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Case study

# Occurrence of organic biocides in the air and dust at the Natural History Museum of Rouen, France

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ABSTRACT

Using over 100 years of biocides for preservation of collections of natural history museums has led to significant pollution of specimens and the environment of museums. Staff may be exposed to these substances as well by skin contact or by breathing dust and volatiles compounds. In this work, we present the results of a screening of volatile and semi-volatile organic compounds in the air and dust from the Natural History Museum of Rouen (Normandy, France). It is shown that the concentration in the air of the different substances is acceptable and below regulatory limits. Nevertheless, concentrations in dust especially for DDT and DDD are high and require special precautions and a regular dusting.



## 1. Research aim

The aim of this study is to investigate the contamination of indoor air pollution in a Natural History Museum by volatile organic compounds used in the fight against insect or mold infestation. Concentrations of these substances in air and dust have to be determined and compared to the regulatory limits. Finally, the possible impact of these substances on the staff has to be assessed and safety precautions given when handling museum specimens.

## 2. Introduction

The problem of indoor air pollution in museums has become a growing concern. Most often, the air quality is studied in order to protect collections from atmospheric degradation but rarely to protect staff and visitors by ensuring compliance with regulations. In the case of the Natural History Museum of Rouen (Normandy, France), the situation is especially problematic as the air quality may be affected by the extensive use for over 100 years of toxic compounds used for conservation and the fight against pests attack. These toxic organic compounds (pesticides, solvents...) or inorganic compounds (arsenic, mercury...) are found on collections itself but also in the form of dust or volatile compounds in the air, which may present a risk to both staff and visitors.

Many studies have shown significant contamination of specimens or objects in museums collections by inorganic and organic compounds [1–3]. For instance, arsenic with arsenic trioxide and arsenate V employed from 18th century until the 20th century is abundantly found on old specimens as well as recent one. The presence of inorganic metallic contaminants in collections has been well studied due to the easy determination of these metals using portable X-ray Fluorescence Spectrometry (XRF) [4]. During the 20th century, synthetic organic insecticides were intensively used. DDT (Dichlorodiphenyltrichloroethane) is probably one of the most emblematic pesticides. Treatments of natural history collections with DDT were common from the 1950s until the late 1970s. This very effective substance against pests was one of the major insecticides used during this period. This compound is now prohibited and is classified as reprotoxic and probably carcinogen by the Environmental Protection Agency (EPA). It is the same for lindane or paradichlorobenzene, which for its part was used until the late 1990s. Today, treatments with insecticides such as pyrethroids are still applied, when integrated pest management and non-chemical methods remains ineffective. Other compounds used for the conservation or as solvents may also be present in the air. This is for example the case of formaldehyde, long used for fluid-preserved collections [5].

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Over the years, these compounds have been accumulated in rooms and on collections [6,7]. It thus may present a risk to staff.

If contamination of collections has been fairly well studied, it is not the same for the air pollution where few publications on this topic are known [5,7]. For these reasons, the Natural History Museum of Rouen wished to make an inventory of the indoor air pollution. The objective was to identify the pollutants in the air and then to determine their concentration. These data will lead to an action plan that will put in place adequate prevention and decontamination measures. A periodic air monitoring will then be conducted to assess the sustainability of these actions.

An initial screening of pollutants and then quantification of these pollutants in the air was performed at the Natural History Museum of Rouen; the objective was to determine the exposure of staff and visitors to these substances and to map the pollution in the museum. Measurement campaigns have then been conducted in different locations: storage rooms, exhibition rooms and laboratories over 2 years. The study was also supplemented by determining the exposure of workers using personal air sampling pumps to assess the impact on their health during a typical working day in different services. During the two campaigns, 188 air and dust samples were collected and analyzed. We present here our results.

## 3. Result and discussion

### 3.1. Sampling

Active air sampling (200 ml $min^{-1}$, 8 h, Escort Elf Sampling Pump, Supelco) was done using glass tube filled with different type of absorbents or filter that trap volatiles compounds or dust. Temperature and relative humidity were recorded during sampling.

### 3.2. Volatiles and semi-volatiles compounds (except formaldehyde) sampling and analysis

Activated coconut charcoal (Orbo 32.6 mm × 75 mm, Supelco), and XAD-2 (Orbo 609, 6 mm × 110 mm, Supelco) adsorbent were used in the sampling tube. The absorbent was desorbed by solvent extraction (1 mL, ethyl acetate for coconut charcoal, and 1 mL of methanol for XAD-2 resin). This solution was analyzed using a GC/MS system (Varian, 3900/Saturn 2100 T). Compounds were separated on a Zebron 5MS column (30 m × 0.25 mm, 0.25 μm, Phenomenex). Identification was made using NIST library search (NIST03, National Institute of Science and Technology). For identified compound, reference standards were injected for retention time and mass spectra comparison. All identified compound were quantified using their own response factors. For calibration, the linear regression mode was used. Duplicate sampling and analysis were performed.

### 3.3. Formaldehyde sampling and analysis

The adsorbent used was silica coated with DNPH (LpDNPH S10, Supleco). The adsorbent was desorbed by acetonitrile (5 mL). The solution was analyzed by HPLC (HP 1050, Agilent, Germany) with a UV-visible detector at 360 nm. The column was a Luna 2 C18 (150 mm × 4.6 mm, 5 μm, Phenomenex, USA). The mobile phase was acetonitrile/water (60/40) with a flow rate of 1 mL/min. Formaldehyde as DNPH derivatives was quantified using a standard solution of formaldehyde-DNPH derivative (Supelco).

### 3.4. Dust sampling and analysis

For dust in the air analysis, we used air monitoring cassettes with glass fiber filter (25 mm A/E glass fiber filter 1 μm pores, Supelco) attached to the air sampling pump. Dust was also collected directly in the windows, in the storage boxes but also in the dust bags used for cleaning of premises. The filter or directly the dust was extracted by dichloromethane under sonication for 10 min in a seal tube. Quantification of volatiles and semi-volatiles molecules (except formaldehyde) was performed by GC-MS as already described.

### 3.5. Reference values and regulations

According to the French regulation, the employer must carry out regular measurement of worker exposure to hazardous chemicals in the atmosphere of the workplace (Article R4412-27 of the French Labor Code). Levels of chemicals in the air have to be compared with reference limits. In this article, we will focused on the reference values advocated by the Occupational Safety Health Administration (OSHA): the Total Weight Average Permissible Exposure Limits, TWA PEL, that are more regularly updated than French one (Occupational Exposure Limit OEL). In Table 2, reference values for the identified chemical compounds are listed. TWA is defined as the employee's average airborne exposure in any 8-hour work shift of a 40-hour workweek, which shall not be exceeded. The 8-hour TWA PEL is then the level of exposure established as the highest level of exposure an employee may be exposed to without incurring the risk of adverse health effects. This value corresponds to the legal limit at which institutions should refer.

### 3.6. Museum description

The Natural History Museum of Rouen houses an important collection of more than 800,000 objects, which approximately half are exposed. This includes specimens of birds, mammals, invertebrates, minerals, palaeontology and ethnology.

The permanent exhibitions are on the first and second floor of the main building (Fig. 1). The temperature in these rooms is not controlled and varies from 17 to 22 °C during the year. The stockroom is located in the storage building (Fig. 1). The temperature is not controlled and varies from 12 to 29 °C during the year. In all premises, the relative humidity is maintained between 30 and 60%. There is no ventilation and air treatment in the museum and the storage room.

### 3.7. Screening of volatile and semi-volatile organic compounds in air

An initial screening stage of volatiles and semi-volatiles organic pollutants was conducted by GC/MS focused on the presence of chemicals used in the museum since 1876 (Table 1). This

**Table 1**
Chemical treatments and period of application in the Natural History Museum of Rouen.

| Compound | Time period of application in the Museum of Rouen |
|---|---|
| DDT | Until 1982 |
| Lindane | Until 1982 |
| Paradichlorobenzene | 1976–1998 |
| Dichlorvos | 1987–2005 |
| Formaldehyde | Until 2006 |
| Acetone | Since 1983 |
| Petroleum ether | Since 1983 |
| Trichloroethylene | Until 2006 |
| Ethanol | Still in use |
| Turpentine | Still in use |
| Creosote from beech | 1976–2006 |
| Pyrethroids | Until 2011 |