Review of biocides used as prevention and intervention measures for historic artefacts, with special regard to herbaria collections

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Summary: Magdalena Grenda-Kurmanow, *Review of biocides used as prevention and intervention measures for historic artefacts, with special regard to herbaria collections*

This paper is a review of biocides used in historical herbaria collections, but also present in many other types of artefacts. Herbaria with desiccated plants, composed of organic material combined with other organics such as glues, pastes and other cellulose-based and proteinaceous materials are particularly vulnerable to pest infestations. Several chemical compounds have been used either to prevent infestation or to fight an existing pest attack. Most of them are now phased out or restricted in use and production. Biocides pose numerous threats both to artefacts and people working in the heritage sector, such as conservators. This review provides a comprehensive list of biocides used in herbaria with references, chemical identification and material characterisation, in particular with regard to the deterioration processes induced in artefacts. The review is a part of the project "Heritage preservation and ethnobotany. Analysis of the influence of conservation treatment on genetic material of historic herbaria" (project no. 2014/13/N/HS2/03118), funded by the National Science Centre in Poland.

This paper presents a review of biocides used for the preservation of historical herbaria by protecting them from biological damage mainly caused by pests. Many of these biocides have been and are being used also for other historical objects, including archival and library collections. Popular and easily accessible biocidal substances are widely used for pest control. Unfortunately, several compounds proved to have negative impacts not only on insects and microorganisms, but also on other forms of life, including humans, and on the artefacts themselves. As the history of the use of biocides in institutions and conservation studios is poorly documented, this article focuses on the issues related to their use.

Herbaria with desiccated plant material can be regarded as paper-based artefacts, but they also contain biological (plant) material, often mounted with natural adhesives. This combination of components makes herbaria particularly vulnerable to damage caused by insects and rodents. Unstable storage conditions, climatic fluctuations or random events involving higher moisture levels (such as dampness, flooding) also create conditions for mould growth. Herbaria in which the plants are kept loose between pages are also not free from potential damage by insects and microorganisms. Stored with other collections containing materials "attractive" to pests (i.e. natural adhesives), herbaria also suffered damage by pest attacks. Some plant species are more susceptible to insect attacks than others. The most endangered groups of specimens are petaloids, belonging to the monocotyledons, many dicotyledon species, particularly *Asteraceae*, and fungi. On the contrary, bryophytes and lichens are more resistant.[1]

Problems concerning insect damage were well known already at the beginning of the creation of herbaria.[2] The first publication on herbarium preparation, *Isagoge in rem herbariam libri duo* by Adriaan van den Spieghel (1606), already

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[1] Hall 1988.

[2] The years 1530–1540 are considered to be the most probable beginning of the history of making herbaria with dried plants (Bridson, Forman 1999, p. 4).

mentions biocidal and repellent substances.[3] Spieghel describes cloves powder and aloe as additions to the glue he used to mount specimens. In another archival source by Joseph Pitton de Tournefort, there aloe extract (*aloe hepatica*) is mentioned, as well as a decoction of common wormwood (*Artemisia absinthium* L., "absinth") and santonica (*Artemisia cina* O. Berg.),[4] which, however, altered the colour of the botanical specimens.

Other plants and plant compounds that were generally used as natural pesticides and repellents were camphor, extracted from camphor tree oil (*Cinnamomum camphora* (L.) J. Presl.), cassia oil from Chinese cinnamon (*Cinnamomum cassia* (L.) J. Presl.), thymol and carvacrol – present in thyme oil (*Thymus vulgaris*), wild thyme (*Thymus serpyllum* L.) and carom (ajwain, *Trachyspermum ammi* L. or *Carum copticum* L.), neem (*Azadirachta indica* A. Juss.), pyrethrin, extracted from Dalmatian pellitory (*Tanacetum cinerariifolium* (Trevir.) Sch. Bip., previously called *Chrysanthemum cinerariifolium* (Trevir.) Sch. Bip.), linalool, from lavender oil (*Lavandula angustifolia* Mill., previously called *Lavandula officinalis* Chaix), turpentine, distilled from pine resin (*Pinus sylvestris* L.), leafy sprouts of wild rosemary (*Rhododendron tormentosum* Harmaja, syn. *Ledum palustre* L.)[5], sweet flag (*Acorus calamus* L.), cassumunar ginger (*Zingiber cassumunar* Roxb.), cultivated tobacco (*Nicotiana tabacum* L.), strychnine from the strychnine tree (*Strychnos nux-vomica* L.), Javanese long pepper (*Piper retrofractum* Vahl), maidenhair tree seeds (*Ginkgo biloba* L.), citronella oil (*Cymbopogon nardus* (L.) Rendle or *Cymbopogon winterianus* Jowitt), rotenone, present in the roots of many plants of the *Fabaceae* family[6], menthol, cedar oil and bitter almond oil.[7] Several of these compounds were at some point synthesised to expedite their production and to standardise their composition

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[3] Spieghel 1606, p. 81.

[4] Tournefort 1694, p. 547–548.

[5] Today, the wild rosemary is under protection (Drobnik 2009, p. 165).

[6] Drobnik 2009, p. 164–165; Prance, Nesbitt 2005; Purewal 2012.

[7] Hawks 2001.

and effects. Several are still used as biocides, such as pyrethrins, both in natural and synthetic form.

Over time, users and custodians began to notice that the use of biocides is detrimental not only to insects and microorganisms, but also to human health. Our civilization is still struggling with the use of "miraculous" biocidal chemicals that facilitate agricultural production in many areas, reducing its costs, but also cause irreversible changes in natural environments. The most frequently cited example is DDT, which is now conditionally phased out. The production of DDT provided its developer, Paul Hermann Müller, with the 1948 Nobel Prize in Physiology or Medicine because of its insecticidal properties and effectiveness in fighting malaria and yellow fever. Today, DDT is still used to treat malaria. At the time of its intensive use in agriculture, this chemical compound almost led to the extermination of entire bird populations in the USA;[8] being one of the most persistent polluting pesticides, it is still detected in populations of animals inhabiting the Arctic.[9]

Such examples remind us, as conservators, that an awareness of the threats connected with pesticides is crucial to responsibly and effectively care not only for the safety of historical items, but also to protect both the natural environment and human health. Raising such awareness is the purpose of this article.[10]

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[8] Jagannath, Shore, Walker, Ferns, Gosler 2008.

[9] Doyle 2008.

[10] Education and raising awareness on the use of biocides is still needed. During the COVID-19 coronavirus pandemic of 2020, it has once again become clear how easy it is to make catastrophic mistakes in the use of biocides that are harmful to many forms of life at the same time, not necessarily in such a selective way as to meet user expectations. A negative example cited here is the use of sodium hypochlorite (a bleaching agent) in Spain to "disinfect" the beach in Zahara de los Atunes. The economic stimulus and the associated preparations for the reopening of the tourist resort were the reason for the decision to degenerate the natural environment and endanger the health of those who will use this beach (Sochaczewski 2020).

Classification of biocides

Biocides can be grouped according to their mode of action: stomach poisons that must be consumed by pests, contact pesticides that must come into direct contact with an insect, residual products, desiccant insecticides causing dehydration and, eventually, death, insect growth regulators and fumigants. They are available in different formulations: in mixtures with solvents or inert substances, as oil concentrates, as emulsifiable concentrates, wettable powders, dusts, baited insecticides, microcapsules diffusing poison and plastic strips impregnated with insecticide.[11]

The best known and most commonly used pesticide in herbaria is mercury chloride. The first reference to its use is the description of Tournefort (1694), who used mercury compounds in both monovalent (*mercure doux*) and divalent form (sublimate, French *sublimé corrosif*) as additives to the glue used to mount the specimens.[12] However, the list of toxic substances used as preventive measures is considerably longer.

Synthesised biocides, also synthetic versions of natural compounds, are listed in Table 1. This table contains references to publications that provide information on individual substances used in herbarium collections. The literature on biocides themselves is far more extensive, in addition to general studies, in which the use of pesticides is discussed in relation to all museum objects, also covering ethnographic, taxidermy, fluid entomological and economic botany collections.[13] These publications mention all biocides listed in the table below, as well as other substances such as borax, methoxychlor or glyphosate,[14] which were, however, most likely not used in herbaria collections.

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[11] Dawson, Strang 1992.

[12] Tournefort 1694, p. 547–548.

[13] Examples of studies: Dawson, Strang 1992; Hawks 2001; Sirois 2001; Odegaard, Sadongei 2005; Odegaard, Zimmt 2008; Pfister 2008.

[14] Glastrup 1987; Hawks 2001; Odegaard, Zimmt 2008.

It cannot be excluded that in the past, biocides might have been used for the preservation of herbarium specimens, and the development and availability of sensitive analytical techniques, mainly chromatographic, still provides new discoveries. Pesticide residues and degradation products are less evident in herbaria than in zoological items.[15] The most extensive literature concerns the use of the above-mentioned mercury chloride, which is one of the earliest known biocidal substances and one of those pesticides that permanently contaminate and damage specimens and are dangerous to human health, even many years after the original application.[16]

In addition, the CAS (Chemical Abstract Service registry) identification number is listed under the name of each pesticide.[17] When an entire group of compounds (e.g. pyrethrins or carbamates) is listed, the CAS number for the representative substances is given. However, this does not mean that there are no other substances with different registration numbers in the same group. The third column of the table indicates whether the compound has a negative effect on the genetic material of objects and artefacts. Due to the limited number of studies in this area, information on the impact on genetic material has been generalised and concerns a wider group of natural history collections, not only herbaria.[18] In some cases, the results of research in this area are not clear or consistent. In such situations, the table provides a less "optimistic" result, as-

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[15] Purewal 2001.

[16] The characteristics of mercury chloride are given later in the text, together with a description of other pesticides used in herbaria.

[17] https://www.cas.org/about/cas-content

[18] The information in this column was obtained from publications on the effects of pesticides and preservatives on the genetic material of various biological objects in museum collections. Studies and compilations in this area were carried out, among others, by Brown (Brown 1999), Whitten (Whitten, Williams, Glover 1999), Kigawai Stranga (Kigawa, Nochide, Kimura, Miura 2003; Kigawa, Strang, Hayakawa, Yoshida, Kimura, Young 2011; Kigawa, Strang 2011; Strang 1999), Cartera (Carter 2003), Eklund (Eklund 2006), Espeland (Espeland, Irestedt, Johanson, Akerlund, Bergh, llersj 2010) and Purewal (Purewal 2012).

suming that if in one study, a given compound showed a destructive effect, it is a potential threat to other historic objects.

The last column contains information on the genotoxicity (mutagenicity or carcinogenicity) of the listed materials, based on the EPA (United States Environmental Protection Agency) and IARC (International Agency for Research on Cancer) databases.[19] All listed pesticides are toxins with a variety of risks to human health. Some of them have a confirmed muta- and carcinogenic status, and for others, genotoxicity is defined as “possible” or “probable”, according to the classification implemented in the above-mentioned sources. In some cases, although a compound is known to be a neurotoxin and interferes with identification of genetic material in museum objects (as in the case of mercury chloride), there are insufficient data to classify it as a carcinogen or mutagen. There is also often a lack of research on chemicals currently phased out (at least in some regions of the world and most previous uses), such as DDT. Descriptions of individual pesticides indicate whether they are listed in the Stockholm Convention, an agreement governing the use of persistent organic pollutants (POPs).[20] The Stockholm Convention divides toxic substances into three groups: group A – intentionally produced toxic agents that should be eliminated, with specific exemption for certain uses; group B – toxic agents, of which international production should be restricted to manufacture and use to fulfil specific purposes (e.g. DDT for the treatment of malaria); group C – unintentional toxic agents that are products of the decomposition of other substances (e.g. production process side effects) and which should be kept to a minimum.

A brief characterisation of biocides is given below the table, with emphasis on the destructive effects of these substances on various elements of historic artefacts and toxicity to their users, including conservators.

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[19] EPA: www.epa.gov; IARC: www.iarc.fr

[20] Stockholm Convention: http://www.pops.int/. The Stockholm Convention was adopted at a conference on 22 May 2001 and came into force on 17 May 2004. Poland is one of the signatories of the Convention; ratification took place in 2008, and the provisions of the Treaty took effect in 2009.

Tab. 1. List of biocides used in herbarium collections

Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
Inorganic compounds				
Mercury chloride (II), CAS: 7487-94-7; mercury chloride (I), CAS: 10112-91-1	Bridson, Forman 1999; Briggs, Sell, Block, I'ons 1983; Clarck 1986; Croat 1978; Dauwalder 2012; Drobnik 2009; Fellowes et al. 2011; Fallon, Peters, Hunt, Koehler 2016; Grenda-Kurmanow 2016; Grenda-Kurmanow 2017; Hall 1988; Havermans, Dekker, Sportel 2015; Hawks, Bell 1999; Hawks 2001; Hawks, Makos, Bell, Wambach, Burrows 2004; Kataeva, Panichew, van Wyk 2008; Merill 1948; Oyarzun, Higueras, Esbrí, Pizarro 2007; Pfister 2008; Popławska 2018; Purewal 1999; Purewal 2001; Purewal, Colston, Röhrs 2008; Purewal 2012; Rader, Ison 1999; Robinson 1903; Sirois 2001; Tournefort 1694; Townsend 1999; Webber, Ernest, Vangapandu 2011	Crystalline powder used in solutions, added to adhesives	Yes	Insufficient data

Tab. 1. List of biocides used in herbarium collections (cd.)

Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
Arsenic (diarsenic trioxide), CAS: 1327-53-3, lead Arsenate, CAS: 7784-40-9 and other arsenic compounds	Dauwalder 2012; Drobnik 2009; Grenda-Kurmanow 2016; Grenda-Kurmanow 2017; Merill 1948; Pfister 2008; Popławska 2018; Purewal 1999; Purewal 2001; Purewal 2012; Purewal, Colston, Röhrs 2008; Robinson 1903; Sirois 2001; Townsend 1999	White powder / dust, added to adhesives	Yes	Yes
Hydrogen cyanide, CAS: 74-90-8	Drobnik 2009; Grenda-Kurmanow 2016; Merill 1948; Purewal 2001; Purewal 2012	Gas; fumigation	-	Insufficient data
Phosphine, CAS: 7803-51-2	Drobnik 2009; Grenda-Kurmanow 2016; Hall 1988; Purewal 1999; Purewal 2001; Purewal 2012	Solid crystals, yellow to grey colour; fumigation	-	Probably not
Sodium fluorosilicate, CAS: 16893-85-9	Bridson, Forman 1999; Purewal 2012	Colourless; added to adhesives applied to wooden furniture	Possible	No data

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Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
Barium fluorosilicate, CAS: 17125-80-3	Bridson, Forman 1999; Grenda-Kurmanow 2016; Hall 1988; Purewal 1999; Purewal 2001; Purewal 2012; Purewal, Colston, Röhrs 2008	Colourless; added to the adhesive applied to wooden furniture	-	No data
Sulphuryl fluoride, CAS: 2699-79-8	Whitten, Williams, Glover 1999; Purewal 2012	Gas; fumigation	Possible	No data
Sulphuryl chloride, CAS: 7791-25-5	Drobnik 2009	Colourless liquid; fumigation	-	No data
Silica gel CAS: 112926-00-8	Dawson, Strang 1992; Hall 1988; Bridson, Forman 1999, s. 21; Hall 1988; Schofield, Crisafulli 1980	Powder, aerosol	-	No data
Organic compounds				
Aromatic hydrocarbons				
Naphthalene CAS: 91-20-3	Bridson, Forman 1999; Croat 1978; Dauwalder 2012; Dawson, Strang 1992; Drobnik 2009; Fenn 1999; Grenda-Kurmanow 2016; Hall 1988; Merill 1948; Purewal 1999; Pfister 2008; Purewal 2001; Purewal 2012; Purewal, Colston, Röhrs 2008; Strang 1999; Robinson 1903	Solid, white colour; passive fumigation	No	Possible

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Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
		Organochlorides		
DDT (dichlorodiphenyltrichloroethane) CAS: 50-29-3	Bridson, Forman 1999; Dauwalder 2012; Grenda-Kurmanow 2016; Merill 1948; Pfister 2008; Popławska 2018; Purewal 1999; Purewal 2001; Purewal 2012	White powder; dusting, spraying	-	Possible
Lindane (gamma-hexachlorocyclohexane), CAS: 58-89-9	Dauwalder 2012; Drobnik 2009; Hall 1988; Lellinger 1972; Pfister 2008; Purewal 1999; Purewal 2001; Purewal 2012	Crystalline; fumigation, dusting	Possible	Highly probable
LPCP / PCPL – Lauryl pentachlorophenate, CAS: 3772-94-9	Bridson, Forman 1999; Clarck 1986; Drobnik 2009; Grenda-Kurmanow 2016; Hall 1988; Purewal 2001; Purewal 2012; Whitmore, Fosberg 1965	Liquid applied on specimens, soaking, spraying, fumigation	-	Possible
Pentachlorophenol (PCP), CAS: 87-86-5	Coradin, Giannasi 1980; Dauwalder 2012; Purewal 2012	Solid, colourless crystals; dusting, soaking, spraying	Possible	Possible
Sodium pentachlorophenate CAS: 131-52-2	Bridson, Forman 1999		Possible	Possible

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Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
Carbon tetrachloride, CAS: 56-23-5	Croat 1978; Drobnik 2009; Grenda-Kurmanow 2016; Purewal 1999; Purewal 2001; Purewal 2012	Colourless liquid; fumigation, spraying	Possible	Possible
Paradichlorobenzene (1,4-dichlorobenzene), CAS: 106-46-7	Bridson, Forman 1999; Croat 1978; Dauwalder 2012; Drobnik 2009; Fenn 1999; Grenda-Kurmanow 2016; Hall 1988; Merill 1948; Pfister 2008; Purewal 1999; Purewal 2001; Purewal 2012; Purewal 2012; Purewal, Colston, Röhrs 2008; Schofield, Crisafulli 1980	White crystals; passive fumigation	Possible	Possible
Para-chloro-meta-cresol (4-chloro-3-methylophenol, PCMC), CAS: 59-50-7	Grenda-Kurmanow 2016	Fumigation	-	Possible
Ethylene dichloride (EDC, 1,2 dichloroethane) mixed in 3:1 ratio with carbon tetrachloride CAS: 107-06-2	Croat 1978; Drobnik 2009; Grenda-Kurmanow 2016; Purewal 2012	Gas; fumigation, passive fumigation	Possible	Highly probable

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Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
Aldrin, CAS: 309-00-2	Dauwalder 2012	White solid; dusting	-	Possible
Dieldrin, CAS: 60-57-1	Dauwalder 2012	White solid; dusting, spraying	-	Possible
Endrin, CAS: 72-20-8	Dauwalder 2012	White crystals; dusting, spraying	-	Insufficient data
Chlordane, CAS: 57-74-9	Croat 1978	Powder; passive fumigation	-	Possible
Organophosphates				
Dichlorvos (DDVP, 2,2-dichlorovinyl-dimethylphosphate), CAS: 62-73-7	Bridson, Forman 1999; Croat 1978; Dauwalder 2012; Drobnik 2009; Fenn 1999; Grenda-Kurmanow 2016; Hal 1988; Lellinger 1972; Pfister 2008; Purewal 1999; Purewal 2001; Schofield, Crisafulli 1980	Liquid; dusting, spraying, passive fumigation	Yes	Possible
Malathion, CAS: 121-75-5	Croat 1978	Spraying	-	Probable
Chlorpyrifos, CAS: 2921-88-2	Hall 1988	Powder, emulsifiable Concentrate or spray; spraying	-	

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Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
Phenols				
Phenol, CAS: 108-95-2	Clarck 1986; Dauwalder 2012; Grenda-Kurmanow 2016; Hawks, Bell 1999; Pfister 2008; Purewal 2001; Purewal 2012	Fumigation	-	Insufficient data
Thymol (2-isopropyl-5-methylphenol), CAS: 89-83-8	Bridson, Forman 1999; Dauwalder 2012; Drobnik 2009; Fenn 1999; Grenda-Kurmanow 2016; Grenda-Kurmanow 2017; Hall 1988; Pfister 2008; Purewal 1999; Purewal 2012	Fumigation	-	No
Creosote, CAS: 8021-39-4	Drobnik 2009; Grenda-Kurmanow 2016; Pfister 2008	Fumigation	-	Highly probable
Pyrethrins and pyrethroids				
Pyrethrins and pyrethroids, representative CAS IDs: CAS: 121-21-1 (pyrethrin I), CAS: 121-29-9 (pyrethrin II), CAS: 52645-53-1 (permethrin)	Bridson, Forman 1999; Croat 1978; Dauwalder 2012; Hall 1988; Pfister 2008; Purewal 1999; Purewal 2001; Purewal 2012; Schofield, Crisafulli 1980	Liquid, powder; spray, granules, dusting	-	Possible in case of some pyrethroids

Tab. 1. List of biocides used in herbarium collections (cd.)

Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
		Others		
Carbon disulphide, CAS: 75-15-0	Croat 1978; Dauwalder 2012; Drobnik 2009; Grenda-Kurmanow 2016; Pfister 2008; Purewal 1999; Purewal 2001; Purewal 2012; Robinson 1903	Liquid, from colourless to yellow; fumigation	-	Insufficient data
Ethylene oxide, CAS: 75-21-8	Croat 1978; Drobnik 2009; Hall 1988; Popławska 2018; Purewal 1999; Purewal 2001; Purewal 2012	Fumigation	Yes	Yes
Propylene oxide, CAS: 75-56-9	Drobnik 2009	Fumigation	Yes	Not excluded
Methyl bromideorganobromine, CAS: 74-83-9	Coradin, Giannasi 1980; Croat 1978; Drobnik 2009; Grenda-Kurmanow 2016; Grenda-Kurmanow 2017; Hall 1988; Purewal 1999; Purewal 2001; Purewal 2012	Fumigation	Yes	Insufficient data
Methyl iodide CAS: 74-88-4	Drobnik 2009; Kosuge, Akiyama, Tauguchi 2005	Fumigation	Yes	Possible
Formaldehyde, formalin, CAS: 50-00-0, paraformaldehyde, CAS: 30525-89-4	Coradin, Giannasi 1980; Dauwalder 2012; Drobnik 2009; Grenda-Kurmanow 2016; Pfister 2008; Robinson 1903	Colourless gas (formaldehyde); powder, crystals (paraformaldehyde); fumigation	Yes	Yes

Tab. 1. List of biocides used in herbarium collections (cd.)

Name, CAS ID number	Literature referring to the use in herbaria	Formulation / mode of action	Negative impact on DNA of natural history artefacts	Genotoxicity, mutagenic, carcinogenic (source: EPA and IARC)
Carbamates andthiocarbamates CAS: 63-25-2 (carbaryl), CAS: 34681-10-2 (Butocarboxim)	Dauwalder 2012; Pfister 2008; Grenda-Kurmanow 2017 (Butocarboxim)	Crystal; liquid; spraying	-	Possible
Alcohol CAS: 64-17-5 (ethanol)	Bedford 1999; Bridson, Forman 1999; Coradin, Giannasi 1980; Purewal 2001	Liquid; soaking	Ambiguous results	
Petrol CAS: 8006-61-9	Hall 1988	Liquid; soaking	Possible	
Pyridine CAS: 110-86-1	Drobnik 2009; Grenda-Kurmanow 2016	Fumigation	-	Possible
Quaternary ammonium cations, CAS: 7281-04-1	Dauwalder 2012; Pfister 2008	Liquid; spraying	-	
Thiosemicarbazide CAS: 79-19-6	Grenda-Kurmanow 2017	White or yellow powder	Possible	Possible
Caratane / Dinocap (dinitrophenol derivative) CAS: 39300-45-3	Grenda-Kurmanow 2017	Liquid; spraying	-	Possible

Characteristics of selected biocides used in herbaria

The following review is based on a number of cross-sectional studies on pesticides[21] and selected other publications, which describe from one to several selected biocides.[22] The basic names of biocidal products are accompanied by summary formulae as well as variations of chemical names and trade names to facilitate the recognition of compounds by users of this summary.[23] The toxicity of the biocides is signalled in general terms.[24]

Inorganic compounds

Mercury chloride, (I) Hg_2Cl_2 and (II) $HgCl_2$ (sublimate)

An inorganic chemical compound, occurring in the form of calomel, where mercury is at degree I oxidation (Hg_2Cl_2), and the more common so-called sublimate, where mercury is at degree II oxidation ($HgCl_2$). The first evidence of the use of both forms of mercury chloride can be found as early as 1794.[25] Calomel under the influence of UV radiation may decompose into pure mercury and mercury (II) chloride, i.e. the sublimate. The sublimate is volatile at room temperature and has been used in solutions in spirit, in various proportions, sometimes with the addition of phenol, or mixed with arsenic or lauryl

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[21] Purewal 2012; Dawson, Strang 1992; Hall 1988; Drobnik 2009; Sadongei, Odegaard 2005; and Pfister 2008 – these publications will not be cited in each case when describing the individual substances. Information on the harmfulness of the compounds, as in the table, was obtained from the EPA and IARC databases (see footnote 19), which are also not always quoted.

[22] These publications are given in footnotes.

[23] The formulas were abandoned when describing whole groups of compounds (e.g. pyrethrins and pyrethroids) to maintain legibility.

[24] Biocides show different levels of toxicity to human health. Side effects need to be discussed separately for each of these biocides.

[25] Tournefort 1694, p. 547–548.

pentachlorophenate (LPCP).[26] Whole botanical specimens were immersed in the solution or it was applied on them with a brush. After removal from the solution, the specimens were sometimes fragile. Mercury chloride may leave a white layer in the form of hairy crystals, which may have been confused with the taxonomic characteristics of the specimen. To avoid recrystallisation, kerosene was added to the alcoholic solution of the sublimate.

Mercury chloride at second degree oxidation slowly sublimates from the area where it is applied, and therefore, treatment was generally repeated several times. This was also because it was long claimed that after some time, mercury chloride lost its biocidal properties. However, the opposite is true, because mercury chloride settles permanently in the structure of objects.

The mercury present in mercury chloride reacts with sulphur, present both as an air pollutant and a component of paper substrates and animal adhesives. It forms black mercury sulphide (metacinnabar, HgS) and leaves a trace on the paper in the form of concentrated or merged black-edged spots. Over the years, it is reduced to pure mercury, showing a tendency to disproportionation, i.e. self-oxidation and self-reduction. The reduction of mercury accelerates the acid hydrolysis of cellulose.[27] Mercury chloride therefore has a destructive effect on both plant tissues and paper substrate, causing brittleness and structural changes.[28] In specimens, it can cause the breakdown of the cuticle (layer saturated with lipid substances, protecting the plant from water loss).[29] Since it was most often used in alcoholic solutions, repeated application of the solution to specimens and sheets additionally caused rinsing of chlorophyll. Mercury chloride also has a corrosive effect on aluminium. In institutions with a long

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[26] Briggs, Sell, Block, I'ons 1983. Purewal quotes older, historical recipes in which the sublimate is also mixed with alcohol and phenol or its derivative – cresol (Purewal 2012, p. 20).

[27] Collins et al. 2014. The authors state that mercury reduction can be catalysed by the presence of naphthalene vapour, once a popular pesticide and repellent.

[28] Clarck 1986.

[29] Collins et al. 2014.

tradition of using mercury chloride, mercury vapour in the air can be expected, especially in storage cabinets and their immediate surroundings, because pure mercury is highly volatile. Back in the 1980s, mercury chloride was used in the Netherlands and at the Royal Botanic Gardens in Kew (according to a recipe called the *Kew mixture*). In 1988, mercuric chloride continued to be used in African herbarium collections; until the end of the 20th century, it was also used in France. It is a strong neurotoxin.

Arsenic (diarsenic trioxide), As_2O_3, As_4O_6; lead arsenate, $PbHAsO_4$; other arsenic compounds

Arsenic has been known since ancient times and has been used in museum collections since the beginning of the 18th century. In the past, arsenic-based substances were often used as insecticides, herbicides and rodenticides. In natural history collections, they were mainly used on taxidermy objects in the form of arsenic and sodium arsenate. Herbarium collections were dusted with arsenic, lead arsenate ($PbHAsO_4$)[30] or potassium arsenate (*sel de Macquer*, KH_2AsO_4).[31]Arsenic was also used in solution with mercury chloride and phenols. Arsenic settles permanently in the structure of objects and is sometimes visible as a white deposit. It is highly toxic not only as a substance consumed, but also inhaled or absorbed through the skin. It is also a carcinogen. Withdrawn from the 1960s onward, it was used in some institutions until the 1990s.

Hydrogen cyanide, HCN

Other names: Prussian acid, Zyklon B

Hydrogen cyanide has been used as a biocide since the 19th century. It was included in Zyklon B according to a patent in force since 1922. It was later used by

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[30] Purewal states that present lead in herbaria may also come from another pesticide, lead acetate [$Pb(CH_3COO)_2$], suggesting that lead arsenate was commonly used in herbaria (Purewal 2012, p. 20).

[31] Péquignot 2006.

the Nazis in extermination camps during World War II. In the post-war period, it was used in disinfection chambers and to fumigate entire rooms. Hydrogen cyanide is well absorbed by porous structures such as paper and is desorbed over a long period, posing a constant threat to human health. In reaction with water molecules, it forms formic acid and ammonia and is therefore particularly harmful under conditions of increased humidity, causing damage to certain pigments (containing copper) and plant dyes, yellowing of paper, brittleness of animal adhesives and corrosion of base metals.[32]

Phosphine, PH_3

Other names: Phostoxin; Celphos; DeliciaGastoxin

Phosphine is a pesticide intended for use in agriculture, but has also been used in herbarium collections. Only a few years ago, it was still being used in Poland as a disinfectant in the collection of herbaria.[33] It is effective in combating insect eggs[34] and occurs in the form of powder compounds of aluminium phosphide and magnesium phosphide. With moisture from the air, these substances release hydrogen phosphate gas, a strong reducing agent. As a product, it also occurs in combination with ammonium carbamate, which decomposes to ammonia and carbon dioxide. It is extremely flammable and highly toxic. Hydrogen phosphate itself oxidises in the presence of water, forming phosphoric acids. Under conditions of elevated temperature and humidity, it can cause corrosion of copper and its alloys, as well as of silver, gold, aluminium, nickel and sulphur compounds. Therefore, it has a destructive effect on pigments such as ultramarine or copper greens, and gilding fades in reaction with phosphoric acid. Exposure to hydrogen phosphide causes many health effects, but no carcinogenic effect has been found.

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[32] Unger, Schniewind, Unger 2001, p. 279–280, 315; Hahn 1999.

[33] Information from an unpublished nationwide survey of the methods of protecting herbarium collections, conducted by the author in 2013.

[34] Unger, Schniewind, Unger 2001, p. 280.

Barium fluorosilicate, $BaSiF_6$, sodium fluorosilicate, Na_2SiF_6

Barium fluorosilicate was patented as a pesticide in 1827. Barium and sodium fluorosilicates were used interchangeably, mainly as an agent against silverfish. Barium fluorosilicate was more effective, but both agents were used as bait in a paste consisting of sugar, flour and Arabic gum in water. The paste was applied to wooden collection storage furniture. Sodium salt can damage the seeds of herbarium specimens.[35]

Sulphuryl fluoride, SO_2F_2, sulphuryl chloride, SO_2Cl_2

Other names: Vikane; sulphuricoxyfluoride

Used as an alternative to fumigation with methyl bromide and phosphine. Fumigation with sulphuryl fluoride causes yellowing and acidification of papers, especially those containing lignin.[36] According to Whitten, sulphuryl fluoride does not destroy the genetic material in herbarium specimens,[37] but Kigawa identified changes in the protein structure by examining specifically proteinaceous samples (from chicken muscles).[38]

Regarding the destructive effect on other museum objects, destruction of wallpapers and bronze handles was observed during fumigation because of gas condensation. In paintings, non-varnished paint layers containing the pigments azurite, malachite and cobalt and Prussian blue in linseed oil medium and protein binders were also destroyed. Changes in textile dyes, layers of polyvinyl acetate and epoxy resins have also been observed.[39] Sulphuryl chloride shows similar effects on sulphuryl fluoride and was used in a similar way.

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[35] Hall 1988.

[36] Burgess, Binnie 1990a and 1990b.

[37] Whitten, Williams, Glover 1999.

[38] Kigawa, Strang 2011.

[39] Unger, Schniewind, Unger 2001, p. 316.

Silica gel, SiO_2

Silica gel is the most popular desiccant and commonly used in the museum environment. It occurs in the form of a fine powder and is often mixed with pyrethrins and pyrethroids, acting as repellents. In this mixture, it is also available as an aerosol.[40] The use of an aerosol spray provides protection in areas that are more difficult to access (shelf joints, rear walls of shelves) and reduces silica gel deposits. Contact with finely ground silica gel can lead to dryness and irritation of the skin and irritation of the respiratory system. Although spraying is not carried out directly on specimens, excess silica powder residue can enter the object and cause micro-damage, acting as an abrasive layer. The agent is used against many species of insects, including the varied carpet beetle (*Anthrenus verbasci* L.), the silverfish (*Lepisma saccharina* L.) and psocids (book lice, belonging to the order *Psocoptera*). The effect of silica powder is to destroy the outer layer of the insects' cuticle, leading to fatal dehydration.

Organic compounds

Aromatic hydrocarbons

Naphthalene, $C_{10}H_8$

Naphthalene was first synthesised in 1821 and has been used in collections since 1887. It is a polycyclic aromatic hydrocarbon and occurs in the form of white powder or balls, used in storage cabinets and inserted into packaging as a passive fumigant. It can be confused with paradichlorobenzene, which occurs in a similar form and is used in a similar manner. Under storage conditions, an insect repellent smell is slowly released from the naphthalene balls. It can

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[40] The so-called aerogel with pyrethrins and pyrethroids in a concentration of 1%, silica gel occurs in a concentration of about 40%; trade names: Drione, Driaone, Dri-die and Silikil (Dawson, Strang 1992; Hall 1988 Bridson, Forman 1999, p. 21; Hall 1988; Schofield, Crisafulli 1980), currently also Evergreen Pyretrum Dust, CimeXa, Tri-Die Silica & Pyrethrum Dust.

recrystallise on the surface of specimens and can be confused with taxonomic features. Naphthalene deeply penetrates the structure of paper and is therefore difficult to remove from objects. Contact with naphthalene can cause many adverse effects on human health. Despite suspicions, neither carcinogenic nor mutagenic properties have been confirmed. In 2008, the use of naphthalene was banned in the European Union.

Organophosphates

Dichlorvos, dichlorovinyl-dimethylphosphate,$Cl_2C{=}CH(CH_3)_2PO_4$

Other names: DDVP, Dichlorfos, Vapona

Dichlorvos occurs in the form of emulsions, aerosols, pesticide impregnated strips and oil concentrate. It is soluble in many organic solvents, also chlorinated, and in alcohols and was placed on the market as an insecticide in the 1960s. Dichlorvos is used for dusting, spraying or as a passive fumigant. As a product used in museum collections, it can leave a film on object surfaces and can cause colour changes in the dyes, especially red, and in the paper itself. Under conditions of increased humidity, it has an acidic reaction and causes corrosion of silver, tin, lead and soft steel. It is a highly toxic substance, and working in the vicinity of a dichlorvos source (e.g. a toxin-releasing dispenser) causes numerous adverse health effects.

Malathion, $C_9H_{19}O_6PS_2$

Other names: Carbofos, Maldison, Mercaptothion

Pesticide from the group of organophosphates, used in agriculture, horticulture and healthcare, are mainly applied to control mosquitoes and lice. Malathion occurs in the form of a liquid, dust, emulsion and powder to form a paste and has been introduced in the 1950s. It is a compound from the group of phosphoric acid esters and succinic acid derivatives.

Chlorpyrifos, $C_9H_{11}Cl_3NO_3PS$

Other names: Dursban; Lorsban; Dowco, Chlorpyriphos-ethyl; Brodan, Bolton, Detmol, Eradex, Empire, Hatchet, Nufos, Piridane, Scout, Stipend, Tricel, Warhawk

Chlorpyrifos was introduced as a pesticide in 1965 and occurs as a liquid for spraying. It has a corrosive effect on copper and bronze and causes colour changes in red dyes. It is strongly toxic, and exposure to this agent causes a number of adverse health effects, especially in children. Withdrawn from 2014, it is still detected in fruit plants.

Organochlorides

Organochlorine compounds were introduced to the market in the mid-20th century.

DDT[41], dichlorodiphenyltrichloroethane $(C_6H_4Cl)_2CHCCl_3$

Other names: Chlorophenothane, Dicophane

Its use in the treatment of malaria and typhus during the Second World War and its popularity in agriculture after the war made DDT generally available and widely used.[42] It was used in collections from the 1940s, at least until the 1970s, when it was banned in the USA due to significant environmental contamination.[43] It was used for direct dusting of objects as well as in solution, for spraying, sometimes mixed with Lindane or mineral oils. It can have

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[41] Information on DDT, apart from the sources mentioned in the introduction, was obtained from Szulczynska's study (Szulczynska 2000).

[42] Dunlap 1981, p. 3–10. As mentioned in the introduction, the Nobel Prize in Medicine was awarded to Paul Hermann Müller in 1948 for demonstrating the efficacy of DDT as a pesticide and its ability to be used against malaria and yellow fever.

[43] As mentioned in the introduction, the persistence and non-removability of this substance can be demonstrated by the fact that traces of DDT have been identified even in the Arctic (information given on the website of the Stockholm Convention (http://www.pops.int/), see also numerous press reports, e.g. Doyle 2018).

a destructive effect on botanical specimens.[44] The DDT decomposition products, mainly DDE, dichloro-diphenyl-dichloroethylene, are also harmful to human health. Until 2008, it was produced in China and is currently still produced in India.[45] Almost phased out because of the Stockholm Convention, it is classified as a group B toxic compound. In certain regions of the world, it is approved for the treatment of malaria.

Lindane, gamma-hexachlorocyclohexsane, $C_6H_6Cl_6$

Other names: Gamma-BHC, Gamma-HCH, Gammexane, Forlin, Gamophex

Lindane was first synthesised in 1825, and its insecticidal properties were discovered in 1942. It is soluble in many organic solvents. During fumigation, the gas decomposes to phosgene ($COCl_2$) and hydrochloric acid (HCl), which is a powerful catalyst for acid hydrolysis of cellulose. It is therefore particularly unsuitable for use in cellulose-based artefacts, such as paper substrates or herbarium specimens. Lindane is a neurotoxin with an ambiguous effect on genetic material. It is classified in Group A of the Stockholm Convention.

LPCP, lauryl pentachlorophenate $C_{18}H_{23}Cl_5O_2$

Other name: Mystox

It was first used in 1962 in the Natural History Museum in London;[46] used for fumigation as well as for individual use, preventive soaking, lubrication and spraying incoming specimens. It was used at a concentration of 5%, in solution with paraffin or mineral turpentine. When using the solution, it was recommended to carry out resistance tests of the handwritten elements beforehand. Coated papers as well as herbarium grass and fern specimens had to be removed from the collection. Application of LPCP onto the specimens was usually performed more than once. The LPCP solution left stains on the paper, which were

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[44] Bridson, Forman 1999, p. 22.

[45] Berg, Manuweera, Konradsen 2017.

[46] Bridson, Forman 1999, p. 21.

supposed to fade after several years. A substance used in herbarium collections in both temperate and tropical zones. Withdrawn in 1984.

Pentachlorophenol (PCP), C_6Cl_5OH, sodium pentachlorophenate, C_6Cl_6ONa

Other names: Santophen, Pentachlorol, Chlorophen, Chlon, Dowicide 7, Pentacon, Penwar, Sinituho

First synthesised in the 1930s, it was used mainly as liquid for soaking and spraying specimens. Pentachlorophenol, its salts and esters were placed on List A of the Stockholm Convention in 2015.

Carbon tetrachloride, CCl_4

Other names: Tetrachlorometan, Benziform, Benzinoform, Carbon chloride, Carbon tet, Freon-10, Refrigerant-10, Halon-104, Methane tetrachloride, Methyl tetrachloride, Perchloromethane, Tetraform, Tetrasol

Colourless liquid with a sweet smell and formerly used as a solvent, extinguishing and cooling agent. First synthesised in 1839, it was used on a mass scale between 1950 and 1980. In the 1980s, it was withdrawn from general use due to its toxicity to humans and its depleting effect on the ozone layer.

Paradichlorobenzene, $C_6H_4Cl_2$

Other names: P-dichlorobenzene; 1,4-dichlorobenzene, p-DCB; 1 ,4-DCB; PDB; PDCB

Paradichlorobenzene has been used in museum collections since 1913 for passive fumigation and as repellent, fungicide and rodenticide. Generally, it is used in a similar way to naphthalene, inside cupboards, but also as a solution. It is more volatile than naphthalene and five times heavier than air and should therefore be placed on top shelves, never in direct contact with specimens. Paradichlorobenzene is a toxic substance that causes numerous adverse health effects upon exposure.

It reacts with some pigments and dyes by changing their colour: zinc white, lithopone, scarlet pigments, ultramarine, acetyl cellulose-based dyes. It also causes yellowing of paper, fading of inks and increased shrinkage of some resins and plastics. By dissociating, it can have a whitening effect on specimens and archival documents, even when they are tightly packed. It is highly volatile, making it difficult to maintain an even concentration in storage cabinets. When paradichlorobenzene vapour leaks from the storage area, clouds of vapour in the air form next to the sources of the leak, posing a health risk. In some institutions, it is still being used.

Para-chloro-meta-cresol, C_7H_7ClO

Other names: 4-chloro-3-methylphenol, p-chlorocresol, PCMC, rachit, Preventol CMK

Para-chloro-meta-cresol is a chlorinated phenol used for passive fumigation and by tamponing with 0.3% solution, either directly or by soaking the interleaves with 10% PCMC solution in 70% ethanol.[47]

Ethylene dichloride, C_2H_4Cl

Other names: 1,2 dichloroethane, EDC

Ethylene dichloride is a chlorinated hydrocarbon. It was used in a 7:3 ratio in mixture with carbon tetrachloride for fumigation[48] and was deregistered from use in 1984.

Aldrin, $C_{12}H_8Cl_6$

Other names: HHDN, Octalene

Dieldrin, $C_{12}H_8Cl_6O$

Other names: HEOD, Octalox

Endrin, $C_{12}H_8Cl_6O$

Other names: Mendrin, Endrex

Aldrin, dieldrin and endrin are compounds invented in the mid-20th century. They were used more or less until the 1990s, being gradually banned since the 1970s in various countries. They are among the most persistent pesticides, are highly toxic and are potential carcinogens. Dieldrin is an effective pesticide,

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[47] Sobucki 2013, p. 128–129; Zerek B. F. 2017.

[48] Dawson, Strang 1992; Drobnik 2009, p. 166.

while aldrin is oxidised inside the insects to dieldrin. Endrin is a dieldrin stereoisomer. They are all classified as Group A in the Stockholm Convention.

Chlordane, $C_{10}H_6Cl_8$

Other names: Heptachlor, Octachlor, Chlorindan, Kypchlor, Toxichlor, Belt, Ortho-Klor, ChlorKil, Chlorotox, Dowchlor, Oktaterr, Starchlor, Topiclor, Sydane, Termex, Intox

Chlordane is a compound from the group of dienes, such as aldrin, endrin and dieldrin. It is a mixture of isomers of chlorinated hydrocarbons and decomposes to phosgene, chlorides, hydrochloric acid and carbon monoxide. It is a highly persistent compound, classified under Group A of the Stockholm Convention.

Phenols

Phenol, C_6H_5OH, thymol, $C_{10}H_{13}OH$, creosote $C_7H_8O_2$

The antiseptic properties of phenol have been known since the 19th century. Phenol and creosote were added to a solution of mercury chloride in alcohol, sometimes in combination with arsenic. They were also placed in liquid form in cupboards as passive fumigants.[49] Thymol, previously obtained from natural resources, was first synthesised in the 19th century and used as a fungicide for application as a solution or passive fumigation. A solution of 1% thymol in ethanol was sprayed or applied on specimens affected by microbiological infection. Fumigation takes place at elevated temperatures by heating thymol in the solid form. Thymol dissolves some inks and adhesives and may leave stains on paper.[50] As a toxic substance, it can cause adverse health effects upon direct contact and ingestion.

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[49] Drobnik 2009, p. 166.

[50] Thymol was detected in a herbarium from the first half of the 18th century. The analysis was carried out using gas chromatography with solid-phase microextraction (GC/MS-SPME), conducted by Dr. Tomasz Sawoszczuk (Cracow University of Economics) as part of a research project funded by the National Science Centre, No. 2014/13/N/HS2/03118 “Heritage preservation

Pyrethrins and pyrethroids

Pyrethrins are substances of natural origin and are extracted from the Dalmatian pellitory (*Tanacetumcinerariifolium* (Trevir.) Sch. Bip., once called *Chrysanthemum cinerariifolium* (Trevir.) Sch. Bip.). The group of pyrethrins includes six natural compounds, which are components of the raw extract of the Dalmatian pellitory flower. Their insecticidal properties have been known since the 19th century. Pyrethrins are prone to biodegradation under the influence of oxygen and ultraviolet radiation.

Since the 1970s, pesticides based on pyrethroids have been available – a synthetic version of pyrethrins, including permethrin ($C_{21}H_{20}Cl_2O_3$), cypermethrin ($C_{22}H_{19}Cl_2NO_3$) and deltamethrin ($C_{22}H_{19}Br_2NO_3$). Pyrethroids are chemically more stable than pyrethrins but are also easily biodegradable.

Pyrethrins and pyrethroids are contact insecticides and used in the form of microcapsules, powders, oil solutions, in liquid form, sprayed and, in the case of herbaria, mixed with silica gel. They are also combined in piperonyl butoxide to increase their durability and effectiveness. They are widely used to this day, both for prevention and intervention.

Other organic compounds

Carbon disulphide, CS_2

Carbon disulphide has been used in collections since 1887, mainly in disinfection chambers, but also as a fumigant for specific rooms; it is suspected of destructive effect against varnishes.[51] It is highly toxic and was de-registered in some countries in 1984. According to Pfister, some institutions still use it.[52]

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and ethnobotany. Analysis of the influence of conservation treatment on genetic material of historic herbaria".

[51] Unger, Schniewind, Unger 2001, p. 296.

[52] Pfister 2008, p. 28.

Ethylene oxide, C_2H_4O

Other names: 1, 2-epoxyethane, oxirane, Rotanox, Carboxide, ETO

Used for fumigation in specific fumigation chambers, usually in libraries, against microorganisms and insects. However, it was also used as a fumigant for storage rooms. Ethylene oxide was used in a mixture with carbon dioxide (CO_2), methyl bromide (CH_3Br), freons and phosphine (PH_3).[53] If a vacuum can be maintained in the chamber, ethylene oxide also kills insect eggs. Ethylene oxide is accumulated by objects made of leather, rubber, vinyl and fats and is gradually released.[54] It cross-links free hydroxyl groups in materials such as wood and paper, causing a reduction in hygroscopicity.[55] It may have a negative effect on some pigments (lead-tin yellow) and plant dyes, as well as on chicken egg casein.[56] It oxidises copper and its alloys (for example bronze). It also reacts with proteins present in leather and parchment, destroying their structure – they become stiff, brittle and less resistant to biological damage. Reaction with textiles that were previously disinfected with sodium pentachlorophenate has been observed. Polyvinyl chlorides strongly absorb ethylene oxide while losing their tensile strength.[57] Ethylene oxide is a mutagen and a carcinogen.

Propylene oxide, C_3H_6O

Other names: 1,2 epoxypropane, 2-methyloxirane, PPO

Propylene oxide is weaker than ethylene oxide and not as effective. It has been mixed with methyl bromide (CH_3Br) and used as a fumigant.[58]

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[53] Unger, Schniewind, Unger 2001, p. 306.

[54] Hall states that for some objects, the desorption time is up to 2–3 months (Hall 1988). Compare also Hengemihle, Weberg, Shahani 1995.

[55] Unger, Schniewind, Unger 2001, p. 316.

[56] Hall 1988, Hahn 1999.

[57] Unger, Schniewind, Unger 2001, p. 316–317.

[58] Drobnik 2009, p. 166.

Methyl bromide, CH_3Br

Other names: bromomethane, organobromine, Meth-O-Gas, Maltox

Its insecticidal properties were discovered in 1932.[59] In its pure state, it is odourless; it disperses quickly and penetrates walls and floors. It is more effective under conditions of increased humidity and temperature. In reaction with water, it forms aggressive bromine water, which acts corrosively. It is highly reactive and reacts via methylation and bromination of various substances. It should not be used for sulphur-containing materials, including herbarium specimens, leather, coated paper, photographic and parchment. As a result of the reaction with methyl bromide, the colour of these substrates will change, and they will emit a strong odour of thiols (thialcohols), which are acidic substances.[60] It has a corrosive effect on zinc, tin, iron and lead and is therefore destructive to pigments such as lead white, Neapolitan yellow, lead yellow and lead red, which blacken in reaction with methyl bromide.[61] It is a strong solvent for rubbers and other organic materials and may cause brittleness of animal glues and softening of natural resins and varnishes. It is often mixed with chloropicrin (CCl_3NO_2), which is phytotoxic. It is highly toxic and has carcinogenic effects. It was widely used for fumigation of herbarium collections, also for passive fumigation.[62] It was phased out in 2004 as an ozone-depleting agent.

Methyl iodide, CH_3I

Used as a substitute for methyl bromide, for room fumigation and passive fumigation and inside storage cabinets.[63]

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[59] Unger, Schniewind, Unger 2001, p. 301.

[60] See also Unger, Schniewind, Unger 2001, p. 316.

[61] Ibidem.

[62] Drobnik 2009, p. 166.

[63] Ibidem.

Carbamates and thiocarbamates

These substances are derivatives of carbamic acid, invented in the 1950s and used in institutions at least until the 1970s. Poorly soluble in water, more soluble in organic solvents, they are also used as fungicides. Examples of products in this group are Bendiocarb, Carbaryl and Propoxur, which are contact or stomach insecticides. They are available in the form of solutions, dusts, powders for making paste, granules and emulsions. They are highly toxic, and the presence of a pesticide from this group was detected in one of the herbaria from the first half of the 18th century.[64]

Formaldehyde (methanal), CH_2O; formalin, aqueous solution of formaldehyde

Formaldehyde and formalin were used for fumigation. Paraformaldehyde, a formaldehyde derivative, was used to perform fumigation in institutions, leaving a white deposit on objects, including those that were not directly exposed, but were in the vicinity of fumigated objects.[65] It reacts with free amine groups present in protein-binding media, causing hardening. It also hardens parchment and leather and accelerates the degradation of wool, fur and hair.[66] Formaldehyde was also used as a passive fumigant. It is a strong reducing agent.

Alcohol, mainly ethanol (C_2H_5OH), was often used as a solvent in solutions of mercury chloride, arsenic, thymol and PCMC, but also alone. Usually, the solution was applied to the specimens or they were soaked in alcohol. Alcohol can cause discolouration of the plants (especially chlorophyll) and make them brittle.

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[64] Analysis was carried out using gas chromatography with solid-phase microextraction (GC/MS-SPME), conducted by Dr. Tomasz Sawoszczuk (Cracow University of Economics) as part of a research project funded by the National Science Centre, No. 2014/13/N/HS2/03118 "Heritage preservation and ethnobotany. Analysis of the influence of conservation treatment on genetic material of historic herbaria".

[65] Unger, Schniewind, Unger 2001, p. 314.

[66] Ibidem, p. 317.

Petrol – was used to soak the specimens. It has a destructive effect on xanthophylls (dyes from the carotenoid group).

Pyridine, C_5H_5N

First synthesised in the second half of the 19th century, it was used for fumigation of collections, also passively.[67] It is a starting product for various pesticides, including chloropyrifos.

Quaternary ammonium cations

An example of a product belonging to this group is Sterinol (or Atoxin) (10% aqueous solution of dimethylolaurylbenzylammonium bromide).[68] The group consists of ionic agents working as surfactants, which were synthesised for the first time in 1890.[69] They increase the permeability of the cell membrane of botanical specimens, destroying their walls. In contact with the cell membrane, ammonium cations are adsorbed by a negatively charged cell wall, which allows the compound to penetrate the cytoplasm. They can irritate the skin and cause contact allergy.[70]

Thiosemicarbazide (rodenticide); **Caratane/Dinocap** (fungicide) – dinitrophenol derivatives – the presence of these pesticides was detected in a herbarium from the first half of the 18th century.[71]

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[67] Drobnik 2009, p. 166.

[68] Karbowska-Berent 2015.

[69] Lipińska-Ojrzanowska, Walusiak-Skorupa 2014.

[70] Ibidem.

[71] Analysis was carried out using gas chromatography with solid-phase microextraction (GC/MS-SPME), conducted by Dr. Tomasz Sawoszczuk (Cracow University of Economics) as part of a research project funded by the National Science Centre, No. 2014/13/N/HS2/03118 "Heritage preservation and ethnobotany. Analysis of the influence of conservation treatment on genetic material of historic herbaria".

Summary

The list of various biocides used in herbarium collections was generated as a part of the author's research for a doctoral thesis on the conservation of historic herbaria.[72] Herbaria are a narrow group of historic objects on a paper substrate, but the substances used to protect the botanical collections are also present in many other museum and archival collections. As shown in the characterisation of these substances, biocides have a harmful effect on the preservation of individual elements and layers occurring in historic artefacts. They also pose a health risk to users. An obstacle to a realistic assessment of the risks associated with the protection of collections and occupational safety is certainly scarcity or lack of documentation, which is a common problem in many institutions around the world.

This makes it even more important to know the potential risks that conservators encounter in their daily work, as well as the processes that affect the state of preservation of the collection items. In addition, many of the biocides mentioned above are encountered in everyday life. Toxic substances are unfortunately commonly used in agriculture, horticulture and various industrial sectors. Many of them have been phased out, but have not disappeared from the environment, often contributing to irreversible damage to the ecosystem and human health.

The issues related to biocides and the protection of historical artefacts include many aspects that need to be discussed in more detail, a task which is beyond the scope of the present article. These include, but are not limited to, methods of biocide identification in historic objects and methods of decontamination and will be the subjects of separate studies. In addition, the author feels that a toxicological compendium created for the use of Polish conservators is also needed so that they can consciously assess the risks associated with the nature of their work.

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[72] The title of the thesis is "Conservation and restoration of historic herbaria and preservation of genetic material of botanical specimens", initiated in 2016.

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