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Potential Occupational Exposures in the Reiss-Engelhorn-Museen Mannheim/Germany

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Abstract The Reiss-Engelhorn-Museen in Mannheim, Germany requested support from a toxicological laboratory in evaluating occupational exposures before a cleanup and renovation period in 2006. Samples of dust and dirt and scrapings of exhibits were collected from several locations. Following toxicologically relevant compounds could be identified by gas chromatography – mass spectrometry (GC/MS) by comparison with a mass spectra library: dichlorodiphenyl trichloroethane (DDT) and its breakdown product dichlorodiphenyl dichloroethane (DDD) as well as dichlorodiphenyl dichlorethylene (DDE), methoxychlor, nicotine, and camphor. In recent times various insecticides have been used to protect museum artefacts against moths, woodborers and other insect pests. Caution has to be made because the presence of hazardous compounds can result in security problems for museum staff as well as for visitors.

Keywords Pesticides · Museum · Gas chromatography—mass spectrometry (GC/MS) · Occupational exposure

In February 2006, the Reiss-Engelhorn-Museen in Mannheim, Germany, requested support from the toxicological laboratory of the Institute of Forensic Medicine Bonn in evaluating occupational exposures before a cleanup and renovation period in 2006. The museum covers a wide spectrum of archaeology, natural history, ethnology and art, city and theatre history. It should be excluded that workers (museum staff) like curators, conservators, preparators (taxidermists) and museum assistants, who are involved in objects handling (e.g. cleaning, packaging and storing), were potentially exposed to toxic compounds. Former employees explained that in former times in the ethnological collection prophylactic gassing with Eulan (comprehensive term for polychloro-2(chlorine methyl sulfone amide)-diphenylether (PCSD) and/or polychloro-2-aminodiphenylether (PCAD)), lindane containing products, pyrethroid insecticides and with an “Illo gas”, not closer to be defined, were carried out till the middle of the 1990s. In a note from 1996 it is explained that Detmol Tex 808 (chlorpyrifos) was especially used for textiles “occasionally”; in addition, Jacutin incense sticks (lindane) till 1992/93 as well as pyrethrum till 1994/95. The aforesaid Illo gas was probably used in a depot (so-called “safe”) only. There are reports that canisters of this gas were taken to the depot were they opened whereupon the executive restorer quickly ran out to throw up.We were asked to analyze various samples from the Reiss-Engelhorn-Museen evaluating occupational exposures.

Materials and Methods

In 2006 samples of dust, dirt, and scrapings of exhibits were collected from several locations (cross-section of removed dirt and dust from a number of objects in long-term-storage area containing various remains on museums artefacts) using a vacuum cleaner. The sample was stored in a sealable plastic bag at room temperature until further analysis.

An aliquot of the dried sample was dissolved in methanol. The solution was centrifuged (5 min; 3.000 g) and the supernatant was filtered through a Millex 4 mm syringe

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filter (Millipore, Schwalbach, Germany). Aliquots of the samples were directly analyzed by gas chromatography – mass spectrometry (GC/MS).

Additionally an aliquot of a methanolic washing solution revealed from a Moroccan necklet with white cristalline scum and abrasions from this necklet solved in methanol were analyzed. Samples from the general workplace environment and from personal breathing zones were not collected.

GC/MS analyses were performed in full scan mode (m/z 30-550) on a model 6890 series Plus GC, in combination with an Agilent 5973 N MSD MS (Chromtech, Idstein, Germany). Substances were separated on a fused-silica capillary column (HP-5MS, 30 m × 0.25-mm i.d., 0.25-µm film thickness). The temperature program applied was as follows: 70°C maintained for 1 min, 5°C/min increase up to 280°C with following 75°C/min increase up to 300°C (held for 2 min); the total run time was 23 min. Temperatures for the injection port and detector were set at 150°C and 280°C, respectively. Injection was carried out in splitless injection mode and helium at a flow rate of 1.0 mL/min was used as carrier gas.

Recorded mass spectra from various extracts were compared with library spectra according to Pfleger et al. (2000) who described a procedure for a systematic toxicological screening analysis. For quality assurance a test solution of various compounds recommended by this group was analyzed each working day prior to real samples to verify the usefulness and sensitivity of the GC/MS system and procedure.

Results and Discussion

With a GC/MS procedure normally used as a systematic toxicological screening procedure dichlorodiphenyl trichloroethane (DDT) and its breakdown product dichlorodiphenyl dichloroethane (DDD) as well as dichlorodiphenyl dichlorethylene (DDE; 4% in technical DDT), methoxychlor, nicotine, and camphor were found as potential hazardous compounds in samples from a cross-section of removed dirt and dust in the long-term-storage area of the Reiss-Engelhorn-Museen (Table 1). Recorded mass spectra resulting from analyses of various samples were compared with reference library spectra. A qualitative analysis only was performed due to missing references concerning the sampled material. In Fig. 1 a positive result for methoxychlor, DDT and its breakdown product DDD is demonstrated.

The determination of drometrizole which is used in sunscreens to absorb UV radiation was interpreted as an artefact.

DDT is a well known organochlorine insecticide that was especially used in the first half of the 20th century and was later banned as a persistent organic pollutant in most countries. Methoxychlor, which is also a synthetic organochlorine, was used as a replacement for DDT, because it is faster metabolized and does not lead to bioaccumulation. Camphor can be used as moth repellent or antimicrobial substance and in embalming. Solid camphor releases fumes that form a rust-preventative coating. Therefore it is stored in tool chests to protect tools against rust. Camphor crystals are as well used to prevent damage to insect collections by other small insects. Nicotine (nicotine sulphate) is also sold commercially in form of a pesticide.

In our opinion in the Reiss-Engelhorn-Museen DDT as well as methoxychlor and camphor were occupational poisons used for pest control in former times. Nicotine is seldom used as a pesticide and could also be transferred from smoking visitors or employees of the museum.

In recent times different insecticides have been used to protect artefacts against moths, woodborers and other

Table 1 Sample list and results

Origin	Description	GC/MS results
Sample of the hazardous substance vacuum cleaner after cleaning all objects from the depot "Halle" (B4, 10a, 1st floor)	Cross section sample	DDT, its breakdown product DDD, dichlorodiphenyl dichlorethylene (DDE; 4% in technical DDT) methoxychlor, nicotine, camphor
Depot "Tresor" (B 4, 10a, 1st floor)	Methanolic washing solution from a Moroccan necklet with white cristalline scum	DDT, its breakdown product DDD, dichlorodiphenyl dichlorethylene (DDE; 4% in technical DDT)
Depot "Tresor" (B 4, 10a, 1st floor)	Abrasion from the Moroccan necklet solved in methanol	DDT, drometrizole

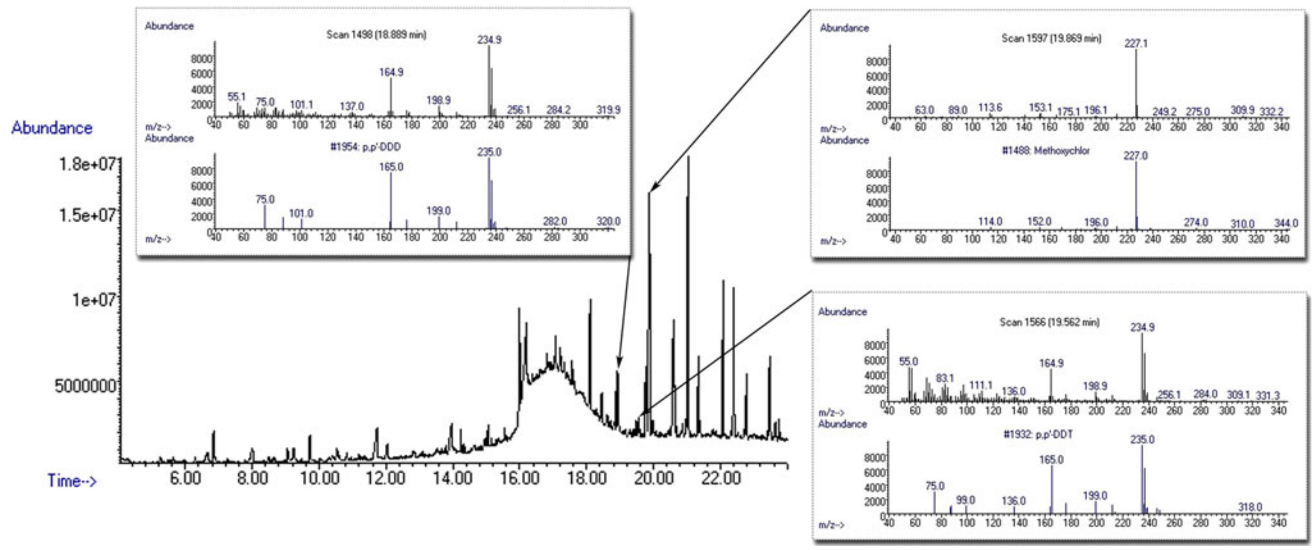

Fig. 1 : Gas chromatogram and recorded mass spectra from the cross section dust sample with corresponding libary spectra from methoxychlor, DDT and DDD (Pfleger et al., 2000) as proof for their presence

insect pests (Goldberg, 1996; Hawks, 2001). There are reports mainly from the 1980s, e.g. from the National Museum of Denmark (Glastrup, 1986) where DDT, naphthalene and methoxychlor (and possibly lindane, aldrin and dieldrin) were detected or from the Departement of Natural History of Bristol Museum (Muir, 1981) where traces of arsenic and mercury together with naphthalene and DDT were found. In the Natural History Museum, Colorado, one detected DDT exposures (Centers for Disease Control, Prevention 1983).

Purewal (2001) who found mercury, arsenic, barium, and naphthalene on historic plant collections presented results from a literature research on chemicals being used on herbarium material by 22 institutions from 12 countries and listed following substances: arsenic trioxide, barium fluorosilicate, carbon disulphide, carbon tetrachloride, DDT, ethylene oxide, lauryl pentachlorophenate, lindane, mercuric chloride, methyl bromide, naphthalene, p-dichlorobenzene, phosphine, pyrethrum, hydrogen cyanide, and dichlorovos. Arsenic and mercury could especially be found in mammalogy and ornithology collections (Sirois, 2001). Recently Palmer reviewed analytical methods for the determination of mercury, arsenic, and pesticide residues on museum objects (Palmer, 2001).

In the past few years positive findings were reported as well, e.g. for p-dichlorobenzene, naphthalene, thymol, lindane, dieldrine, and DDT on museum objects repatriated to the Hupa tribe in California (Palmer et al., 2003). According to Dawson and Strang (1992) at least since the end of the 1980s it is well known that organochlorides are not useful for handling in museums.

Today museums have converted to chemical-free means, e.g. freezing, vacuum cleaning or a combination of flash-freezing and subsequent cleaning to preserve artefacts from destruction by insects. Other safety measures:

- objects are visually checked intensely at regular intervals and are removed if necessary;
- depots are ventilated and restructured; the air movement causes a retreat of adult moths capable of flight;
- an object filing in certain for moths unattractive areas can protect against infestation;
- fight with beneficial animals: these attack only a certain development stage of the pest at a time. In our case small ichneumon flies destroyed the oviposition of the moths;
- to shrink-wrap endangered objects in polyethylene foil serves the protection from infestation (anew) and prevents as well, if necessary, a propagation of unrecognized infestation in the depot;
- display of attractants (fresh feather bundles or animal skins), sticky traps - merely to monitor – can not decimate existing infestation.

However, in older collections the presence of hazardous compounds can not be excluded resulting in security problems for the staff as well as for visitors and chemical-toxicological analyses are recommended for exclusion. Since the middle of the 1990s a conversion of the preventive measures to a controlled deep-freezing and recently heating procedures occurred due to acute infestation. Once the use of beneficial animals was given a try during an acute infestation (ichneumon flies were to destroy the ovipositon of the moths). However, the main focus in the everyday work lies in systematic prophylaxis, “integrated pest management sytems”, i.e. locks in the depot access area, regular controls by application of pheromone traps, UV traps for the supervision of the insect flight, training of the staff etc.

In 2006 in the case of the Reiss-Engelhorn-Museen after a mechanical cleaning procedure a relevant exposure to the toxic agents could be excluded. However, caution should be taken with organic materials, especially wood, skin, fur, and feathers (Merkord, 1994).

Especially in museums with older objects and the suspicion of former use of pesticides caution has to be taken because museum staff like curators, conservators, preparators and museum assistants but also visitors can potentially be exposed to toxic compounds. Because the potential presence of hazardous compounds chemical-toxicological analyses are recommended for exclusion of any risks.

References

Centers for Disease Control, Prevention (1983) DDT exposure in a Natural History Museum—Colorado. MMWR 32:443–444

Dawson J, Strang TJK (1992) Solving museum insect problems: chemical control. Canadian Conservation Institute, Ottawa

Glastrup J (1986) Insecticide analysis by gas chromatography in the stores of the danish national museum's ethnographic collection. Stud Conservat 32:59–64

Goldberg L (1996) A history of pest control measures in the anthropology collections, national museum of natural history, smithsonian institution. JAIC 35:23–43

Hawks C (2001) Historical survey of the sources of contamination of ethnographic materials in museum collections. Collect Forum 16:2–11

Merkord J (1994) Gefahren im Umgang mit Fungiziden & Bioziden. Restauro 3:170–173

Muir D (1981) Health hazards in natural history museum work. Museums Journal 80:205–206

Palmer PT (2001) A review of analytical methods for the determination of mercury, arsenic, and pesticide residues on museum objects. Collect Forum 16:25–41

Palmer PT, Martin M, Wentworth G, Caldararo N, Davis L, Kane S, Hostler D (2003) Analysis of pesticide residues on museum objects repatriated to the Hupa tribe of California. Environ Sci Technol 37:1083–1088

Pfleger K, Maurer HH, Weber A (2000) Mass spectral and GC data of drugs, poisons, pesticides and their metabolites, 2nd edn. Wiley-VCH, Weinheim, Germany

Purewal V (2001) The identification of four persistent and hazardous residues present on historic plant collections housed within the national museum and galleries of wales. Collect Forum 16:77–86

Sirois PJ (2001) The analysis of museum objects for the presence of arsenic and mercury: non-destructive analysis and sample analysis. Collect Forum 16:65–75