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The use of 'poisonous insecticidal solutions' in bookbinding: coping with historic pesticide treatments in the archive

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Abstract

Records from a popular series at The National Archives were found to bear warning labels that they have been bound using a 'poisonous insecticidal solution'. Research into historic sources suggested that the agents used by bookbinders in the early twentieth century were mercuric chloride, copper sulphate, and beechwood creosote; these may have been replaced by organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDT) mid-century. Analysis by X-ray fluorescence (XRF) spectroscopy confirmed the presence of mercury in labelled, bound items. A number of OCPs were detected using gas chromatography/mass spectrometry (GCMS) including DDT, gamma-hexachlorocyclohexane (Lindane, γ-HCH), Dieldrin, pentachlorophenol (PCP), dichlorodiphenyldichloroethylene (DDE), and 1-chloronaphthalene (1-CP). Tests confirmed the presence of these agents on all items tested regardless of format (e.g. tagged files and bound volumes) or period of creation, suggesting the OCPs were introduced to the items after the binding process. An occupational hygienist (OH) consultancy was engaged to carry out in-situ air monitoring during production, digitisation, and general handling of the items. Risk assessments were developed based on the results, allowing readers and staff to once again access the collection with safety measures including the use of personal protective equipment (PPE).

Keywords Pesticides, Insecticides, Biocides, Archives, Libraries, Organochlorines, Book and paper, Health and safety, Hazardous collections

Introduction

The collection

The National Archives is the official archive of the United Kingdom's government, ensuring preservation and access to records spanning more than 1000 years. The collections include millions of medieval, early modern and modern records created by the UK central government and major courts of law, ranging from maps to manuscripts, service and operational records, and collections from a number of government offices (e.g. Home Office, War Office, etc.). The 'FCO' collections cover material from the Foreign and Commonwealth Office and their predecessors, and include the series FCO 141—the records of former colonial administrations, also known as the 'Migrated Archives' [1]. This series is sensitive, not

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Fig. 1 Top: examples of tagged files in original and contemporary folders (left, centre), and an original binder (right). Bottom: examples of bound notebooks and registers

only because of its contents, but also due to the history of its transfer to The National Archives [2, 3]. The records in the collection originate from 41 territories around the world and are composed primarily of tagged files—loose documents and correspondence held together by a cord-tag and contained in folders and binders (Fig. 1, top)—though there are also bound items (ledgers, notebooks, and printed books, Fig. 1, bottom).

During a conservation survey of the FCO 141 collection, a series of bound items from Nigeria were discovered to bear a notice that they have been bound using an insecticide (Fig. 2). On inspection, different types of notices were found either adhered or stamped on the right or left paste-down of the bound items from this territory over a time period from 1940 to 1959. The application of the labels was inconsistent—not all identical notebooks of a sequence within the series contain the notice. In some instances, the notice was not immediately visible due to the later addition of stickers or a new paste-down.

A quick scan of the preservation literature on pest management indicated that the kinds of agents used for insect treatment during this period could range from mercuric chloride to synthetic organic insecticides. The

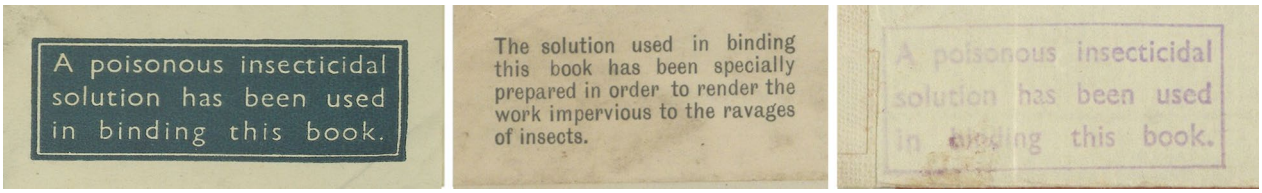

Fig. 2 Examples of three types of warning labels found on bound notebooks from Nigeria from 1943, 1940, and 1958 (from left to right)

National Archives immediately suspended access to the collection to readers, and ceased any conservation and digitisation activity until the nature of the hazards could be established, and an appropriate risk mitigation strategy could be implemented.

Brief history of insecticide use in collections

The historic use of biocides, and specifically insecticides in historic collections is a well-known and documented area of research in preventative collection care [4–7]. Both inorganic (arsenic-, mercury- and lead-based compounds) and organic (DDT, γ-HCH, PCP, naphthalene, para-dichlorobenzene (PDB), ethylene oxide, methyl bromide, carbon tetrachloride, formaldehyde) agents have been used on collections around the world to prevent damage or loss by a variety of pest classes. Recent collection care-specific literature and guidance in this area almost exclusively deals with ethnographic, anthropological, and natural history collections. The nature of the materials in these collections predisposes them to pest damage, and consequently, prior to Integrated Pest Management programmes many organisations applied toxic agents to their repositories, cabinets, and galleries. In rare cases, these practices were documented; however, the nature of the agents and the scale of use has only recently come under detailed scrutiny. Detection and identification of insecticides has been carried out in a number of natural history museums [8–11], ethnographic/anthropological collections [12–18], and several historic buildings [19–21]. In particular, organisations holding objects used in ritual practices, and now being repatriated, have been at the forefront of recent studies [22–26].

Far less contemporary published literature and safe handling guidance is available for archive and library collections. Application and detection of mercuric chloride (often referred to as corrosive sublimate) to herbarium papers has been described and studied, while Querner et al. recently showed that endsheets in Chinese rare books were sometimes treated with red lead as an insecticidal measure [27–30]. The use and consequences of fumigants have been explored by others, and a recent publication has demonstrated widespread use of carcinogenic polychlorinated biphenyls (PCBs) in mass-market paperback book adhesives [31–33]. However, studies on the implications of the historic use of synthetic organic insecticides, and in particular OCPs, to handling and research collections are rare. In 2020, a review of historic archive and library practices in Portugal was published [34]. Recently, Harvard University Libraries described their risk mitigation approach after the discovery of DDT in a rare book collection acquired from Pakistan [35]. In contrast to the majority of studies described here, the labels found on the FCO 141 items suggest that the insecticide was incorporated directly *into* the bookbinding materials rather than sprayed or applied as a preventative measure at a later date. To understand more about historic pest management methods in the bookbinding, library and archive sectors, a literature review was undertaken.

Desk research

Despite a dearth in recent investigation into historic pesticide practices in bookbinding and in library and archive collections, documentary evidence of these practices can easily be found. A 1973 UNESCO guidance entitled 'Conservation and Restoration of Archive Materials (prepared with special attention to problems encountered 'in regions with unfavourable climatic conditions') suggests that solutions or resins containing DDT, Dieldrin, Lindane, chlordane, malathion, or chloronaphthalene can be 'thoroughly applied to the bookshelves, care being taken to cover all areas, including cracks, crevices and the underside of the shelves' [36]. Weiss and Carruthers mention the use of corrosive sublimate and a variety of other agents that can be applied to bookshelves in *Insect Enemies of Books*, especially when dealing with books for export to the tropics [37].

When it comes to the addition of insecticides to the bookbinding materials, evidence can be found in historic manuals, as well as research papers [38]. In *Bookbinding, and the Care of Books* [39], the incorporation of corrosive sublimate into pasting paper is suggested for the prevention of attack by bookworms and other insects. Weiss and Caruthers compiled a bibliography of ancient to modern references to agents used to deter insects from destroying written heritage. The first mention of corrosive sublimate is noted as 1788, but the agent begins to appear

more frequently in references throughout the nineteenth century and is suggested for incorporation into the binder's paste, into the paper pulp, and for application to the inside of book covers.

Bracey and Barlow's paper *Urea–Formaldehyde Resin as a Vehicle for Semi-Permanent Insecticidal and Fungicidal Coatings on Bookbindings and Bookcases* [38], describes contemporary methods for insect control, and specifically, the Crown Agents for the Colonies Specification No. 40, which recommends 'the use of a solution of 1 per cent. mercuric chloride and 0.5 per cent. of beechwood creosote in methylated spirit to be painted on the inner and outer faces of the binding boards and the bookcloths'. The authors go on to note that many bookbinders do not follow the specification because of health and safety concerns for their employees and the potential to breach newly introduced Factory Acts. Instead, Bracey and Barlow propose the substitution of mercuric chloride with DDT in the bookbinding glues and pastes, and demonstrate that this can be accomplished without affecting the adhesive and drying properties of the pastes.

Bracey and Barlow's manuscript led to the discovery of the Crown Agents for Oversea Governments and Administrations purchasing files (CAOG 12/87 and CAOG 12/88) as well as the Colonial Office Insecticide Committee Research Unit's records (CO 927/139), incidentally located in The National Archives. Within these records, we find the aforementioned Standard Specification No. 40, which describes how books for use by colonial government administrations, e.g. ledgers, registers, etc., should be bound in order to prevent damage by insects (Additional file 1: Fig. S1a). Letters accompanying this record indicate that this method has been used for at least 40 years (e.g. from ca 1900). Communications from 1907, including widely circulated advice provided Dr T.E. Thorpe, the Principal Chemist of the Government Laboratories, also describe the application of corrosive sublimate to government records as well as the use of naphthalene on bookcases, cupboards, presses and boxes, and the application of carbon disulphide if infestation has already occurred. The application of corrosive sublimate on books is cited by Dr Thorpe as having been used as early as 1888 in China. It is suggested that 'it would be of great service if the Crown Agents for the Colonies were to make it a condition of any contract they might enter into for the supply of bound books to tropical Colonies that they should be treated on the lines suggested by Dr. Thorpe'.

From communications found in CAOG 12, it is clear that most government issued books were bound in England[1] and then sent abroad. Indeed, this can be confirmed by a handwritten note by an administrator on the right past-down of FCO 141/13515: 'Ask Govt. Printer for better quality paper in next ledger book.' (Additional file 1: Fig. S2, emphasis in original). Critically, Specification No. 40 includes the statement, 'A small printed label stating that a poisonous insecticidal solution has been used in the binding shall be pasted inside the front cover of each book'—identical to what is seen on many FCO 141 bound items.

Tracing the history of insecticide use for bookbinding and in government libraries and archives through the communications in the CAOG 12 series demonstrates use of the following agents from 1907 to 1951: DDT, permethrin, Aldrin, γ-HCH, Dieldrin, creosote, PCP, mercuric chloride, sodium fluoride, copper sulphate, carbon disulphide, and ethylene oxide. Communications from ca 1949–1951 explicitly describe the substitution of mercuric chloride for DDT as well as spraying cupboards and bookshelves with a solution of 5% DDT in white oil. It was the Colonial Insecticides Committee Research Unit that hired Bracey and Barlow to develop a new method of incorporating DDT into bookbinding pastes and glues. The pair go on to test DDT, Dieldrin, Aldrin, γ-HCH, and PCP incorporated into a urea-alkyd resin that requires *accelerator AC 54* (10% sulphuric acid in butanol) for curing. This agent is deemed unsuitable for use in paper and leather products by the government despite the researchers' demonstration of the insecticidal efficacy of their new product.

Our approach: from determining hazard to risk assessment

Unfortunately, records from the CAOG 12 series end in 1951 and there is no indication as to whether new government guidance was issued for bookbinding of items with OCPs, nor as to whether the use of mercuric chloride and beechwood creosote was discontinued. The records in the FCO 141 series span 1835 to 2012, so it was assumed that both mercury and a variety of OCPs might be present in the binding glues and pastes in the items. Furthermore, because there was historic indication that government archives, libraries, and administrative offices were applying insecticidal agents to shelves and in storage areas, we suspected that OCPs may be present on the items in the series regardless of format or date of creation.

[1] Binders mentioned include Camelot Press Ltd and a 'modern binding-works in Southampton' – though we believe this is a reference to Samuel Jones Ltd formerly located on Southampton Way in Camberwell, London. A label in FCO 141/13419 indicates that it was bound by Waterlow & Sons, Ltd also based in London.

There are a number of recent publications and studies detailing methods for non- or minimally destructive analysis of OPCs in heritage objects as well as methods to detect off-gassing of agents that require no sampling at all. [40–43] Unfortunately, these methods are not available through commercial laboratories, and new, streamlined testing kits for the GLAM (gallery, library, archive, museum) sector are still under development.[2] The popularity and sensitivity of the FCO 141 collection required rapid analysis and action, including invasive sampling for destructive analysis by GCMS. Sampling of archival and library items, and in particular those that do not bear an 'iconic' status is a complex and rapidly evolving area in Collection Care research. Although the value of library and archival materials is often directly attributed to the information contained therein rather than the media, there has been a recent growth in appreciation and research into the *artefactual value* of these materials [44]. Sampling of our collections for scientific or scholarly research study currently requires approval by a panel of experts and the Director for Research and Collections. In this instance, where the health and safety of our readers and staff were paramount, sampling to determine the nature and scale of insecticide use was approved by the Executive Team of the organisation.

Beyond establishing whether the collection was a potential hazard, it was necessary to determine the risk it posed to staff, visitors, and readers. Research in this area is scant, with several studies exploring the acute and chronic risk to staff via air sampling or biological testing (e.g. urine and blood tests) [10, 11, 21]. Much like items in 'handling collections', library and archival material is regularly accessed by members of the general public alongside staff. Users spend hours in close contact with the records, whether carrying out conservation treatment or close reading. In addition, the digitisation process, which introduces a potential for slightly elevated temperatures or light-levels, was a concern as these conditions may accelerate the volatilisation of some agents. However, making this collection permanently inaccessible to the public or to staff to avoid any risk was not an option. Indeed, even its temporary withdrawal during testing was deeply concerning to the research community.

Our approach was to carry out XRF spectroscopy on bound items (with and without insecticide labels) to determine if mercury was still present and to commission external GCMS analysis on bound items and tagged files (in historic and contemporary folders) to establish if OCPs were detectable and to identify the agents found.

[2] See the German MUSA initiative: http://musa-projekt.de [accessed 09 November 2022].

Table 1 Years of patent and early use of relevant OCPs [5]

Year described	Year of US patent	Federal registration	Agent
1942	1944	1952	DDT
1948	1954	1948	Dieldrin
1951	1954	1954	Endrin
1825	1940	1952	γ-HCH (Lindane)
1948	1948	1948	PCP

If OCPs were detected and the items deemed to present a hazard, we would work with an occupational hygiene (OH) expert to determine the rate of emission or transfer of the insecticide(s) during handling for production, digitisation, and research. The outcomes of these tests would be used to create risk assessments and recommendations for the safe handling of the items by different kinds of users, and for their long-term storage.

Methods and materials

Item selection and sampling

The conservation team had surveyed approximately 1 000 items (from six territories) out of ~ 20 000 in the series when the labels were noticed. Of these pieces, 49 were noted as 'bound' and all originated from Nigeria. Our initial concern was around the presence of insecticidal agents in the binding glues and pastes; therefore, 12 of the bound items were selected for analysis via X-ray fluorescence (XRF) and Fourier transform infrared (FTIR) spectroscopy in-house, and gas chromatography-mass spectrometry (GCMS) externally. Items were selected to cover a range of years (1940–1960) pre- and post-commercial availability of OCPs (Table 1). Twenty samples from both labelled and non-labelled items were analysed. Following the results from this initial round of testing, another 20 items from five other territories were selected for GCMS analysis (one sample per item). These items covered a wider period of production (1900 through 1961) and primarily consisted of tagged files in historic and contemporary folders.

Samples (0.06–0.27 g) from bound items were obtained using a scalpel from the paste-downs, the spines, and anywhere along the gutter where binding glue was visible. Samples were of mixed composition and often included paper, board, binding glue, textile, and sewing thread. Where possible, a sample of the glue was set-aside for FTIR analysis. Samples from tagged file folders were obtained by cutting a narrow band (~ 1 mm) along the bottom or top edge of the folder. All sampling was documented and care was taken not to affect any area with written or printed text. Gloves were changed between each sampling and the benchtop, scalpel and

tweezers were wiped thoroughly with isopropyl alcohol-water mixture (30/70% v/v). Samples were placed in 1.5 mL polypropylene conical vials and secured in small sealed plastic bags. Ten samples were sent to Integrated Contamination Management (ICM) working with PAZ Laboratorien GmbH respectively ALAB GMBH in Germany for GCMS, Raman and XRF spectroscopic analysis; thirty samples were sent to FERA Science Ltd in the UK for GCMS analysis.

Instrumental—the national archives

A Niton XL3t Ultra GOLDD + handheld XRF spectrometer was used in mining mode (Cu/Zn), changing filters for main (40 kV, 50 μA, 90 s acquisition time) and light elements (15 kV, 100 μA, 30 s acquisition time), with a 3 mm spot size. Niton Data Transfer Version NDT_REL_8.2 Software was used for data processing. FTIR was carried out to identify the adhesive used in bound items. An Agilent 4300 handheld spectrometer using a diamond Attenuated Total Reflectance accessory (ATR) positioned in a benchtop stand was employed. Samples were analysed in the 650–4000 cm^{-1} range; 64 scans averaged, with 4 cm^{-1} resolution and HappGenzel appodization. Data was analysed using the Agilent MicroLab Expert Software and reference spectra were obtained through the IRUG User's Library.

Instrumental—PAZ laboratorien GmbH and ALAB GmbH

As above, a Niton XL3t GOLDD + with a 50 kV silver tube with silver anode was used. Spot size of 3 or 8 mm was used depending on the sample. For chromatography, samples were extracted using acetone/cyclohexane (1:1), PCP was derivatised with acetic-acid-anhydride. Samples were analysed by gas chromatography with electron capture detector (GC/ECD) using a 30 m HP5MS column (diameter 0.25 mm, film 0.25 μm) as well as using GCMS in single-ion mode with a 50 m HP5MS column (diameter 0.2 mm, film 0.33 μm). Samples were identified and quantified against calibration solutions of: γ-HCH, PCP, DDT and DDT degradation products (p,p-DDT, o,p-DDT, p,p-DDE, o,p-DDE, p,p-DDD, o,p-DDD), 1,4-dichlorobenzene, camphor, 2-chloronaphthalene, 1-chloronaphthalene, di-chloronaphthalene, tri-chloronaphthalene, tetra-chloronaphthalene, and naphthalene.

Instrumental—FERA science ltd

Full details are provided in the Additional file 1. In brief, samples were extracted with ethyl acetate (1.0 ml) by ultra-sonication for 30 min in 1.5 ml microcentrifuge tubes. The extraction mixture was centrifuged at 12000 ± 2000 G and supernatant was analysed by gas-chromatography coupled with tandem mass spectroscopy (GC-MS/MS). Stable isotope labelled internal standards for representative compounds were added prior to extraction. The analysis of samples included following steps to ensure the results generated meet the criteria set in the SANTE requirements for pesticide residues analyses. All solvents used were of HPLC grade or purer. All other chemicals were Analytical Grade or purer. Positive and negative control samples were included to demonstrate method performance. Multi-level calibration solutions were used to accurately quantify any residues detected. These calibration solutions included all pesticides sought. All samples tested (along with control samples) were bracketed with the multi-level calibration solutions to demonstrate the instrument performance throughout the duration of the run [45]. Gas chromatographic methods coupled with selective tandem Mass spectroscopy instruments provide unequivocal evidence to support any residues detected.

Occupational hygiene testing

OH testing was carried out by Synergy Environmental Solutions Ltd. The survey was carried out in accordance with the guidance provided within HSE document HSG 173 Monitoring Strategies for Toxic Substances and was designed to provide data on the levels of exposure over the duration of a single day and exposures during specific tasks.

The survey at the National Archives involved three main tasks: production, reading and digitisation. These tasks were identified as processes that can generate airborne particles, increasing the exposure risk through inhalation. The sampling period was at least 25% of the expected task duration to ensure representative results. The monitoring period was 150 min and 180 min for reading and digitisation, respectively. In the case of production, a task-based sample was selected, assessing the complete task carried out in 22 min.

Personal samples were taken from the lapels of the workers within their breathing zones. The sample pumps (Casella Apex2) were calibrated before and after sampling using a calibrated flow meter (Casella FlowDetective™) traceable to national standards. Samples were submitted to i2analytical, a UKAS accredited laboratory that participates in, and performs satisfactorily in an external Physical Testing (PT) Scheme.

Two members of staff wearing a half-face mask (Drager X-plore 3300) and two filters for organic and inorganic vapours, mercury, and particulates (ABEK1Hg-P3RD), nitrile gloves, disposable coveralls and safety glasses enacted three scenarios:

1. Production of records from the repositories [Staff member 1, 22 min]: searching record codes on the

rolling racks, looking into boxes for the correct document and replacing it; placing documents in a trolley.
2. Research and close reading [Staff member 1, 420 min]: Reading and reviewing of documents in a room, flipping through documents and pages while looking for specific information.
3. Digitisation [Staff member 2, 405 min]: Placing records above the digitising workbench, using scanning software with a high-definition camera to image the relevant pages, and replacing records into boxes.

Ethylene oxide was measured following the requirements of NIOSH method 1614: a known volume of air (Flow rate: 0.2 $l.min^{-1}$) was passed through a solid sorbent tube (SKC226-178) containing HBr-coated charcoal. The samples were desorbed with 1 mL of dimethylformamide and analysed using Gas Chromatography.

For fluoride and hydrofluoric acid, samples were obtained following the requirements of NIOSH method 7906: known volumes of air (Flow rate: 2 $l.min^{-1}$) were drawn through a pre-filter of cellulose nitrate (0.8 µm pore size and 37 mm) followed by a treated filter of cellulose nitrate impregnated with Na_2CO_3 separated by an inert chemical spacer. Samples were subsequently analysed by Ion Chromatography with conductivity detection.

Mercury was determined following the NIOSH method 6009. A known air volume (Flow rate: 0.2 $l.min^{-1}$) was passed through a solid sorbent tube (SCK 226-17-1A) containing a section of 200 mg Hopcalite held by glass wool plugs. The samples were then desorbed with a nitric acid solution, followed by hydrochloric acid and deionised water; the solution was analysed by atomic absorption spectroscopy.

For pentachlorophenol and chloronaphthalenes, samples were collected in sorbent tubes 226-30-04 and analysed using the in-house method at i2analytics (Flow rate: 0.6 $l.min^{-1}$). The pentachlorophenol followed a DCM extraction and GCMS. For the case of chloronaphthalenes, the analysis followed current soil/water methods that semi-quantify against a standard of 1-chloronaphthalene following a DCM extraction. All other substituted chlorobenzenes were determined by ion extraction sum of all alkyl series isomers and semi-quantitation against 1-chloronaphthalene, reported as each alkyl group in total isomer concentration. The methodology is based on the EPA 8270/625.

For phenol, cresol, and xylenol detection, samples were taken as per the requirements of NIOSH method 2546 and OSHA 32: known volumes of air (Flow rate: 0.1 $l.min^{-1}$) were drawn through XAD-7 sampling tubes (SCK 226–95) and desorbed with methanol. The samples were then analysed using High-Performance Liquid Chromatography (HPLC) with ultraviolet detection at 218 nm.

For Volatile Organic Compounds (1,4-dichlorobenzene, naphthalene, carbon disulphide), samples were taken in accordance with the requirements MDHS 96: a known volume of air (Flow rate: 0.2 $l.min^{-1}$) was drawn through an SKC 226–01 activated carbon sorbent tube that collected the airborne volatile organic compounds. The sorbent tube was sealed for transportation after use and analysed by gas chromatography (GC-FID).

Samples for the 'pesticide suite' (details in Additional file 1) analysis were determined using an in-house method of i2analytics, where a volume of air (Flow rate: 2 $l.min^{-1}$) passes through a 226-92 PUF sorbent tube. DCM extraction was used, followed by GC-QQQ analysis of all the compounds based on standard external calibration for all analytes. This method is based on the pesticide method in soil/water, which follows the recommendations EPA 505/525. The survey results were compared to current occupational exposure limits published within the Health and Safety Executive document EH40/2005 Workplace Exposure Limits (Fourth Edition 2020) and levels specified in the Control of Substances Hazardous to Health Regulations 2002 (as amended). Where a WEL was not present, alternative national limits were used as guidance, if available.

Results

XRF, FTIR, GCMS analyses

Results from all three types of analyses (XRF, FTIR, and GCMS) are summarised in Table 2; full data from GCMS analysis are presented in the Supplementary Information (Additional file 1: Table S1). The adhesives were analysed via FTIR where possible in order to support GCMS methodological development and to establish whether mercuric chloride was present in both gelatine and starch pastes. Results show that gelatine, rather than starch, was primarily used in the areas tested: to secure pastedowns, adhere the cover paper to the boards and along the spine of the bound items. In most cases, this material was brittle and brown, as would be expected for aged gelatine. Because the items in FCO 141 have not been through any type of conservation treatment after acquisition, loose and detached material from the binding structure could be easily collected (Fig. 3). Besides featuring in bound items, the insecticide warning stamps were frequently found in tagged binders composed of two boards attached with a cloth spine (Fig. 1 top, right). Adhesive in these items was applied in very thin layers and sampling for FTIR was difficult in most cases. Gelatine was detectable on one such item, and it has been assumed that this is the adhesive used in similar binder types.

Table 2 Summary of results of GCMS, XRF, and FTIR analyses of samples tested

Catalogue No.	Year	Label	Territory of origin	Organochlorines[1]	Hg[2]	Adhesive if bound[3]	Sample area description
FCO 141/18732	1941	N	Zanzibar	None	N	Starch	Crystalline material on left fly leaf
FCO 141/18732	1941	N	Zanzibar	DDT	N/T[6]	Gelatine	Right turn-in with spine textile
FCO 141/13423	1943	Y	Nigeria	HCH[4], PCP, DDT	Y	Gelatine	Right turn-in, adhesive along spine
FCO 141/13419	1940	Y	Nigeria	HCH, PCP, DDT, 1-CN	Y	Gelatine	Left paste-down, spine textile, textile over sewing support
FCO 141/13516	1945–46	N	Nigeria	DDT, DDE HCH, Dieldrin	N	Gelatine	Right cover paper and turn-in
FCO/141/13464 V3	1958–59	Y	Nigeria	DDT	N/D[6]	Gelatine	Sewing support, textile tie, left board
FCO/141/13464 V3	1958–59	Y	Nigeria	DDT	N/D	Gelatine	Back board
FCO 141/13467 V2	1958–60	N	Nigeria	DDT, DDE, HCH, Dieldrin	N	Possibly gelatine	Textile from bottom of spine
FCO 141/13467 V2	1958–60	N	Nigeria	DDT	N	Gelatine	Sewing support, textile tie, left board
FCO 141/13467 V2	1958–60	N	Nigeria	DDT	N	Gelatine	Back board
FCO 141/13506	1955–57	Y	Nigeria	DDT, DDE, HCH, Dieldrin	Y	Gelatine	Right turn-in, spine textile, textile cover and adhesive
FCO 141/13506	1955–57	Y	Nigeria	DDT	Y	Starch & gelatine	Loose material from spine in gutter including sewing thread and adhesive
FCO 141/13504	1951–53	Y	Nigeria	DDT, DDE HCH, Dieldrin	N/D	Gelatine	Right turn-in, spine textile, textile cover and adhesive
FCO 141/13504	1951–53	Y	Nigeria	DDT	N/D	Gelatine	Loose material from spine in gutter including sewing thread and adhesive
FCO 141/13503	1949–51	Y	Nigeria	HCH, PCP, DDT	Y	Gelatine	Right turn-in, spine textile, textile cover and adhesive
FCO 141/13503	1949–51	Y	Nigeria	PCP	Y	Gelatine	Loose material from spine in gutter including sewing thread and adhesive
FCO 141/13477 V3	1957	Y	Nigeria	PCP, DDT	N/T	Starch	Right fly leaf with white bloom
FCO 141/13477 V3	1957	Y	Nigeria	HCH, PCP, DDT	N/D	Possibly gelatine	Spine textile
FCO 141/13490	1958	Y	Nigeria	HCH. PCP, DDT	N/D	Possibly gelatine	Spine textile
FCO 141/13428	1946–47	N	Nigeria	DDT	N	Gelatine	Spine textile and right cover paper
FCO 141/6441	1926–27	N	Kenya	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Bottom edge of folder
FCO 141/15564	1946	N	Singapore	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Bottom edge of folder and textile spine
FCO 141/13661	1951–61	N	Northern Cameroon	DDT, DDE, HCH, Dieldrin, endrin	N/T	Tagged folder	Bottom edge of folder and textile spine
FCO 141/5641	1953–61	N	Kenya	DDT, DDE, HCH, Dieldrin	N/T	N/T	Left turn-in, cover paper, paste-down, and spine textile
FCO 141/5576	1956	N	Kenya	DDT, DDE, HCH	N/T	N/T	Right turn-in, paste-down, spine textile and adhesive
FCO 141/5502	1932	N	Kenya	DDT	N/T	N/T	Right turn-in, paste-down, spine textile and adhesive, bottom of fly-leaf
FCO 141/17891	1957–59	Y	Tanganyika	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Right board and spine textile; blank paper edge of file 136
FCO 141/15678	1949	N	Singapore	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Right board and spine textile
FCO 141/15508	1913–14	N	Singapore	DDT, DDE	N/T	N/T	Left paste-down and board, spine textile and adhesive
FCO 141/7435	1938–41	N	Malaya	DDT, DDE, Dieldrin	N/T	Tagged folder	Bottom edge of folder
FCO 141/5648	1931–37	N	Kenya	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Right bottom edge of folder

Table 2 (continued)

Catalogue No.	Year	Label	Territory of origin	Organochlorines[1]	Hg[2]	Adhesive if bound[3]	Sample area description
FCO 141/17883	1958–59	N	Tanganyika	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Left bottom edge of folder
FCO 141/15874	1900	N	Singapore	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Bottom edge of folder; loose, blank paper detached near tag
FCO 141/13575	1906	N	Nigeria	DDT	N/T	Tagged folder	Bottom edge of folder; top edge of blank file
FCO 141/7048	1949	N	Kenya	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Bottom edge of folder
FCO 141/17888	1957–61	Y	Tanganyika	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Right board and spine textile
FCO 141/15511	1901	N	Singapore	DDT, DDE	N/T	Tagged folder	Right bottom edge and loose material along spine of folder
FCO 141/7434	1929	N	Malaya	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Left bottom edge of folder
FCO 141/13697	1932–54	N	Nigeria	DDT, DDE, HCH, Dieldrin	N/T	Tagged folder	Loose fragments from folder and bottom edge of file 8
FCO 141/5542	1954	N	Kenya	DDT, DDE, HCH	N/T	Tagged folder	Left bottom edge of folder

[1] Qualitatitve summary of GCMS results from different labs; [2]Qualitative summary of mercury detection from analyses carried out at The National Archives and PAZ Laboratorien GmbH; [3]As determined from FTIR analyses on bound items; [4]HCH = HCH-γ (Lindane); [5]FTIR spectrum dominated by binding components (paper, textile); adhesive type based on format and conservator observation; [6]*N/D* not detected, *N/T* not tested—only bound items were tested for mercury

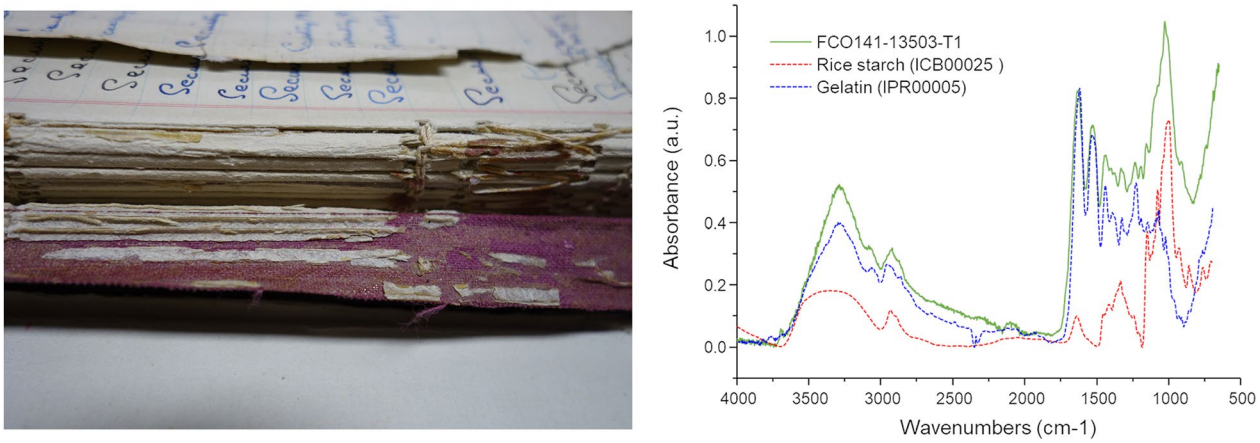

Fig. 3 Detail from FCO 141/13503 showing detached spine with loose and crumbling adhesive (left), and FTIR spectrum of adhesive with reference spectra for gelatine and starch. It is more likely that the carbohydrate signals corresponding to 'starch' in the sample are due to the presence of paper pulp in the glue sample, than starch adhesive

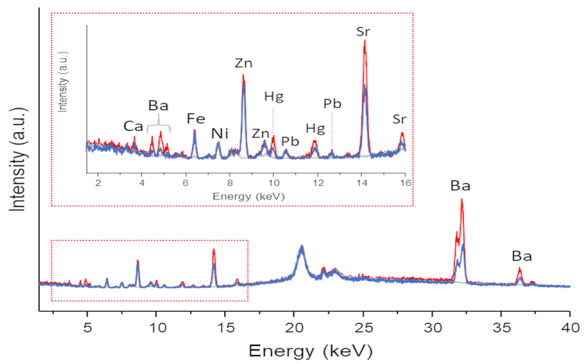

Fig. 4 XRF spectra (main range) of adhesive in gutter of FCO 141/13506 (red and blue), a bound register of the same format as that shown in Fig. 1 bottom, right. The baseline spectrum is in grey

XRF spectroscopic analyses confirmed the presence of mercury in all items that contain a warning label. An example XRF spectrum of a labelled item can be seen in Fig. 4. Multiple areas were analysed on each item, focusing on parts of the binding where adhesive was visible or expected to have been applied in large quantities. Nonetheless, the mercury signal is very weak and in some instances, may be masked by the presence of other elements in the testing area. XRF analysis carried out at The National Archives and PAZ Laboratorien GmbH was qualitative; however, even if calibration standards had been employed, it would not be possible to back-calculate the total amount of mercury present in the items, as its overall distribution over the surface of the objects cannot

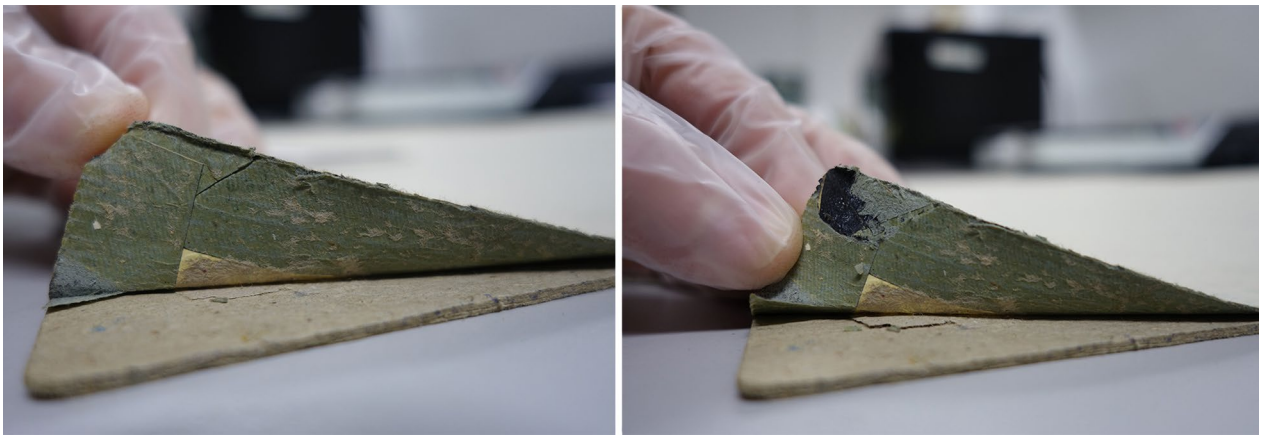

Fig. 5 Detail from right turn-in before (left) and after (right) sampling from FCO 141/13515. The degraded yellowed adhesive can be seen along the green card

be established with localised XRF testing. During XRF testing, PAZ Laboratorien GmbH also noted very high levels of chlorine on most items, corresponding to the suspected presence of OCPs.

Samples for GCMS analysis (Fig. 5) were obtained from a variety of items in the collection covering six territories and including bound volumes and binders with and without insecticide warning labels as well as original and contemporary tagged folders, which did not feature warning labels. Samples were extracted according to different methodologies by the two laboratories and analysed against slightly different 'pesticide suite' standards. One or more historic insecticides were detected in all samples tested but one—a starch adhesive scraped from the flyleaf of a bound item from Zanzibar. However, a second sample from the right turn-in of this item tested positive for p,p-DDD and p,p-DDE.

The most common agents detected in the samples were p,p-DDT, o,p-DDT, Dieldrin, γ-HCH, PCP, and Endrin. Testing by FERA Science Ltd also showed the presence of pp-DDD and pp-DDE, breakdown by-products of DDT in many of the samples [46]. These compounds were also detected in the analysis carried out by ALAB GmbH but are included as a sum within the DDT result. PCP was detected in many samples tested by ALAB GmbH, but is not part of the standard suite used by FERA Science Ltd, and may therefore be present in these samples as well. Both laboratories quantified each of the organic insecticidal agents detected in the samples. However, as with the XRF analyses, we cannot speculate on the overall quantity nor distribution of the agents on each item. Instead, the analyses were sufficient to confirm that many, if not all items in the collection bear residual insecticidal agents, and should therefore be treated as a hazardous collection.

Occupational hygiene testing

In order to establish whether the collection poses a risk to staff and readers, levels of exposure were measured with the support of an occupational hygiene consultancy. Results from the OH survey on the levels of exposure over the duration of a single day or during the execution of specific tasks are summarised in Table 3 and compared against occupational exposure limits. Results from static monitoring indicated that for the agents in the pesticide suite, phenol, cresol, xylenol, mercury, and ethylene oxide, no discernible mass was detectable after blank correction. The same results were found for task-based personal sampling during document production and long-term personal sampling during document digitising and reading for 1,4-dichlorobenzene, naphthalene, carbon disulphide, pentachlorophenol, and chloronaphthalenes. Therefore, under the conditions of testing, the exposure risk to these elements through inhalation is not significant for operatives carrying out the described tasks.

An unexpected finding was the detection of hydrogen fluoride (presumed from fluorine) from static monitoring during document production, digitising and reading at background concentrations of 0.04 mg/m^3, 0.002 mg/m^3 and 0.004 mg/m^3, respectively. These levels do not indicate excessive short-term exposure during document production or long-term exposure during document digitising and reading.

Discussion

Hazardous collections

Initial XRF and GCMS testing on bound items, both with and without labels, indicated the residual presence of a variety of insecticidal agents and their breakdown products. The XRF results confirmed that mercury

Table 3 Summary of workplace airborne contaminant testing results from Synergy Environmental Solutions Ltd. Limits of detection are available in the Additional file 1: Table S2

Task	Analyte[a]	Sample Volume (L)	8 h Exposure Limit (mg/m^3)	Average Blank Mass (mg)	Analyte Mass (mg)	Corrected Mass (mg)	As determined conc. (mg/m^3)
Document Production (22 min)	Pentachlorophenol	13.5	0.5	0.01	0.01	0	0
	1-chloronaphthalene		0.23	0.01	0.01	0	0
	pp-DDD	44	N/A	0.0001	0.0001	0	0
	pp-DDE		N/A	0.0001	0.0001	0	0
	pp-DDT		0.5	0.0001	0.0001	0	0
	op-DDT		0.5	0.0001	0.0001	0	0
	Dieldrin		0.25	0.0001	0.0001	0	0
	Endrin		0.1	0.0001	0.0001	0	0
	γ-HCH		0.5	0.0001	0.0001	0	0
	Mercury (gaseous)	4.2	0.02	0.0002	0.0002	0	0
	Mercury (particulate)	44	0.02	0.001	0.001	0	0
	Hydrogen fluoride (as F)	45	1.5	0.0028	0.0047	0.0019	0.04
Digitisation (480 min)	Pentachlorophenol	90	0.5	0.01	0.01	0	0
	1-chloronaphthalene		0.23	0.01	0.01	0	0
	pp-DDD	90	N/A	0.0001	0.0001	0	0
	pp-DDE		N/A	0.0001	0.0001	0	0
	pp-DDT		0.5	0.0001	0.0001	0	0
	op-DDT		0.5	0.0001	0.0001	0	0
	Dieldrin		0.25	0.0001	0.0001	0	0
	Endrin		0.1	0.0001	0.0001	0	0
	γ-HCH		0.5	0.0001	0.0001	0	0
	Mercury (gaseous)	30	0.02	0.0002	0.0002	0	0
	Mercury (particulate)	298	0.02	0.001	0.001	0	0
	Hydrogen fluoride (as F)	300	1.5	0.0028	0.0035	0.001	0.002
Reading Room Research (420 min)	Pentachlorophenol	94	0.5	0.01	0.01	0	0
	1-chloronaphthalene		0.23	0.01	0.01	0	0
	pp-DDD	322	N/A	0.0001	0.0001	0	0
	pp-DDE		N/A	0.0001	0.0001	0	0
	pp-DDT		0.5	0.0001	0.0001	0	0
	op-DDT		0.5	0.0001	0.0001	0	0
	Dieldrin		0.25	0.0001	0.0001	0	0
	Endrin		0.1	0.0001	0.0001	0	0
	γ-HCH		0.5	0.0001	0.0001	0	0
	Mercury (gaseous)	33	0.02	0.0002	0.0002	0	0
	Mercury (particulate)	322	0.02	0.001	0.001	0	0
	Hydrogen fluoride (as F)	322	1.5	0.0028	0.0042	0.0014	0.04

[a] Only results for agents detected via GCMS are shown here; full results are available though all were non-detectable

(probably as mercuric chloride) had been used in the labelled bound items. Testing did not detect this agent in identical items from the same time period that did not bear a warning label. However, because the mercury signal was very weak even when detected, we cannot discount its presence from non-labelled items entirely, especially with knowledge of documented historic practices.

The first round of testing revealed that OCPs such as γ-HCH, PCP, and Dieldrin were detectable on items pre-dating their commercial availability (Tables 1 and 2). These results suggest that OCPs were applied on the items or in the areas where they were stored at a later time. Furthermore, the presence of multiple types of OCPs on the same item suggests multiple applications, or application of patented mixtures (e.g. Impra Hgf, used in

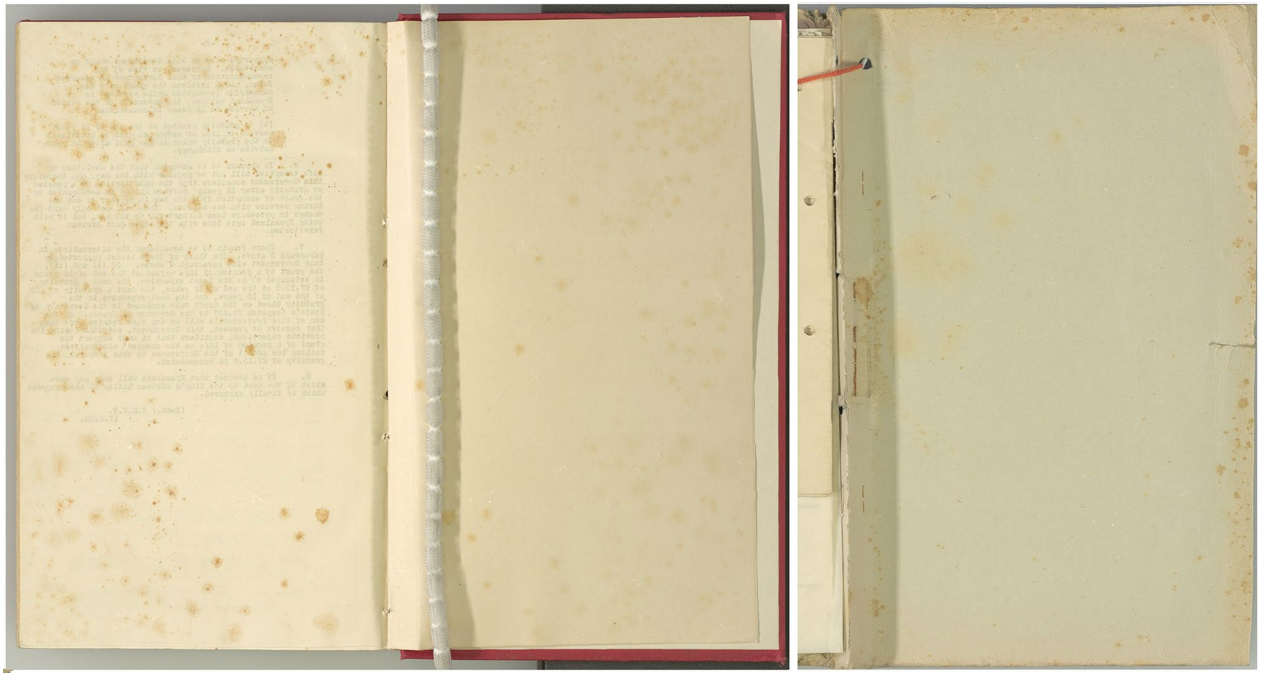

Fig. 6 Left flyleaf and text block of FCO 141/5502 (left) and right folder flap of FCO 141/5648 (right) showing discoloured spotting resembling spray pattern that may be a result of insecticide application

Germany, contains γ-HCH and PCP) [47]. These results indicate that mercury is not the only agent of concern, and that the absence of a warning label on the items does not preclude its potential to present as a hazard.

To determine whether this observation affected non-bound collection items, and those originating from other territories, a second round of GCMS testing was carried out primarily on tagged files. Indeed, while surveying items for the follow-up analysis, insecticide-warning stamps were discovered on items from other territories as well. Once again, a range of OCPs were detected on all items tested, either individually applied, or in mixtures. Some of the items in this testing set were produced as early as 1900, again demonstrating that the insecticidal agents were applied after the item creation. According to the results from ALAB GmbH, the quantities of PCP in items produced before 1947 are similar to those in items produced later; it is therefore not possible to distinguish between primary or secondary contamination.

The tests carried out cannot be used to determine when the insecticides were applied (beyond the obvious post-commercial availability, WWII period). We can speculate, at least for those items containing mercuric chloride, that the agents were applied at the time of production, in Britain, and by the binding-works. However, for the remainder of the items surveyed, there is no way to determine in what form the agents were applied, nor where and by whom they were applied. To our knowledge, documentation around this has not been kept. Within the CAOG 12 records, we find clues, but we do not have information for specific record series or regular practices in different territories, offices, or archives.

Although the presence of the insecticidal agents is not visible on the items (no crystalline or powdery materials were noted, as might be the case on ethnographic objects), a spray-like pattern was observed on some items in the series (Fig. 6). Both of these records were returned from Kenya but they show different types of OCP contamination. Future research may aim to establish if these patterns correspond to insecticide use, or whether they are incidental and unrelated.

Risk management

In this study, three workplace exposure tests were carried out over the duration of a single day and during the execution of specific tasks. The testing was limited to monitoring only risk by inhalation, and for acute exposures (i.e. tests were not carried out continually to monitor for cumulative exposure over the course of days, weeks, or months). Though most of the agents found on the items do not readily volatilise in ambient conditions, they can be inhaled through dust and particulates on and around the documents. The main routes of exposure for PCP are inhalation and ingestion, but it is less well absorbed dermally [48]. DDT and its persistent transformation products also occur mainly through diet, but other exposure

routes, such as inhalation or dermal contact, cannot be excluded [49]. This is similar for γ-HCH, though the substance has been shown to have cutaneous absorption in rats [50]. For Dieldrin and 1-CP, the most significant routes of exposure are absorption through intact or damaged skin, via the eyes or through inhalation of vapours, dust, and aerosols, as well as through ingestion. Although exposure to these components is not significant through inhalation, it might result in a residual risk through dermal contact or ingestion.

Realistically, in the archive or library setting, inhalation of dusts and particulates and dermal absorption are the most likely routes of exposure. Staff and readers are already required to follow safe handling procedures when working with any of the collections at The National Archives: frequent hand washing, exclusion of food and drink near the documents, caution against chewing on pencils or eyeglasses, or licking of fingers when browsing documents. In parallel to the OH assessment, a literature review of the approaches other organisations have taken when dealing with known insecticides in their collections was also carried out (Additional file 1: Table S3). In most cases, recommendations are made to ensure that artefacts are made inaccessible to the public—a step that cannot be implemented at The National Archives. Handling recommendations span a variety of approaches: from a signed acknowledgement form and encouragement to wear nitrile gloves to strict requirements that staff and researchers handle the items wearing full PPE (nitrile gloves, lab coats, aprons, finger sleeves) and PPR (masks with FFP3 fine particulate dust filters) while working under extraction and cleaning using HEPA (high efficiency particulate air) filter vacuums.

The current OH workplace airborne contaminant assessment suggests that the control measures applied during document production, digitising, and reading appear to be adequate to prevent acute exposure through inhalation (Table 3). The unexpected, detectable hydrogen fluoride levels could not be correlated with historic insecticide use. Although sodium fluoride may have been used for this purpose, this salt is not expected to spontaneously form hydrogen fluoride gas under ambient conditions. In order to determine if the detected hazardous agents are absorbed dermally during handling, biological testing would be required. Furthermore, monitoring in the repository areas where the FCO 141 collection is stored would be beneficial. The current testing was constrained by access demands to the collection, necessitating rapid action and a workable solution that could be implemented as an interim solution.

Consequently, the following recommendations were made and implemented to further minimise exposure risk through ingestion and dermal contact: (1) items are to be viewed and handled in designated and restricted locations; (2) disposable nitrile gloves with a minimum breakthrough time of at least one hour are required to be worn by staff, external readers and any other individual who may handle the documents; (3) high levels of housekeeping are to be maintained, ensuring areas where the documents are handled are cleaned after use (e.g., vacuum cleaning followed by damp wiping); (4) eating and drinking are to be fully restricted when handling the documents (as is the general handling guidance at The National Archives); and (5) because personal objects such as mobile phones, laptops and any other objects that could be subject to cross-contamination, these shall be wiped down prior to being removed from the area where document handling occurred.

Conclusions

This study describes the initial analysis and response to a suspected hazard in the collections of The National Archives. This practice-lead project has several limitations associated with the nature of a reactive research scenario situation in an organisation, rather than a traditional laboratory (e.g. number and selection of records for sampling, invasive and destructive nature of the analyses, acute vs chronic occupational exposure testing). Our results demonstrate that a variety of OCPs are found on all items tested in the FCO 141 series, regardless of period of production, format, or originating territory. Although our initial hopes were that the detected hazards would correlate with the warning labels identified on some items, this was confirmed only for mercuric chloride. Therefore, plans to carry out a survey of the FCO 141 series in order to locate all items bearing warning labels were set aside, and focus shifted to establishing the risk posed by collection items to staff and readers during handling.

In the available time and within the constraints of an active and open archive, we carried out workplace exposure testing for airborne contamination by the agents detected via XRF and GCMS analyses. These preliminary results suggest that current practices during handling do not result in detectable concentrations of harmful agents through inhalation. Due to the difficulty in testing for dermal absorption for mercury and the various OCPs found on the items, biological testing was not carried out. However, safety measures that would prevent this risk were implemented for all staff and members of the public when handling the collections.

Several key questions remain open for the organisation and for other archive and library collections. As has been shown, historic literature and correspondence demonstrates relatively widespread use of mercuric chloride in book-binding practices at least until the Second World

War, as well as the application of OCPs on shelves and in storage areas where documents and books were kept. These practices seem to have been particularly prevalent in 'tropical environments' or, as described by Kathpalia in 'regions with unfavourable climatic conditions' as perceived by Western standards [36]. Further testing should be carried out across collections where documents have been returned from abroad. However, this does not preclude the possibility that many archives and libraries carried out such treatments in Western regions as well, especially during the peak of OCP production and use, in the period after the Second World War. With precautionary measures in place for the FCO 141 series, we may now look to carry on further testing, potentially working with heritage partners that can do so in minimally invasive and possibly non-destructive ways.

Several methods have been proposed for decontamination of heritage items from historic pesticides without compromising their integrity. These include the vacuum removal of surface contaminants, remediation by specialist bacteria, extraction using liquid or supercritical carbon dioxide, solvent cleaning, washing under vacuum, exposure to increased temperatures under vacuum, and removal through aqueous α-lipoic acid solutions [7, 51]. However, the application of these methods is not easily adaptable to large-scale bound or tagged file collections such as the FCO 141 series, especially where visible, powdery residues are not present. Furthermore, as demonstrated by a bioassay carried out at Harvard University Libraries, removal of DDT from books using a vacuum with a (high-efficiency particulate absorbing (HEPA) filter could not fully remove biologically active residues [35]. Other methods, such as thermal desorption [52] have yet to be demonstrated for safe use on book and paper collections. For the moment, these methods will not be pursued at The National Archives. Instead, documentation and appropriate labelling with hazard notifications on the boxes and in the digital ordering system will be implemented to ensure safe handling precautions are followed during access according to the procedures established and described in this paper.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-023-00866-y.

Additional file 1: Figure S1. The Crown Agents for the Colonies, Standard Specification No. 40—Binding of Book. CAOG 12/88/6. **Figure S2.** Right paste-down of FCO 141/14515 with handwritten note deriding quality of paper in ledgers issued by the Government Printer. **Figure S3.** Calibration line for DDT-pp; range from 0.002 µg/ml to 0.05 µg/ml. **Figure S4.** Chromatogram for DDT-pp; 0.05 µg/ml calibration solution, Positive control at 0.02 µg/ml, negative control and a positive sample, respectively. **Tables S1.** The GC-MS/MS results from FERA Science Ltd are presented in the three tables below followed by the results from ALAB GmBH. **Table S2**. Limit of detection for each sampling method used for occupational health testing by Synergy Environmental Solutions Ltd. **Table S2.** Summary of health and safety approaches taken by other organisations with regard to insecticide-treated collections. Sources are included in main manuscript reference list.

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Author contributions
LVA was lead scientist for this research and carried out sampling, desk research, FTIR and XRF spectroscopic analysis, data interpretation, and wrote the manuscript. SN lead the GCMS analysis and interpretation through FERA Science Ltd. BK and BP carried out GCMS and XRF analyses through ALAB GmbH and PAZ Laboratorien GmbH, respectively. FM and HW designed, carried out, and interpreted occupational hygiene measurements. MV and JV supported the research, critically read and supported the writing of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
GCMS and OH data generated or analysed during this study will be made publically available through The National Archives Freedom of Information repository online: https://www.nationalarchives.gov.uk/about/freedom-of-information/information-requests/ [accessed 09 November 2022]. All datasets (e.g. GCMS tabulated results, OH data, FTIR, XRF spectra) are available in the Additional file 1, from the corresponding author on reasonable request.

Declarations

Competing interests
The authors declare no competing interests.

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