threshold Limit Values-TLV, American Conference of Governmental Industrial Hygienists, ACGIH) (Miller 1997).

<u>ACGIH OEL for workers</u>: 10.0 parts per million (ppm) is the ACGIH TLV for both PDB and naphthalene. These were established in 2000 and 1986 respectively. Based on more recent carcinogenicity and toxicology studies, the ACGIH is currently evaluating PDB OEL status (ACGIH 2014) against more recent studies including the following.

<u>USEPA IRIS Target OEL recommended for workers</u>: 4.0 ppm is a more conservative OEL based on the Inhalation Reference Concentration (RfC) derived from no observed adverse effects levels per its comprehensive review of toxicity and environmental impact data, and adjusted for an 8-hour workday (USEPA 2003).

Personal inhalation exposure studies, PDB
From 1997-2012, 21 personal air samples were collected from staff applying PDB and during post-treatment curating and cleaning of vertebrate zoology specimens. Results converted to 8-hour time-weighted average shift-long concentrations to standardize them for comparison to the OELs were:

- Case application: 0.404 and 0.578 ppm.
- Initial accessing post-treatment period, 13 cases: 1.85 and 2.66 ppm.
- Post-treatment curation and cleaning, extensive decontamination cleaning, and collections care inspections: 17 samples ranging 0.093 - 0.221 ppm.

Statistical analysis of these data shows that, with 95 percent confidence, the likelihood of a future exposure exceeding the ACGIH TLV of 10 ppm is less than 2 percent (1.412 percent). When analyzed against the more conservative IRIS RfC, the likelihood of a future exposure exceeding 4.0 ppm is slightly higher (5.63 percent). A good indicator of health risk control is if the analysis indicates, with 95 percent confidence, the chance is less than 5 percent that future exposures might exceed the OEL (an American Industrial Hygiene Association recognized statistical standard).

However, all the exposures were detectable levels of a potential carcinogen and so efforts to reduce risks further must be examined. Data indicates that the two greatest contributors to exposure were initial post-treatment case access for removal of remaining PDB, and inspections, suggesting no additional future applications of PDB would significantly reduce exposure potentials from residues.

Sampling methodology
Personal exposure and ambient samples for PDB were collected on activated charcoal (SKC 226-01) sorbent tubes, and for naphthalene on Chromosorb 106 sorbent tubes, via calibrated sampling pumps. Analysis was performed using NIOSH Method 1003 and OSHA 35 Method, respectively. Exposure assessments were conducted per validated standard industrial hygiene methodologies (SSM 2007).

IMPACT ON COLLECTIONS AND COLLECTION STORAGE MATERIALS

Visual evidence suggests that both PDB and naphthalene treated specimens retain these chemicals in lipids and other fats. The chemicals tend to recrystallize in deposits of unsaturated fats on the surface of bone and may even recrystallize elsewhere on proteinaceous specimens. Treated cases also retain PDB and naphthalene in/on the case interiors. Wood and other cellulosic materials appear to adsorb and absorb these chemicals, with subsequent recrystallization. Glass, painted and unpainted metals also show recrystallization and in instances where painted surfaces are white, also show accumulations of tightly adhered insect carcasses that appear to have resulted from fats solubilized from the insects in response to the pesticides. These are likely to be present on other surfaces exposed to these chemicals (e.g., unpainted wood), but are difficult to see against anything other than a white ground.

This residual PDB and naphthalene within closed collections cases results in accumulated, persistent vapor concentrations. As dangerous to health as these chemicals can be, there are reasonably available and affordable controls to at least reduce health risks to working staff. However the damage to the collection itself and its storage environment is long-lasting, sometimes irreversible, and always expensive to mitigate.

In the PDB application studied at NMNH, efforts to clean the painted metal storage cabinets, which could not be removed to other sites for this work, required use of respiratory protection, discarding and replacing all storage trays and drawer liners, discarding numerous drawers deemed too contaminated with insect carcasses to merit cleaning, and many hours of staff time spent in trying to remove both the residual insecticide and the adhered insect remains from the case interior surfaces. Not all surfaces could be readily accessed for cleaning. PDB is soluble in a number of solvents, according to its Safety Data Sheets, but the least toxic appears to be ethanol. PDB is only slightly soluble in water and not in ammonia-based cleaners. Fire safety controls and personal protective equipment were required for the ethanol scrubbing. While somewhat successful, these efforts resulted in a substantial amount of hazmat (hazardous materials) that required expensive disposal.

Staff at NMNH considered the use of scavengers on the inside of case doors (PDB and naphthalene have a strong affinity for activated charcoal, for instance). Scavengers would not significantly reduce pesticides absorbed in the specimen, but would reduce the ambient accumulated vapor and reduce exposure upon accessing the case. Monitoring of concentrations and subsequent change-out schedules for the scavengers would have required budgetary and staff resource commitments that were not available.

Methods to decontaminate the specimens themselves, whether bone, tanned skins, or study skins are still under discussion. A major concern is that no impact on the scientific utility of the specimens should result from any decontamination effort. While recrystallized PDB can be removed from bone using ethanol, and the same solvent could remove some of the PDB solubilized in unsaturated fats, it is likely that contamination would persist in saturated fats. Removal of saturated fats would weaken the bone and is not deemed to be desirable. Ethanol soaking was not considered to be acceptable for skins, which would remain as a potent source of residual vapor in the cabinets.

ENVIRONMENTAL MONITORING TO MEASURE CASE DECONTAMINATION EFFECTIVENESS

PDB treated cabinets

NMNH collection management and conservation staff attempted various cabinet cleaning and decontamination strategies in 14 vertebrate skeletal collection cases post-PDB application. After cleaning, each case was opened for 15 minutes and a source air sample collected at its face, five feet above the floor, representing a person's breathing zone when accessing the contents. Pre-cleaning sample results ranged from 1.42 - 10.27 ppm (mean 4.7). Post-cleaning results ranged from 0.554 - 4.86 ppm (mean 1.3). Statistical analysis of these two sample population indicated that their respective 95 percent upper and lower confidence levels did not overlap and therefore the two sample sets were distinct. These data suggest that the removal efforts were effective in reducing accumulated source PDB concentrations. However, despite two years of cleaning attempts, similar case source concentrations still would be expected, with 95 percent confidence, to exceed the 10 ppm TLV greater than 5 percent (5.7 percent) of the time. Further, with 95 percent confidence, case source concentrations post-cleaning would in all probability exceed the more conservative IRIS OEL of 4.0 ppm over 18 percent of the time, a hazardous situation that requires an ongoing program of cleaning and ventilating of residual PDB residue.

While PDB may be an effective insecticide, the negative consequences of its application are not trivial. Case access restrictions necessitated (and would continue to result in) time and resource expenditure not required by a less toxic alternative. In the study presented in this paper, collections staff time and resource constraints on labor-intensive case cleaning prevented full release of these cases for almost two years post-treatment. Applying chemicals in a storage area requires access restrictions to all users of the area, and may disrupt multiple departments' visitor research plans and study tours.

Naphthalene

Between 1999 and 2003, a project was completed to physically remove (by chipping and HEPA vacuuming) residual caked naphthalene from approximately 900 entomology cabinets. Sixteen ambient samples were collected in areas throughout the storage room before the project began, with results ranging from 0.050 - 0.10 ppm. Ambient samples collected in the same locations post-removal ranged from 0.021 - 0.052 ppm. Statistical comparison of these two sample population indicated that their respective 95 percent upper and lower confidence levels did not overlap and therefore the two sample sets were distinct. These data suggested that the removal effort was successful in reducing the overall ambient concentrations of naphthalene in the storage area. These concentrations are all orders of magnitude less than the 10.0 ppm OEL.

However, because OELs are targeted for healthy workforce, and may not be as protective for the general population that includes the very young or very old, and those with pre-existing medical conditions or sensitivities to agents of exposure, the USEPA/Agency for Toxic Substances and Disease Registry establishes community based minimal risk levels (MRL), for this purpose. The MRL for naphthalene, converted to an 8-hour workday, with uncertainty factors to account for the general population, would be 0.015 ppm (ATSDR 2011). To reach this with a second round of removal efforts would require replacing the wooden drawers completely (at prohibitive expense) or gradually airing out drawers emptied of specimens within fume hoods to permanently volatilize residual naphthalene in the wood (effective but extremely time consuming).

RECOMMENDATIONS FOR RISK CONTROL AND REMEDIATION

The following recommendations, based on these studies, are applicable to any facility for effectively controlling and remediating risk to both health and collections from exposure to PDB or naphthalene.

<u>Elimination of PDB and naphthalene applications</u>. Data in the PDB study indicated that the greatest contributor to staff exposures was accessing the cases immediately after the active treatment period. Eliminating future use of these organic chemicals greatly reduces the overall exposure potential from accessing past treated cases. Eliminating the use of these applications is also in line with the intent of U.S. federal regulations (USEPA 1996) to prevent registration and use of pesticides with unreasonable adverse risk to humans and the environment. Where multiple pesticides or treatments are available, the one least harmful to the environment and to human and animal health must be attempted first.

<u>Research on effective yet safer chemical alternatives</u>. Regardless of a robust IPM system, infestations may require the use of chemical pesticides. Scientific studies in the collections care community are essential to find effective pest control methods that are a safer alternative to PDB or naphthalene in terms of the scientific utility of the specimens. While effects of some chemicals have been researched well (e.g., Kigawa 2011), this is an area that merits continued study.

<u>Staff exposures</u>, particularly in collections care tasks, need to be controlled through a continuing health management program, to include:

1. <u>Warning labels, providing awareness and safety instructions</u>, affixed to previously treated cases, alerting users to the possible presence of residual pesticides from past treatments. The signage should advise users to consult with supervising collection managers for more guidance on safe access and handling procedures.

2. <u>Staff training in the exposure hazards from treated cases and the safe work practices required by the facility to control their risks</u>. Safe work practices should include, as a minimum:
    a. Respirator use for any case involving significant time at the case or inside the case for cleaning or inspections.
    b. Barrier gloves when handling treated specimens or cleaning cases.
    c. Ventilating treated cases before access.
    d. Removal of specimens of interest for research to a cart or table, in a well-ventilated area.

<u>Strict adherence by all units to a museum integrated pest management (IPM) program that would prevent or significantly reduce infestations from occurring</u>. A facility IPM program should be followed by all collecting units with incoming items:

1. Improved pre-storage preparation techniques for species that are known to retain lipids.
2. Extensive inspection of all incoming specimens for pests, including quarantine, treatment with non-toxic and low-impact methods such as anoxic methods or freezing, and final inspection for eggs or live-hatch prior to movement into storage.
3. Robust and consistent storage area pest monitoring and case inspection procedures.

4. Timely reports of potential infestations to the appropriate staff.
5. Treatments for infestations that rely on least-toxic-to-humans fumigation/pesticide applications in accordance with all applicable regulations, or use of non-toxic methods of eradication.

CONCLUSION

Prevention of infestations is key to sound IPM programs. Pest inspection and, where warranted, measures such as freezing, heat treatments, and anoxia are well documented as to their efficacy in pest eradication. These steps can preclude the need for extremely potent chemicals that leave lingering safety risks. As a caveat, use of heat treatments for any material known or suspected of having been treated with long-lived organic chemicals should be avoided unless adequate capture filtration can be provided for the vapor generated during treatment. Environmental sampling regarding exposure to persistent organic pesticide residues suggests that remediation methods must be researched, validated and implemented for permanent pesticide removal and risk reduction for the benefit of healthy users and healthy collections.

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