Exposure assessment of toxic metals and organochlorine pesticides among employees of a Natural History Museum

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Abstract:

Chemical compounds such as arsenic, mercury and organochlorine pesticides have been extensively used as preventive and curative conservation treatments for cultural and biological collections to protect them from pest and mold infestations. Most of the aforementioned compounds have been classified as carcinogenic, mutagenic and teratogenic and represent a health risk for members of staff exposed to contaminated objects. The present study addresses the internal exposure of 28 museum employees in Museum für Naturkunde Berlin by measuring arsenic species and mercury in urine as well as hexachlorocyclohexane isomers (α-HCH , β-HCH, γ-HCH), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (4,4´-DDT), its main metabolite dichlorodiphenyldichloroethylene (4,4´-DDE) and pentachlorophenol (PCP) in blood serum. This study was carried out in order to assess the internal exposure of Natural History Museum staff members to toxic metals and organochlorine pesticides.

From each participant, involving 8 women and 20 men, two blood samples and five urine samples were taken during a working week. Information about work activity and exposure related factors like dust development through work, use of personal protective equipment, as well as a nutrition diary were obtained after applying a questionnaire. Information on fish and seafood intakes as well as amalgam fillings was also available. The results of the study showed that the museum staff members were exposed to arsenic, mercury, β-HCH and 4,4´-DDE while handling museum objects. However, all results for specimen were below established reference values. To validate the results, further studies are required.

Keywords: Arsenic; Human biomonitoring; Museum collections; Occupational exposure; Organochlorine pesticides, Mercury

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List of abbreviations:

4,4´-DDE = Dichlorodiphenyldichloroethylene
4,4´-DDT = Dichlorodiphenyltrichloroethane
As = Arsen
As(III) = Trivalent arsenic
As(V) = Pentavalent arsenic
AsB = Arsenobetain
BAR = Biological substance reference value
DMA = Dimethylarsinic acid
ES = Elise Spiegel
FIMS = Flow injektion mercury system
GerES = German Environmental Survey
GF-AAS = Graphit furnace atomic absorption
HBM = Human biomonitoring
HCB = Hexachlorobenzol
Hg = Mercury
HPLC-ICP-MS = A high-performance liquid chromatography in combination with inductively coupled plasma mass spectrometry
IPASUM FAU = Institute and Outpatient Clinic of Occupational, Social and Environmental Medicine in Erlangen (University of Erlangen-Nuremberg, Germany)
KD = Katharina Deering
LOD = Limit of Detection
LOQ = Limit of Quantification
MfN = Museum für Naturkunde Berlin
Mm = Monday morning
MMA = Monomethylarsonic acid
OCPs = Organochlorine Pesticides
PCP = Pentachlorophenol
SB = Stephan Bose-O´Reilly
Te = Thursday evening
α-HCH = α-hexachlorocyclohexane
β-HCH = β-hexachlorocyclohexane
γ-HCH = γ-hexachlorocyclohex

1. Introduction

Museum collections, especially those with a focus on organic objects, have historically been treated preventively and curatively with toxic preserving agents such as arsenic and mercury. Numerous studies show that well into the 20th century biocides with additives from toxic metals were used for the preservation of natural history specimens (Martin, 1879). Accordingly, research on the use of toxic substances in museum as preservatives has identified a wide range of toxic metals and pesticides in recent decades (Goldberg, 1996; Hawks, 2001; Omstein, 2010). Due to the highly repeated use of different pesticides in the past, a "poisonous cocktail" was applied on the objects. As a result, restorers, conservators, curators and scientists have been and still often exposed to toxic substances in their daily work without their knowledge (Spiegel et al., 2016). And this is surprising since the health risks posed by the use of formulations with toxic metals as a preservation agents is well known to the early taxidermists and scientists (Martin, 1879; Naumann, 1848). In this regard, Arndt (1932) published a systematic study of occupational diseases in natural history collections, pointing out that health problems can occur after handling taxidermal objects.

A large and growing amount of literature has been published on pesticides in air, dust and objects as early preservatives in museum collections (Banks, 2015; Briggs et al., 1983; Charlton et al., 2014; Cross and Odegaard, 2009; Gribovich et al., 2013; Marcotte et al., 2014; Marcotte et al., 2017; Marte et al., 2006; Oyarzun et al., 2007; Palmer et al., 2003; Seifert et al., 2000; Torge et al., 2011). Several authors have examined mercury and arsenic in museum collections, showing high concentrations compared to general background levels. Schieweck et al. (2005) and Holt et al. (2017) found organochlorine pesticides (OCPs) in a museum and a historical building. A previous study has examined and compared the concentrations of these compounds in several museums, including the Museum für Naturkunde Berlin (MfN) (Deering et al., 2019). However, there are no studies addressing the exposition of these chemical compounds in museums` employees. Recently, one study reported the concentrations of arsenic species, but only in five employees. (Mithander et al., 2017). To the best of our knowledge, the present study is the first performing both, an ambient monitoring in 17 rooms and collections accompanied by a human biomonitoring of toxic metals and OCPs in 28 individuals from the museum staff. Specifically, urine and blood samples have been analyzed in order to quantify inorganic arsenicals and organic arsenicals, arsenobetaine (AsB), mercury (Hg) in urine and several OCPs, including α-hexachlorocyclohexane (α HCH), β-hexachlorocyclohexane (β -HCH), γ-hexachlorocyclohexane (γ-HCH), 4,4´-dichlorodiphenyltrichloroethane (4,4`-DDT) and the main metabolite dichlorodiphenyldichloroethylene (DDE), hexachlorobenzene (HCB) and pentachlorophenol (PCP).

Especially the toxic metals are well known as cancerogenic, mutagenic and reprotoxic. On average, the content of toxic metals as well as OCPs in museum air and dust samples, is below concentrations found in occupational medicine studies, with exposures arriving from smelting and mining metals and minerals. Working in a museum is associated with long-term chronic exposure. This is also evident in a procedure for the determination of occupational diseases, which was carried out in 2015 by the Institute for Preventive Medicine and Occupational

Medicine of the Statutory Accident Insurance. They diagnosed a restorer with an urothelial carcinoma after chronic exposure to arsenic during working life as an occupational disease. This diagnosis was considered as a disorder related to the occupation of the patient and specifically his exposure with arsenic (Hagemeyer et al., 2015). This is the only published case of an assessment of occupational illness with a restorer in connection with toxic preservatives. However, it is supposed that other cases remain undiagnosed or unpublished. Therefore, the published case does not necessarily reflect the full dimension of exposure to toxic substances in museums. Our study was carried out in order to assess the internal exposure of Natural History Museum staff members to toxic metals and organochlorine pesticides.

2. Materials and methods

2.1. Study population

This study was approved on December 29, 2016 (Nr.: 802-16) by the Ethics Committee of the Faculty of Medicine, Ludwig-Maximilians-Universität, Munich, Germany. The call for volunteers has been achieved through several information events at the MfN. The intention was to recruit at least 20 participants for the study. Inclusion criteria for the selected individuals were the following: (i) being employed in contaminated exhibitions or depot rooms for at least 6 months, and (ii) to have worked at least 10 hours per week with the collection items; (iii) employees who were not exposed during the last two weeks were not included in the assessment. In the end, a total of 28 employees participated in the study. After being personally informed by authors of this study (KD, ES), the volunteers signed the informed consent form.

A questionnaire was developed (KD, ES) to distinguish work-related exposures from other exposures. Participants had to answer questions about their intake of fish and seafood as well as amalgam fillings as opportunities for exposure to arsenic or mercury. In addition, they answered questions about health issues related to their work, the use of personal protective equipment and other issues (e.g. use of gloves, dust exposure, dermal contact). This study was conducted according to the Declaration of Helsinki.

2.2. Analytical processes

2.2.1. Sample collection

From all the participants, four blood samples were collected in a clot activator tubes (S-Monovette®, Co. Sarstedt, 9 ml Z, Clotting Activator for Serum) and five urine samples were collected in 250 ml polypropylene vessels. All the samples were obtained during one study week at the MfN. Two blood samples (n = 28) and one urine sample (n = 28) from each participant were gained Monday morning before they started their individual daily work. From Monday afternoon to Thursday afternoon, participants brought their urine (n = 119) after end of working hours. Two blood samples (n = 26) from the participants was obtained after end of their working week. First, both blood and urine samples were stored at 5°C. The blood samples were transferred the same day to laboratory in Munich where the samples were centrifuged to collect serum. The urine samples were refilled in

two urine sample tubes each Monovetten (Co. Sarsedt, Luer, 10 ml), stored at 5°C. and transferred at the end of study week to the same laboratory. All samples (urine and blood serum) were stored at -20°C until analysis.

2.2.2. *Determination of total arsenic in urine*

Total arsenic in urine was analyzed by graphite furnace atomic absorption spectroscopy (GF-AAS) at a detection wavelength of 193.7 nm. Urine samples were diluted six-fold with 0.01 % Triton-X in 0.13 % nitric acid. 20 µl of this dilution were automatically pipetted into the graphite tube of the GF-AAS (AAnalyst 600, Perkin Elmer, Rodgau, Germany). 5 µg Pd (as $Pd(NO_3)_2$) and 3 µg $Mg(NO_3)_2$ were added as matrix modifiers. The furnace program was according to the recommendations of the manufacturer. Quantification was based on the standard addition method. In detail, 5 and 10 pg arsenic were directly added to the sample in the graphite tube, respectively. Limit of detection (LOD) was 0.2 µg/l.

Samples with total arsenic levels above 15 µg/l were analyzed for arsenic species at the Institute and Outpatient Clinic of Occupational, Social and Environmental Medicine in Erlangen (University of Erlangen-Nuremberg, Germany) by HPLC-ICP-MS according to a procedure proved and published by the Deutsche Forschungsgemeinschaft (Schramel et al., 2018). (LOD: 0.07 µg/l)

2.2.3. *Determination of total mercury in urine*

Total mercury in urine was analyzed using a Flow Injection cold vapor system (FIMS 100, Perkin Elmer, Rodgau, Germany) at a detection wavelength of 253.7 nm. For analyses, 1.5 ml urine sample, 0.20 ml hydrochloric acid (30%,), 0.20 ml 3% $KMnO_4$ solution and 4.1 ml ultrapure water were mixed and introduced into the system. Reduction of Hg was carried out in the manifold by adding a 1.3% $SnCl_2$ solution. Quantification was based on external calibration. (LOD: 0.1 µg/l)

2.2.4. *Determination of organochlorine pesticides in serum*

The following analytes were liquid-liquid extracted: hexachlorobenzene (HCB), several isomers of hexachlorocyclohexanes (HCH, including alpha-HCH, beta-HCH and gamma-HCH (lindane)), 4,4'-DDT and its main metabolite, 4,4'-DDE. First, 20 µl of internal standard (IS, 1 mg/l δ-HCH in methanol) and 2 ml formic acid were added to 2 ml serum. Then, 4 ml of a hexane-toluene-mixture (1:1; v/v) were added and the sample was mixed with an overhead shaker for 5 min. The organic phase was transferred to a separate tube and the sample was again extracted again. The organic phases were combined, spiked with 100 µl n-decane and concentrated to a final volume of approximately 200 µl using an automated concentration system (XcelVap, Horizon Technology, Uppsala, Sweden).

1µl of the final solution was injected into an Agilent 7890A GC coupled to an Agilent 7000 mass spectrometer (Agilent, Waldbronn, Germany). Separation was carried out on a VF-5MS GC column (30 m × 0.25 mm × 0.25 µm; Agilent, Waldbronn, Germany). Helium 5.0 was used as carrier gas in constant flow mode (flow = 1.5 mL/ min). The split flow was set at 64.5 mL/min. Injector and transfer lines were heated to 250 and 280 °C, respectively. The oven program was as follows: 70 °C (1 min), 25 °C/min to 150 °C (3 min), 20 °C/ min to 280

°C (1 min). Mass spectra were obtained at 70 eV (source: 230 °C, H2 quench gas: 2.25 ml/min, N2 collision gas: 1.5 ml/min) in MRM mode. The retention times and MRM parameters for the analytes were as follows (retention time, transition quantifier, transition qualifier): HCB: 9.3, 284 → 249, 284 → 214; HCHs: 9.3 (α-HCH) / 9.9 (β-HCH,γ-HCH) / 10.4 (δ-HCH, IS), 219 → 183, 181 → 109; 4,4-DDE: 12.8, 246 → 176, 318 → 248; 4,4-DDT: 13.4, 235 → 165, 235 → 199. Quantification was based on matrix-assisted calibration. In detail, pesticide-free serum was spiked with various concentrations of the analytes.

Pentachlorophenol (PCP) was also liquid-liquid extracted: 50 µl of internal standard (1 mg/l tribromophenol in methanol) and 2 ml saturated sodium bisulfate solution were added to 2 ml serum sample. For extraction, 4 ml hexane were added, and the samples were mixed with an overhead shaker for 5 min. Thereafter, 100 µl acetone was added and the sample was centrifuged for 5 min at 1370 g. The organic phase was transferred to a separate tube and the sample was extracted again. The organic phases were combined, spiked with 100 µl n-toluene and evaporated to dryness using an automated concentration system (XcelVap, Horizon Technology, Uppsala, Sweden). Then, 500 µl acetic anhydride were and the sample was incubated for 5 min while shaking. After addition of 4 ml of a 0.1 M potassium carbonate solution, the analytes were extracted with 3 ml hexane for 15 min with an overhead shaker. The organic phase was transferred to a separate tube and the sample was extracted again. The organic phases were combined, spiked with 100 µl n-toluene and evaporated to dryness. Finally, the residue was dissolved in 100 µl toluene.

1µl of the final solution was injected into an Agilent 7890A GC coupled to an Agilent 7000 mass spectrometer (Agilent, Waldbronn, Germany). Separation was carried out on a VF-5MS GC column (30 m × 0.25 mm × 0.25 µm; Agilent, Waldbronn, Germany). Helium 5.0 was used as carrier gas in constant flow mode (flow = 1.5 mL/ min). Injector and transfer lines were heated to 250 and 280 °C, respectively. The oven program was as follows: 70 °C (1 min), 20 °C/min to 250 °C (0 min). Mass spectra were obtained at 70 eV (source: 230 °C, H2 quench gas: 2.25 ml/min, N2 collision gas: 1.5 ml/min) in MRM mode. The retention times and MRM parameters for the analytes were as follows (retention time, transition quantifier, transition qualifier): PCP: 9.3, 284 → 249, 284 → 214; tribromophenol: 9.3, 219 → 183, 181 → 109. Quantification was based on matrix-assisted calibration. In detail, PCP-free serum was spiked with various concentrations of PCP. (LOD for all OCPs: 0.1 µg/l)

2.3. Statistical analysis

The characteristics of the study population are shown in Table 1, as counts and proportions (%). For descriptive analysis, median, percentiles and range of the studied compounds were presented. Statistical differences between covariates were tested for significance using Mann-Whitney U test. The concentrations are presented as volume-based (µg/l) for arsenic and mercury (total) in urine, and for OCPs in serum. This allows to compare the levels with the occupational biological health limit values (Biologischer Grenzwert, BGW, defined in TRGS 903), as well as with other studies. The concentrations below the LOD were replaced by ½ the LOD. Multivariate linear regression analyses were used to assess the association of several covariates with arsenic, mercury and OCPs concentrations. Before inclusion in the models, concentrations were transformed into the natural logarithm.

Statistical analysis and graphics were performed using the statistical software SPSS 25, R (R Core Team) and ggplot package (Wickham, 2016).

3. Results and discussion

3.1. Characteristics of study population

A total of 28 participants (8 women and 20 men) between 27 and 65 years of age (mean of 49.4 ± 10.6 years old) were included in the study (Table 1). As it can be seen in Table 1 the individuals were divided into three age groups. Almost one third of the participants were classified in the younger group age (27-45 years old, 9 participants), 36% in the middle age group (46-56 years old, 10 participants), and 32% in the eldest age group (57-65 years old, 9 participants). The participants had different occupational activities, namely taxidermists, collection caretakers, curators and conservators. Due to the small number of participants, it is possible to draw conclusions from the activitygroup to natural persons. Therefore, the different job tasks are not mentioned in this study. However, they are known to the authors of the study. For a better understanding, the groups have additional information as to whether they are in direct contact with the objects or not. Concerning work tasks, 25% of the participants had a continuous contact to objects (Activity 1), almost half of the individuals often had direct contact to objects (Activities 2 and 4), while 29% were classified in the group of having seldom direct contact to objects (Activity 3). More than two thirds of the participants (79%) declared that they had direct skin contact to animal dermoplastics or other objects of the collection during study week. 44% of participants did not wear gloves during skin contact activities and 21% reported toxic dust formation during their work. Concerning participants' information on individual characteristics, more than one third of the participants had amalgam fillings (43%), while more than one half eat fish and seafood in a weekly frequency. None of the interviewees had contact with arsenic, mercury or OCPs during their private activities (data not shown)

3.2. Arsenic exposure

Arsenic concentrations were above the LOD (0.2 µg/l) in all analyzed samples. Median urine concentrations of As during the study week ranged between 7.7 µg/l on Monday morning and 5.0 µg/l on Thursday evening. No significant differences were found by day of analysis (Figure 1). In addition, total As concentrations in participants´ urines (n=147) were highly variable, with a median level of 6.4 µg/l, ranging from 0.30 µg/l to 339 µg/l (Table S1). 78% of the concentrations were lower than the reference values (RV) derived from the 95th percentile from a normal control group by the German Federal Environmental Agency, on 15 µg/l (dashed brown line in Figure 1) or 45 µg/l (dashed grey line in Figure 1) depending on not having or having fish and seafood consumption in previous 48h before analysis, respectively (Bekanntmachung des Umweltbundesamtes, 2003). In the studied population, all the participants which declared low or no fish and seafood consumption had systematically low As concentrations, while those individuals eating fish and seafood in a weekly basis had higher As levels (Figure S1). The differences were statistically significant (p-value < 0.05).

Arsenic is classified by the International Agency for Research on Cancer as a group 1 carcinogen to human. Inorganic arsenic affects a broad range of organs and systems and can also cause non-cancer health effects (ATDSR, 2016). There are a large number of current studies to arsenic exposure and its health effects, which have been summarized in several papers. Naujokas et al. (2013) offer a good overview in their review: Arsenic can cause various types of cancer such as bladder, lung, liver, kidney and skin cancer. In addition, arsenic can affect the development processes of infants at the prenatal and early postnatal period, the nervous, respiratory, immune, cardiovascular and endocrine system with various health issues.

A total of 32 samples which showed higher arsenic concentrations (above the RVs, diagonal dashed lines in Figure 1) underwent additional analyses (see Materials and Methods). Tables 2 and 3 and Figure 2 show the concentrations of As-species measured in 33 urine samples of 11 participants. Median values of As(III) and As(V) were 0.20 µg/l, ranging from < LOD to 0.40 µg/l in both species. Any of the aforementioned inorganic As species exceeded the Biological Substance Reference Value (BAR) of 0.5 µg/l set by the German Research Foundation (Deutsche Forschungsgemeinschaft, 2018). Median concentrations of the organic As species were 27.34 µg/l for AsB (ranging from 1.7 µg/l to 295 µg/l), 6.9 µg/l for DMA (ranging from 2.2 µg/l and 41.9 µg/l) and 0.40 µg/l for MMA (ranging from 0.20 µg/l and 2.8 µg/l) (Table 2). For AsB, 58% of the samples analyzed exceeded the reference values set by the Institute and Outpatient Clinic for Occupational, Social and Environmental Medicine of the Friedrich-Alexander-University Erlangen-Nuremberg, IPASUM FAU, of 23 µg/l, while for DMA, 24% of the samples exceeded the BAR, set on 10 µg/l (Table 2).

The results of the analyses showed a highly variable level of the total of arsenic in the participant's urines (N: 147, median: 6.40 µg/l; min.: 0.3 µg/l; max.: 339 µg/l). After a species analysis had been carried out for 22% (N: 33) of the samples who had a higher total arsenic content than 15 µg/l, it has been shown that the AsB was found in the highest concentrations (Table 2 and Figure 2, green). AsB is absorbed mainly by biological material such as marine food and, due to the rapid and complete excretion after consumption, is considered to be much lesser toxic than inorganic As (Lehmann et al., 2001; Spratlen et al., 2018). Whereby this is questioned in more recent studies (Hille-Rehfeld, 2016; NN, 2003). What is certain, however, is that the AsB was not absorbed due to working with contaminated objects, but due to the dietary intake. As(III) and As(V) in dust and airborne particles are absorbed via inhalation and dermal contact (Ouypornkochagorn and Feldmann, 2010). After ingestion, the inorganic arsenic species are mainly converted to the mono- and dimethylated forms of arsenic. These compounds have a lower toxicity than the organic species, and are excreted through urine (Spratlen et al., 2018).

The variations of inorganic As and its metabolites within each participant through the study week (Figure 2, Table 3) could be due to fish consumption since DMA content can also be present in seafood (Özcan et al., 2016). In this regard, no increase in concentration due to the work activity over the course of the week is visible. However, the urinary concentrations of inorganic arsenic and MMA species in the participants is comparatively high in relation to the general population and cannot be solely explained by fish and seafood consumptions. Julshamn et al. (2012) could detect only very small amounts of inorganic arsenic species in fish. In addition Heinrich-Ramm et al. (2001) reported that As(V) and As(III) (Heinrich-Ramm et al., 2002) is usually found in

people who are occupationally exposed to As. In comparison with the present study, Heitland and Köster (2008) detected more As(III) but lower As(V) levels in a general adult population from Northern Germany (Table 2). In another study performed on 322 people from France living naturally As-contaminated environment, rarely As(V) was found in the urine (Fillol et al., 2010). On the other hand, comparisons with a similar study performed on museum staff handling preserved animal skins, lower content of As(III) and As(V) than the present study was found. Only one worker had an moderate uptake of arsenic during handling contaminated skins (Mithander et al., 2017).

Apart from fish and seafood, As concentrations were associated with skin contact to collection objects, with statistically significant results (Fig. 3). However, the other studied variables, including occupational activity, use of gloves and dust development during work activity, were not associated with urinary arsenic levels (Mann-Whitney U test > 0.05). Ciarrocca et al. (2012) investigated the relationship between the arsenic content in environmental air and the internal load of total of arsenic in 122 employees. The two variables correlated significantly. The higher values of As(III) and As(V) in the urine of the museum staff could also be related to the arsenic levels measured in the air and dust of the MfN (air: median = 3ng/m³, min = 1.5 ng/m³, max. 47.8 ng/m³; dust: median = 35.4 µg/kg, min = 4.3 µg/kg, max = 3507 µg/kg) (Deering et al., 2019). A statistical correlation between the total sum of arsenic and some work-related factors can also be found within this study. Figure 3 shows that the use of gloves is protective for arsenic (one way significant at $p<0.1$) and a rise of total arsenic is also associated with a higher dermal contact to taxidermic objects. These results suggest that the participants could have been moderately occupationally exposed to inorganic arsenic, especially As(V), during their daily work. There are some previous studies that have established a link between long-term low-dose chronic arsenic exposure and adverse health risks, including non-melanoma skin cancer (Kim et al., 2017), hypertension (Yu et al., 2017), cardio-metabolic outcomes (Spratlen et al., 2018) and type 2 diabetes mellitus (Pan et al., 2013; Spratlen et al., 2018). In this regard, it is recommended to use the necessary occupational safety measures in order to minimize the exposure to inorganic arsenic.

3.3. Mercury exposure

86% of the samples analyzed were above the LOD (<0.1). Median mercury concentration for the whole study week ranged between 0.10 - 0.25 µg/l, with the highest median concentration found on Monday morning, and decreasing slightly over the study week (Figure 4 and Table S1).

None of the participants exceeded the HBM-1 reference value of 7 µg/l in urine (Figure 4, dotted grey line). In addition, urinary Hg levels in present study are half as those reported in German environmental survey (GerES) performed in Germany in 1998 (geometric mean of 0.43 µg/l) (Becker et al., 2002).

In our previous report performed at the MfN, levels of Hg in dust and airborne particles at different rooms of the museum were comparatively low, with median concentrations of 3.6 mg/kg in dust and 0.80 ng/m³ in air, respectively. Nevertheless, Hg exposure in museums, especially in herbaria or historic buildings with old mirrors

should be considered, since some studies performed in museums have already reported much higher levels of Hg in indoor air and dust (Briggs et al., 1983; Marcotte et al., 2017; Measday and Goodall, 2018; Oyarzun et al., 2007; Torge et al., 2011). In this regard, and even with low urinary mercury concentrations, the present study was able to find associations with work-related variables, such as dust development during work and skin contact (Figure 3), with statistically significant results ($p<0.05$).

Concerning individual characteristics of the studied participants, urinary Hg concentrations were associated with amalgam fillings. Individuals having amalgams had higher urinary Hg levels than those without, with statistically significant results ($p<0.05$) (Figure S2). This relationship is widely known and published in many previous studies. By contrast, no significant associations between fish intake and urinary Hg levels were found ($p>0.05$), in contrast to what was already shown in previous reports (Jirau-Colón et al., 2019; Pirard et al., 2018). This could be explained by the low sample size in our study, and therefore missing statistical power.

3.4. Organochlorine pesticides exposure

The concentrations of OCPs are presented in Table 4. 4,4'-DDE and PCP were detected in all the analyzed samples, followed by HCB (detected in 90% of the samples), β-HCH (60%) and 4,4'-DDT (detected in only 20% of the samples). α-HCH and γ-HCH were not detected in any of the samples, which is in accordance with previous reports (Becker et al., 2002). Except for 4,4'-DDE and PCP, the concentrations of the measurements taken on Thursday evening (Te) were slightly higher than those taken on Monday morning (Mm) (Figure 5). The highest median concentrations were found for 4,4'-DDE (Mm: 0.76 µg/l – Te: 0.89 µg/l), followed by PCP (Mm: 0.42 µg/l – Te: 0.44 µg/l), HCB (Mm: 0.13 µg/l – Te: 0.19 µg/l), β-HCH (Mm: 0.11 µg/l – Te: 0.16 µg/l) and 4,4'-DDT (Mm: 0.11 µg/l – Te: 0.13 µg/l).

It is well known that organochlorine pesticides, as lipophilic chemicals, bio-accumulate over time in the body. Accordingly, older people have higher values than younger people and a strong relationship between age and OCP-concentration has been previously reported in several studies (Becker et al., 2002; Ben Hassine et al., 2014; Freire et al., 2017; Hardell et al., 2010; Pirard et al., 2018). The present study was able to detect such increasing association with age (Table 4). However, compared with the reference values from the German Environmental Survey from1998 (Becker et al., 2002), the OCP concentration from this study are far below (Table 4). This could be explained by the fact that OCP values in Europe have decreased within the last decades (Hardell et al., 2010). There is no actual study about the distribution of organochlorine pesticides in blood serum for the population of Germany available. However, as clearly shown in the table, none of the measured values are even close to the reference values from 1998. For PCP there are no reference values from the German Environmental Study, therefore the toxicologically justified HBM-1 (40µg/l) value was used for an assessment. Also, the values measured in this study are well below the HBM-1 value, which indicate there is no harm according to current evaluation, and require no action (Schulz and Kolossa-Gehring, 2010). Peper et al. (1999) examined the effects of long-term low exposure in Germany to wood-preserving chemicals containing PCP and γ-HCH, reporting

blood concentration of 43.6 µg/l, respectively 0.085 µg/l, respectively. Again, the measured values of this study are significantly lower.

When OCP concentrations are compared with the different occupational activities of the participants, some factors are noticeable (Figure 6). The concentrations of 4,4'-DDT and γ-HCH are higher among the activity group 4 (involving often direct contact to objects). On the second day of analysis (Thursday) the concentrations of 4,4'-DDT are also higher among activity group 2 (also related to often direct contact to objects). On the other hand, the concentrations of PCP among participants performing activity 3 are slightly higher than in the rest of participants, even this activity involves seldom direct contact to objects. In contrast, certain work-related activities have been associated with the levels of OCPs (Figure 3). For instance, dust exposure is associated with higher concentrations of β-HCH ($p<0.05$) and the use of gloves is protective for DDT ($p<0.05$). However, for 4,4´-DDE, β-HCH and HCB, the concentrations are negatively associated with dermal contact. Regarding the previous report performed at the MfN Berlin, the ambient monitoring measurements were comparatively high for γ-HCH in the (median: 0.27 mg/kg, range: 0.10 mg/kg – 130 mg/kg) and air (median 65.5 ng/m³, range: 14 ng/m³ - 320 ng/m³). (Deering et al., 2019) The degradation product of γ-HCH, γ-PCH, was also measured in air (median: 125 ng/m³, range: 10 ng/m³ - 230 ng/m³), involving high levels as well. However, those compounds are rarely found in human matrices, but due to the similarity of chemical structures of γ-PCH and γ-HCH, it can be assumed that γ-PCH poses an additional carcinogenic risk to employees. The other compounds were measured in dust and air in lower amounts. Therefore, it is not surprising that the OCP compounds were detected in low concentrations in the analyzed serum samples. Nevertheless, the links between the measurements and the occupational variables show that there is a relationship and therefore counteractive action should be taken in principle. Especially since the health risks of low-dose exposures of organochlorine pesticides have been more intensively investigated recently. Thus, Lee et al. (2010) describes a relationship between a low-dose mixture of OCPs and type 2 diabetes mellitus. Rignell-Hydbom et al. (2009) found a relation between 4,4´-DDE in blood serum and an increase of type 2 diabetes mellitus in Swedish women. It should also be noted that most OCPs, even in small doses, can act as endocrine disruptors and can cause endocrine cancers in various organs. The synergistic effects with other OCPs and chemicals are not well studied (Bergman et al., 2013).

3.5. Limitations and strengths of the study

The generalization of these results is subject to certain limitations. For instance, the data was based on a limited number of participants. Another further limitation of this study is related to the As speciation analysis, which was only performed in a subset of samples, and not among the total urine samples collected. As a result, significantly fewer data could be compared with other studies.

Nevertheless, this study has arisen knowledge on the current exposure risks among employees of a natural history museum. And, for similarly other affected museums, the authors of this study published an guideline for handling contaminated objects in museums, libraries and archives (Spiegel et al., 2019). According to the results of this study in combination with the results of other studies, it is recommended to take occupational safety measures in each museum, historic library and herbarium. These occupational safety measures have already been

implemented in the Museum für Naturkunde Berlin. With this study, the museum received comprehensive data and assumptions about the risks of pesticides emanating from the objects in its collections. The data helped to develop a better understanding of the extent, sources and causes of contamination. They are building the basis for further adjustments and developments in order to better protect employees.

4. Conclusion

This is the first study assessing the body burden of arsenic, mercury and organochlorine pesticides in 28 employees of a museum of Natural History Museum. These components have been historically used as biocides to preserve natural history collections. The measurements were taken at the same period of time than indoor air and dust monitoring, hence an elaborate assessment has been performed. Relatively high urinary concentrations of inorganic arsenic, especially As(V), were found in the participants compared to other studies. In addition, various work-related factors, such as wearing gloves and high dust development during work, have been significantly correlated with blood and urine levels of As, Hg and OCPs. Given the potential health risks posed by the exposure to these chemicals and lack of knowledge of possible synergic effects, occupational safety measures should be taken into account among museum staff. According to the results of this study in combination with the results of other studies, it is recommended to ensure occupational safety measures in each museum, historic library and herbarium. Further research is needed to assess the pathways in more detail from exposure to toxic substances in contaminated museum collections to absorption and distribution of such substances in humans.

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Conflict of interest: The authors declare that they have no conflict of interest.

Tables

Table 1: Socio-demographic and occupational characteristics of the study participants at the MfN (n=28)

	N	%
Age		
27 - 45 years	9	32
46 - 56 years	10	36
57 - 65 years	9	32
Total	28	100
Work task		
1 (continuous contact to objects)	7	25
2 (often direct contact to objects)	9	32
3 (seldom direct contact to objects)	8	29
4 (often direct contact to objects)	4	14
Fish or seafood consumption		
Never	2	9
Monthly	13	57
Weekly	8	35
Amalgam fillings		
No	16	57
Yes	12	43
Use of gloves		
No	11	44
Yes	14	56
Direct skin contact		
No	6	21
Yes	22	79
Dust developments		
Never or rarely	22	79
Often or solely	6	21

Table 2: Concentrations of arsenic speciation in urine (in µg/l urine) and comparison to other studies in Germany.

		Arsenic species				
		As(III)	As(V)	DMA	MMA	AsB
This study (Museum staff N = 33)	**Positive findings in %**	**35**	**58**	**100**	**93**	**100**
	Median	0.2	0.2	6.9	0.4	27.3
	Min	< LOD	< LOD	2.2	2.2	1.7
	Max	0.4	0.4	41.9	41.9	295.0
	LOD	0.07	0.07	0.07	0.07	0.07
Mithander et al. (2017) (Museum staff handling preserved animal skin, N = 10)	**Positive findings in %**	**20% (> LOQ)**		**100**	**40**	**NA**
	Median	NA	NA	NA	NA	NA
	Min	< LOQ	< LOQ	3.1	< LOQ	NA
	Max	2.3	0.3	25.0	9.8	NA
	LOD / LOQ	0.07 / 0.2	0.07 / 0.2	00.07 / 0.2	0.07 / 0.2	NA
Heitland and Köster (2008) (Northern Germany, general adult population, N = 82)	**Positive findings in %**	**73**	**31**	**99**	**89**	**88**
	Median	NA	NA	NA	NA	NA
	Min	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
	Max	2.3	0.6	18	2.7	23
	LOD / LOQ	NA / 0.1	NA / 0.1	NA / 0.1	NA / 0.1	NA / 0.1
	Reference values (µg/l urine)	0.5**	0.5**	10**	*2***	23*

**reference values were determined at the IPASUM FAU*
***Biological Substance Reference Values (BAR) obtained from Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) (Deutsche Forschungsgemeinschaft, 2018)*
NA = Not available; < LOD = under detection limit

Table 3: Urinary species analysis in nine participants during the study week at the MfN in comparison with the biological reference value (concentrations in µg/l)

Participant		As(III)	As (V)	DMA	MMA	∑As+DMA +MMA	AsB
2	Monday morning	0.1	-	41.9	2.8	44.8	295.0
	Monday evening	0.2	-	23.7	0.8	24.7	139.3
	Wednesday evening	0.3	-	16.8	1.7	18.8	83.5
	Thursday evening	0.2	-	6.6	0.7	7.5	21.8
3	Monday morning	-	0.2	7.3	0.4	7.9	42.7
	Monday evening	-	0.4	3.8	0.2	4.4	23.2
4	Tuesday evening	-	-	5.2	0.3	5.5	26.8
	Wednesday evening	-	-	2.2	-	2.2	36.7
	Thursday evening	-	0.1	4.9	0.3	5.3	16.3
5	Monday morning	-	-	10.0	0.2	10.2	5.8
	Monday evening	-	-	6.2	-	6.2	65.6
	Tuesday evening	-	0.3	8.6	0.3	9.2	12.4
6	Monday morning	0.4	0.4	22.1	1.2	24.1	117.7
	Monday evening	0.3	-	8.2	0.4	8.9	120.1
	Tuesday evening	0.1	-	3.1	0.2	3.4	126.9
	Wednesday evening	-	0.2	22.9	1.3	24.4	62.5
	Thursday evening	-	-	4.1	0.3	4.4	35.7
7	Monday morning	-	0.3	6.9	0.3	7.5	61.7
	Monday evening	-	0.1	6.8	0.5	7.4	27.9
	Tuesday evening	0.1	0.2	8.4	0.3	9.0	48.0
	Wednesday evening	-	0.1	4.5	0.2	4.8	22.8
	Thursday evening	-	0.3	3.4	0.3	4.0	22.3
9	Monday morning	-	0.4	5.6	0.4	6.4	12.8
	Thursday evening	-	0.4	21.1	1.0	22.5	21.8
10	Wednesday evening	-	0.2	10.8	1.0	12.0	2.8
	Thursday evening	-	-	6.8	0.8	7.6	4.7
11	Monday morning	0.1	0.2	3.8	1.0	5.1	28.3
	Monday evening	0.3	0.2	4.9	1.4	6.8	27.6
	Tuesday evening	0.1	-	3.7	0.6	4.4	26.5
	Wednesday evening	-	0.2	3.0	0.6	3.8	15.8
	Thursday evening	-	0.4	1.4	0.3	2.1	8.1
BAR	biological reference value*	0.5	0.5	10	2		

**Biological Substance Reference Values (BAR) obtained from Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) (Deutsche Forschungsgemeinschaft, 2018)*

Table 4: OCP-concentrations in blood serum (in µg/l) for age-groups. For comparison, reference values and HBM values were used.

		Median	Minimum	Maximum	Reference value*	HBM-1 values**
β-HCH	27 - 45 years	0.05	0.05	0.21	0.3	-
	46 - 56 years	0.05	0.05	0.17	0.3	-
	57 - 65 years	0.17	0.05	0.39	0.5 – 0.9	-
HCB	27 - 45 years	0.13	0.05	0.39	0.5 – 2.5	-
	46 - 56 years	0.10	0.05	0.27	2.5 – 3.3	-
	57 - 65 years	0.29	0.05	0.93	3.3 – 5.8	-
4,4´-DDT	27 - 45 years	0.05	0.05	0.05	-	-
	46 - 56 years	0.05	0.05	0.82	-	-
	57 - 65 years	0.05	0.05	0.72	-	-
4,4´-DDE	27 - 45 years	0.42	0.17	1.32	1.5 – 4 (WG) 3 – 11 (EG)	-
	46 - 56 years	0.66	0.19	1.48	7 (WG) 18 (EG)	-
	57 - 65 years	1.34	0.21	3.0	8 – 11 (WG) 31 (EG)	-
PCP	27 - 45 years	0.29	0.24	0.53	-	40
	46 - 56 years	0.43	0.23	0.75	-	40
	57 - 65 years	0.52	0.22	1.5	-	40

** GerES 1998 received from (Schulz et al., 2011)*

*** HBM values received from (Schulz and Kolossa-Gehring, 2010)*
"-" = no values available
WG = western part of Germany
EG = eastern part of Germany

Figures:

Figure 1: Boxplots showing the As concentrations in urine (in µg/l) during the study week from Monday morning to Thursday evening. Dotted grey line indicates the reference value of 45 µg/l (fish consumption 24h before sampling). Dotted brown line indicates the reference value of 15 µg/l (without fish consumption 24h before sampling). Diagonal dashed lines indicate the concentration-level in which additional species analysis was performed. (Becker et al., 2002)

Figure 2: Proportion of Arsenic species over the total As for 11 participants during study week.

Figure 3: Beta-coefficients from multivariate regression models for As, Hg and OCP pesticides adjusted by several covariates.

Figure 4: Boxplots showing the Hg concentrations in urine in µg/l during the study week from Monday morning to Thursday evening. Dotted grey line indicates the HBM-1 value of 7.6 ug/l.

Figure 5: Boxplots showing the OCP concentrations in blood serum during the study week.

Figure 6: Boxplots showing the OCPs concentrations in blood serum during the study week by the different activity groups. Each activity involves continuous (1), often (2, 4) or seldom (3) direct contact to objects.

Supporting information (SI)

Table S1: Descriptive statistics of total As and total Hg in urine in µg/l, for the study week.

		N	Minimum	Percentile 25	Percentile 50 (Median)	Percentile 75	Maximum
Total Hg concentration	Monday morning	28	< LOD	0.10	0.2	0.6	1.8
	Monday evening	27	< LOD	0.08	0.2	0.3	2.0
	Tuesday evening	27	< LOD	0.08	0.2	0.5	2.6
	Wednesday evening	27	< LOD	0.06	0.1	0.4	2.4
	Thursday evening	28	< LOD	< LOD	0.1	0.3	1.8
	Total	**137**	**< LOD**		**0.2**		**2.6**
Total As concentration	Monday morning	28	0.3	2.4	7.7	12.9	339.0
	Monday evening	27	0.7	2.4	6.4	12.8	164.0
	Tuesday evening	27	0.8	3.6	6.9	10.8	136.0
	Wednesday evening	27	0.7	1.6	5.7	14.8	90.0
	Thursday evening	28	1.0	1.6	5.0	11.8	39.7
	Total	**137**	**0.3**		**6.4**		**339.0**

Table S2: Descriptive statistics of total As in urine (in ug/l) for individual and work-related variables.

		Monday morning (before working week started)					Thursday evening (end of working week)				
	N	Min.	25%	Median	75%	Max.	Min	25%	Median	75%	Max.
Fish diary											
Eats fish or seafoot never	2	1.3	1.3	5.1	8.8	8.8	1.1	1.1	1.4	1.6	1.6
Eats fish or Seafood monthly	8	0.8	2.0	4.0	7.7	10.8	1.4	2.2	3.6	7.1	35.5
Eats fish or seafood weakly	13	0.3	6.1	10.2	33.4	339.0	1.0	1.5	5.9	11.5	32.1
Work task											
Activity 1	7	0.3	1.3	2.7	9.2	9.7	1.1	1.5	12.1	32.1	35.5
Activity 2	9	0.8	6.8	8.8	10.2	60.8	1.0	1.6	2.0	6.7	16.8
Activity 3	8	2.1	4.0	20.5	79.2	339.0	1.0	1.5	5.2	19.8	39.7
Activity 4	4	1.0	3.2	8.1	12.9	14.9	3.5	3.8	5.0	7.0	8.1
Direct skin contact to objects											
No	6	1.0	2.1	7.6	55.9	125.0	1.4	1.5	2.6	7.3	39.7
Yes	22	0.3	2.7	7.9	10.8	339.0	1.0	1.6	6.3	12.1	35.5
Wearing gloves											
No	11	1.3	5.0	8.9	33.4	339.0	1.0	1.4	3.0	10.2	29.3
Yes	14	0.8	2.1	6.5	9.7	125.0	1.1	1.6	7.0	12.1	39.7
Dust generation											
Never or rarely	22	0.3	2.7	6.9	10.8	125.0	1.0	1.5	3.3	10.2	39.7
Often or solely	6	0.8	2.1	9.7	55.9	339.0	1.0	6.7	9.7	27.2	29.3

Table S3: Descriptive statistics of total Hg in urine (in µg/l) for individual and work-related activities (Museum of Natural History Berlin, n=28).

		Monday morning (before working week started)					Thursday evening (end of working week)				
	N	Min.	25%	Median	75%	Max.	Min	25%	Median	75%	Max.
Amalgam fillings											
No	16	< LOD	0.1	0.1	0.3	0.7	< LOD	< LOD	< LOD	0.2	0.6
Yes	12	< LOD	0.3	0.4	1.0	1.8	0.1	0.1	0.30	0.6	1.8
Fish diary											
Eats fish or seafoot never	2	0.1	0.1	0.3	0.5	0.5	< LOD	< LOD	0.3	0.5	0.5
Eats fish or seafood monthly	8	< LOD	0.1	0.1	0.2	1.8	< LOD	0.1	0.1	0.2	0.4
Eats fish o seafood weakly	13	0.1	0.1	0.3	0.7	0.9	< LOD	< LOD	0.1	0.3	0.7
Work task											
Activity 1	7	0.1	0.1	0.4	1.1	1.2	< LOD	< LOD	0.5	1.2	1.8
Activity 2	9	< LOD	0.1	0.1	0.8	1.8	< LOD	< LOD	0.1	0.1	0.7
Activity 3	8	< LOD	0.1	0.1	0.4	0.7	< LOD	< LOD	0.1	0.2	0.3
Activity 4	4	0.3	0.3	0.3	0.3	0.3	0.1	0.2	0.3	0.4	0.5
Direct skin contact to objects											
No	6	< LOD	0.1	0.1	0.3	0.6	< LOD	< LOD	0.1	0.3	0.5
Yes	22	< LOD	0.1	0.3	0.7	1.8	< LOD	< LOD	0.1	0.4	1.8
Wearing gloves											
No	11	< LOD	< LOD	0.2	0.7	0.9	< LOD	< LOD	0.1	0.2	0.7
Yes	14	0.1	0.1	0.2	0.6	1.8	< LOD	< LOD	0.2	0.4	1.8
Dust generation											
Never or rarely	22	< LOD	0.1	0.2	0.4	1.8	< LOD	< LOD	0.1	0.3	0.6

Often or solely	6	0.1	0.1	0.7	1.1	1.2	< LOD	0.2	0.6	1.2	1.8

Figure captions for SI

Figure S1. Boxplots showing As concentrations during the study week depending on each group of fish and seafood consumption (never, monthly or weekly basis).

Figure S2. Boxplots showing Hg concentrations during the study week depending on having or not having amalgam fillings.

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