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Jean Tétreault

Canadian Conservation Institute, Department of Canadian Heritage, 1030 Innes Road, Ottawa, Ontario K1B 4S7, Canada;
jean.tetreault@canada.ca

Since the first pollutant limits for museums and archives emerged in the 1970s, various documents have proposed specifications to guide pollutant control for the protection of heritage collections. Three approaches to avoiding damaging pollutant levels are examined in this paper: specifications based on maximum allowable levels, on dosimeters and on testing products. The evolution of recommended maximum levels of gaseous pollutants is documented, showing that, over time, limits were progressively lowered but then more recently relaxed, and that lists expanded to include more key pollutants. Dosimeters have been developed as an alternate way to characterize pollutant levels, but their use in museums and archives remains limited. Tests that distinguish products that emit damaging pollutants from those that do not have been more widely adopted as a means of selecting appropriate products for use in collection spaces, especially enclosures. To date, evidence to support specifications has often been weak or may not reflect what actually occurs in the museum environment.

Depuis que les premières limites de polluants pour les musées et les archives sont apparues dans les années 1970, divers documents ont proposés des spécifications pour orienter le contrôle des polluants dans les institutions patrimoniales. Le présent document examine trois approches permettant d'éviter des niveaux de polluants nocifs : des spécifications basées sur les niveaux maximaux admissibles, sur des dosimètres et sur l'évaluation des produits. L'évolution des niveaux maximaux recommandés de polluants gazeux est documentée et montre qu'au fil du temps, les limites ont été progressivement abaissées, puis assouplies plus récemment, et que les listes ont été élargies pour inclure davantage de polluants clés. Les dosimètres ont été développés comme moyen alternatif pour caractériser les niveaux de polluants, mais leur utilisation dans les musées et les archives reste limitée. Les essais permettant de distinguer les produits émettant des polluants nocifs de ceux qui ne le sont pas ont largement été adoptés comme moyen de sélectionner de produits appropriés pour une utilisation muséale, en particulier les enceintes. Jusqu'à présent, les justifications des spécifications ont souvent été faibles ou peuvent ne pas refléter ce qui se passe réellement dans l'environnement du musée.

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INTRODUCTION

From the 19th to mid-20th centuries, large cities like London, England were polluted. A lot of soot and sulphur dioxide (SO_2) was produced by industrial activities, cooking and heating systems, and emitted from gas lights. In museums and archives, soot deposition was observed on paintings,[1] and embrittlement of papers[2] and leather book bindings[3,4] was noted. Severe degradation of lead and shells was also reported in enclosures containing products known to emit high levels of acetic acid, such display cases made of oak.[5-7] Knowledge about how materials are damaged by pollutants increased over the 20th century.[8,9]

By the mid-20th century, scientists were beginning to propose techniques for measuring pollutant levels in museums and for mitigating their effects on collections. The inclusion of gas filters or a water scrubber system for blocking the infiltration of outdoor pollutants into museums was considered for heating, ventilation and air conditioning (HVAC) systems,[8,10] and some quantitative methods based on wet chemistry were used to determine the concentration of SO_2, nitrogen dioxide (NO_2) and ammonia (NH_3).[11] Thomson of the National Gallery in London, who was an important figure in environmental guidelines for museums and art galleries, emphasized the need for both in his review on air pollution:[12] "Adequate control of air pollution is useless without adequate monitoring ... Monitoring need not be continuous, and can be manual or automatic, but in every case it should be regular …"[13] This statement was repeated in the second, 1971 edition of *The Conservation of Antiquities and Works of Art* written by Plenderleith, the first director general of the International Centre for the Study of Preservation and Restoration of Cultural Property (ICCROM) and Werner, Keeper of the British Museum.[14] In the 1960s, some guidelines already incorporated permissible ranges for relative humidity (RH) and temperature for general collections in museums and archives.[15,16] These climatic parameters were relatively easy and inexpensive to measure. Electronic pollutant monitoring devices developed for outdoor environments, such as pulsed fluorescent SO_2 analysers, facilitated the rapid collection of data on pollutant levels inside major museums in the 1970s;[11] however, their use remained limited due to their cost.

By the late 20th century, the measurement of pollutant levels combined with the analysis of degradation products was increasingly used to identify products that emitted harmful volatile compounds. In the mid-1980s, for example, the museum community became highly interested in formaldehyde, which was already known to affect human health, when it was reported that it had caused significant amounts of white efflorescence on lead objects stored in a plywood cabinet. The efflorescence was identified as lead formate. A level of 37 ppb (parts per billion)[17] of formaldehyde was found in the cabinet and it reportedly originated from the urea-formaldehyde resin in the plywood.[18,19] This generated a high interest on the measurement of carbonyl compounds (aldehydes and organic acids) in museums.[20]

Although some experts have suggested that there are no safe pollutant limits for collections preservation,[21-23] many heritage professionals want to know what they should do in terms of air filtration or choice of products to protect artifacts in their care. Over the past 40 years, this has led to the development of specifications or guidelines on the control of gaseous airborne pollutants for the care of collections in museums and archives. This paper reviews the evolution of these specifications with a particular interest in how they have been justified. Pollutant control specifications for museums can be divided into three categories: (i) specifications based on maximum levels of pollutants, (ii) specifications based on dosimeters, and (iii) specifications based on testing products.

SPECIFICATIONS BASED ON MAXIMUM LEVELS OF POLLUTANTS

Specifications based on pollutant limit levels are commonly used in standard documents for the safeguard of collections. Such specifications were first developed in the UK in the 1970s and in the USA in the 1980s, with an emphasis on the care of archival records. The same specifications were sometimes applied to general collections. Many heritage institutions around the world adopted the British and American specifications, which were adapted and updated over time. This section documents the evolution of such specifications as reflected in key published documents (**Table I**, **Appendix I**).

Thomson (1978)

Garry Thomson, scientific adviser to the Trustees and head of the Scientific Department at the National Gallery in London, was interested in comparing pollutant levels in the clean countryside to those in industrial areas. Based on observations that old papers and leather bindings stored in areas with low pollution levels were in better condition than those stored in polluted areas,[2,12,24] he recommended that SO_2 and NO_2 levels in collection spaces should be similar to those found in a clean environment (≤ 10 µg/m^3) for the preservation of mixed collections (**Table I**). The level recommended for ozone (O_3) was not more than 2 µg/m^3, which was about 10 times lower than that found outside in non-polluted air. Thomson justified this lower level due to the high capacity of O_3 to react with everything indoors, resulting in a small concentration remaining whether air-conditioned or not. The upper limits recommended for SO_2, NO_2 and O_3 were outlined in his book *The Museum Environment*, first published in 1978.[25] Thomson indicated that these levels were already attainable by using HVAC systems with air recirculation.[26] As an added benefit, these systems could also control the levels of other acidic gases and strong oxidants.

Thomson recognized that there was a push for environmental guidelines from the museum community without having yet the appropriate knowledge to justify them.[27] Thomson also listed other outdoor- and indoor-generated pollutants such as sea salt aerosol, hydrogen sulphide (H_2S), hydrogen chloride (HCl) and organic acids without proposing maximum levels. However, he did suggest use of simple corrosion tests, including the so-called Oddy test,[28] for products used in the vicinity of collections if harmful vapours were suspected.[29] In the second, 1986 edition of his book, recommendations for control of pollutants remained the same.[30]

Table I. Maximum pollutant levels recommended by published specifications in µg/m^3 (ppb).

	BS 5454 1977	Thomson 1978	NBS 1983	NRC 1986	BS 5454 1989–2000	NISO 1995	UNESCO 1998	NARA 2002	PAS198 2012*
Acetic acid			BCT‡					10 (4)	*250* (100)
Formaldehyde			BCT‡					5 (4)	*375* (300)
Formic acid									*958* (500)
Nitrogen dioxide		10 (*5.2*)	5 (*2.6*) §	BCT‡	10 (*5.2*) §	*19* (10)	1 (*0.5*)	5 (2.6)	*19* (10) §
Ozone		2 (*1*)	25 (*12.5*)	2 (1)		*20* (10)	2 (*1*)	4 (2)	*20* (10)
Reduced sulphides									(10)
Sulphur dioxide	50 (*18.7*)	10 (*3.7*)	1 (*0.4*)	1 (0.4)	10 (*3.7*)	*27* (10)	1 (*0.4*)	2.7 (1)	*2.7* (1)
Total suspended particles			75				75		
Hydrogen chloride			BCT‡						
Metallic fumes			BCT‡						

*based on lowest threshold from different materials

‡best control technology

§values reported are based on NO_X which include NO and NO_2; the unit conversion in italics is based on NO_2

italic number: unit converted by the present author

National Archives, USA (1983–1986)

“Priceless records allowed to rot,” claimed Jack Anderson, columnist at the *Washington Post*, in 1979.[31] In his article, Anderson drew attention to many examples of neglect such as risk of fire, lack of security, inadequate storage, and lack of proper strategies to limit chemical deterioration. Although perhaps an exaggeration, this warning nevertheless forced the National Archives to react quickly. A preservation advisory committee was formed in 1980 and made twelve recommendations in 1981, one of which was to develop recommended air quality criteria for archival storage and preservation.[32] The advisory committee also mentioned that the criteria would be implemented in Presidential Libraries.

National Bureau of Standards

In 1983, the National Bureau of Standards (NBS) hosted a two-day workshop on environmental conditions for archival records storage with 25 participants including conservators, scientists, staff from NBS, and members of the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE).[33,34] In the early 1980s, most research focused on the effect of SO_2 on archival products. The group admitted that little information was available on the effects of nitrogen oxides (NO_X) and O_3 on paper-based records, but they were assumed to be harmful. During that workshop, there was little discussion on quantitative dose-response relationships; instead, the talks focused on control technologies.[35] The May 1983 NBS report[33] mentioned that “participants agreed that the state of the art control of gaseous contaminants should be specified, but that economic analyses should be relied upon to help in establishing specifications for particulate control.”[36] In other words, the HVAC operating costs of maintaining pollutants at the recommended levels should be sustainable.

In their final specifications document,[34] the NBS committee recommended levels no higher than 1 µg/m^3 for SO_2, 5 µg/m^3 for NO_X, 25 µg/m^3 for O_3 and 75 µg/m^3 for total suspended particulate (fine particles) for archival storage (**Table I**).[37] At that time, it was expected that these levels could be measured by direct reading analyzers and controlled by an HVAC system. “Best control technology” was to be used to control acetic acid, formaldehyde, HCl and “metallic fumes.”[37] Moreover, building products and furnishings in storage areas were to be properly selected to avoid or minimize pollutant emissions. Access to storage areas was also to be restricted to optimize climate control, and no smoking was to be allowed. No justification was provided for the control of acetic acid, formaldehyde and HCl. Probable sources of acetic acid and formaldehyde were noted, but no damage resulting from the presence of these volatile compounds was mentioned in the report. Metallic fumes were probably included in the control list, as it was known that some metals introduced during paper manufacture act as catalysts in the degradation of paper.

Although their air quality specifications were meant for the long-term preservation of archival records, the NBS committee stated clearly that the recommended levels must also be compatible with human occupancy. Since no quantitative data related to soiling damage was investigated closely by the committee, the limit of 75 µg/m^3 for total suspended particles was adopted from the 1971 limit in the National Ambient Air Quality Standards, USA.[38] This control limit was far from being conservative, as Thomson had already reported an average outdoor level of only 40 µg/m^3 in the city of London in the 1970s.[39] At that time, the level of fine particles in non-polluted areas was around 20 µg/m^3. By comparison, in 1959, the level of fine particles rarely exceeded 10 µg/m^3 in an exhibition area of the National Gallery, London with air conditioning that included dust filtration.[40] The participants of the NBS committee were mindful that the air quality criteria should be acceptable, measurable, achievable and economically sustainable. In 1984, Banks, a member of the advisory committee, noted that “in absence of quantitative dose-response relationships, the trend has been toward best available technologies criteria for SO_X, NO_X, O_3, and particulates.”[41]

National Research Council

Only three years after the NBS report, the National Research Council (NRC) in the USA recommended new limits for the preservation of paper-based records in a chapter of their book entitled *Preservation of Historical Records*.[42] In this new text, the 1 µg/m^3 limit was retained for SO_2, the limit for O_3 was reduced to 2 µg/m^3, and the best available technology was required for NO_2 and nitric acid (**Table I**).[43] Control of particulates was based not on a concentration limit but rather on the ≥ 90% efficiency of fine particulate filters as determined by the ASHRAE dust spot efficiency test.[44] In addition, the NRC stated that the level of pollutants measured should consist of averages based on data collected over 24-hour periods. The committee members agreed that O_3 was at least as harmful to materials as nitrogen oxides, and concluded that SO_2, NO_2 and O_3 should be controlled at the same order of magnitude. The NRC added a list of volatile compounds known to cause damage to materials typically found in archives, without providing more information or references. These pollutants were nitrous acid, formic acid, acetic acid, hydrochloric acid, hydrogen sulphide, ammonia, and oxidants such as peroxyacetal nitrate and hydrogen peroxide.

The NRC recognized that the low levels recommended for pollutants could make monitoring challenging. In the early 1980s, direct reading monitors had a detection limit of around 4 to 6 µg/m^3 for O_3, SO_2 and NO_2.[45] Manual methods, such as those using air sampling with absorbing agents, were able to measure to the lower recommended levels at the time, but only with very large air samples. According to the NRC, the limit of detection provided by direct reading monitors was close enough to the recommended maximum limits to be acceptable. Quarterly or semi-annual measurements were recommended to determine when gaseous filtration systems needed to be renewed.

The NRC text underlined an important point related to implementation of recommended environmental specifications: the pollutant limits should be achieved at the surface of the archival document.[43] The NRC recognized that the recommended levels might be achievable, sometimes at much lower cost, by using microclimates, including passive approaches such as document boxes, although research data to confirm this was needed. The chapter also gave recommendations for the preservation of photographic film, magnetic recording media and optical discs, but no specific requirements were provided, with the exception of avoiding oxidizing atmospheres or using best control technology for controlling pollutants.

Baer and Banks, who were both involved in the 1986 version of the American standard document, wrote a conservation note after the release of the second edition of Thomson's book and stated in their first paragraph: "It is essential to note that all authorities warn against the simplistic application of standards without specific reference to the special needs of individual collections."[46]

British Standards Institution (1977–2012)

1977

The British Standards Institution (BSI) released its first version of recommendations for long-term storage and exhibition of archival records, BS 5454, in 1977.[47] At that time, the document contained no specifications for the control of NO_2 and O_3, but SO_2 levels were not to not exceed 50 µg/m^3 (**Table I**). The document provided advice on the selection of products for storage containers and display cases, underlining the high risk of corrosion for lead artifacts, such as seals from historical documents, in the presence of acidic emissive products (e.g., oak and fresh paint). The BSI document also included specifications about the leakage of display cases; specifically, that their design should allow sufficient air infiltration, and that those points of ventilation should have dust filters. This feature minimizes the accumulation of internally generated pollutants but, as a trade-off, permits the infiltration of external gaseous pollutants.

1989

The 1989 version of BS 5454[48] specified a gas filtration unit in the HVAC system when SO_2 and/or NO_X levels were higher than 10 µg/m^3 (**Table I**). The airtightness of display cases was related to RH control in the room: where RH was well controlled throughout the year, cases should have a vent with a dust filter; but where RH was not well controlled, cases should be airtight and include silica gel.

2000

In the 2000 version,[49] BS 5454 retained the 1989 limits for SO_2 and NO_X (**Table I**). The standard document also incorporated specific recommendations with lower pollutant targets for storage environments for photographic materials that had been published by UNESCO in 1998[50] (see below). Specifications related to the airtightness of display cases were more detailed than in 1989. If the RH and temperature were well controlled, the design of the case could allow a leakage rate of 1 air exchange per day (AE/d), a leakage rate characteristic of a fairly airtight case according to Padfield.[51] For rooms with unsatisfactory environmental conditions, the BSI document recommended display cases with a maximum leakage rate of 0.1 AE/d. Alternatively, cases could incorporate moisture sorbents (such as silica gel) and pollutant sorbents (such as activated carbon). Regular monitoring of pollutants in the rooms was to be done throughout the year and reactive organic compounds monitored inside display cases.

2012

In the 2012 version, the tone of the document changed as recommended maximum limits became guidelines. The document was no longer referred to as a British Standard, BS 5454, but rather as a Published Document, PD 5454.[52] (For the difference between BS, PD and PAS documents from the BSI, see **Appendix II**). Quantitative recommended ranges for RH and temperature were provided for different contexts, but were no longer provided for pollutants. For the maximum recommended concentrations of externally and internally generated pollutants, PD 5454 referred to another document released in the same year, the PAS 198[53] (see below). According to PD 5454, external pollutants found in excess were to be controlled with gas filtration incorporated in the HVAC system. No information was provided about the level of airtightness required for enclosures (display cases, storage cabinets, etc.). There was, however, a special comment about the acceptable level of acetic acid in a repository: if it reached a level higher than 100 µg/m^3, a higher rate of fresh, filtered air intake would be needed.

National Information Standards Organization (1995)

In the 1990s, the National Information Standards Organization (NISO) created a standard of environmental guidelines for libraries and archives in the USA, NISO TR01-1995,[54] in response to constant demand by administrators and environmental engineers in those institutions. A group of people, including many participants involved in previous American standard documents, sat on the standard committee. Agreements on specifications or rigid requirements could not be reached due to the different needs, resources and environmental boundary conditions in archives and especially libraries (high access, inadequate buildings, etc.). The committee underlined that the NISO document should serve as a guide and not as a strict specification. The group recognized that although the limit of detection by actual monitoring instruments could be equal to or less than 1 ppb for some pollutants, it could be challenging for filtration technology to achieve those levels. After reviewing data in the literature on filtration performance, the committee suggested a maximum level of 10 ppb for each of SO_2 (27 µg/m^3), NO_2 (19 µg/m^3) and O_3 (20 µg/m^3) (**Table I**). A full-time monitoring program was suggested as most desirable but, "if funds are short, or if the air in the building is not filtered … only occasional testing using less sophisticated monitoring devices is indicated."[55]

United Nations Educational, Scientific and Cultural Organization (1998)

Nine people from different European countries developed for the United Nations Educational, Scientific and Cultural Organization (UNESCO) a guide on standards and recommended practices for the preservation of a variety of archival products, from paper to optical media, that was published in 1998.[56] To protect paper-based materials from the effects of pollutants, the document simply mentioned the need to filter air with activated carbon. More detailed recommendations were provided for the preservation of photographic materials in archives and libraries,[50] recommendations that were equally or more restrictive than all standard documents prior to 1998. For frequently used materials (mainly copies of originals), the requirements were based on the American National Bureau of Standards 1983 recommendations for low access paper-based materials.[37] For long-term preservation of originals, the maximum level for O_3 was reduced to 2 μg/m^3 (**Table I**), as in Thomson[26] and the National Research Council's 1986 document, *Preservation of Historical Records*.[43] The permitted level of NO_X was lowered to 1 μg/m^3 following a limit proposed by a 1989 National Archives of Canada document written by Hendricks.[57] Close reading of that document, however, shows that Hendricks referred to the National Bureau of Standards 1983 document[37] which, in fact, proposed a limit of 5 μg/m^3.

National Archives and Records Administration (2002)

In early the 1990s, the National Archives and Records Administration (NARA) in the USA was responsible for construction of the new archives building in the state of Maryland. With its state of the art filtration system, NARA targeted pollutants such as SO_2, NO_2, O_3 and aldehydes to keep their levels below 1 to 12.5 ppb[58] (12.5 ppb = 25 μg/m^3, the same limit for O_3 as proposed by Mathey et al. in 1983).[37] In 2002, based on the performance of the new building, NARA produced a policy directive on archival storage standards, NARA 1571,[59] for all the Presidential Libraries in the United States. According to the document, the maximum levels of pollutants permitted for records storage and exhibit areas were based on the lowest concentrations that were measurable and achievable with room air filtration technology at that time. Those levels, in μg/m^3, were 2.7 for SO_2, 5.0 for NO_2, 4.0 for O_3, 5.0 for formaldehyde and 10.0 for acetic acid (**Table I**). No justification based on dose-response was provided for the levels in the standard document, which stated that "there are no known 'safe' lower limits below which pollutants will not cause damage."[60] According to the document, facility managers were in charge of regular monitoring and filtration systems maintenance to ensure compliance. Guidelines on the selection of finishing products were provided, but any product would have to be approved by the preservation department. If needed, tests on the suitability of products could be conducted.

Canadian Conservation Institute (2003)

With the publication of *Airborne Pollutants in Museums, Galleries, and Archives: Risk Assessment, Control Strategies, and Preservation Management* in 2003,[61] the Canadian Conservation Institute (CCI) adopted a new approach to establishing guidelines by focusing on the vulnerability of the collection to pollutants to determine concentration limits. Two risk assessment concepts were considered: LOAED (Lowest Observable Adverse Effect Dose) and NOAEL (No Observable Adverse Effect Level). Data was obtained from a literature review of quantitative interactions of pollutants on materials and was compiled in this book.[62]

Using the concepts of LOAED and reciprocity, it was possible to extrapolate the exposure period required to reach a level of critical damage (or observable adverse effect) on a material, such as a specific change of colour for a given pollutant concentration in specific environmental conditions. The lower the concentration of the pollutant, the longer it would take for critical damage to occur and be observed. Estimation of the rate of damage over time replaced pass/fail concentrations. Museums and archives would select a preservation target for a specific material or collection, such as 10, 30 or 50 years without observing any critical damage, and then control pollutants to the corresponding level. The preservation target chosen should be informed by institutional policies related to access, integrity and preservation of the collection, as well as consideration for actual conditions (e.g., local outdoor environment, building envelope), budget available, sustainability, significance of the objects or collection, knowledge of materials science, and the precautionary principle. An institution could, for example, decide that a silver collection should need cleaning only after 1, 10 or 30 years, and then control pollutants that tarnish silver in a manner that required no more than the desired cleaning frequency.

Where extensive data exists, a low concentration limit can be established following the concept of NOAEL. This is the case with lead corrosion by acetic acid, where data show that maintaining an acetic acid concentration below 400 μg/m^3 at 54% RH or less will prevent trace amounts of corrosion for more than a year.[63] Since untarnished lead – the most sensitive material to acetic acid – has a NOAEL of 400 μg/m^3, the limit for acetic acid was set conservatively at 100 μg/m^3 for the preservation of general collections, with RH kept below 60%. Note that lead alloys and lead with a stable patina will be more resistant to acetic acid, while contaminants (such as salts) on lead may increase its sensitivity to acetic acid.

CCI produced a table of six key airborne pollutants with their respective concentrations (based on LOAED) to meet a range of preservation targets for most objects (**Table II**).[64] LOAED related to hypersensitive materials (such as silver with H_2S) and high risk conditions for materials (such as lead with acetic acid) were excluded from the table and were dealt with separately using special mitigation strategies. Although the table of preservation targets was supported by the compiled LOAED, very few heritage institutions adopted their own preservation targets. This was probably due to a number of factors: a lack of awareness, lack of exemplary models to follow, difficulty in linking critical damage to a loss of value, and the cost of monitoring. More information on the use of the concepts of LOAED, NOAEL and critical damage, and on **Table II**, is found in **Appendix III**.

Table II. Guidelines on levels of airborne pollutants in $\mu g/m^3$ and (ppb) from CCI[64] and GCI.[69]

	CCI maximum average concentration allowed for indicated preservation targets			GCI concentration limit*			
Key airborne pollutants	**1 year**	**10 years**	**100 years**	**action limit: extremely high**	**action limit: high**	**for general collection**	**for sensitive materials**
Acetic acid	1000 *(400)*	100	100	*1500* (600)	*500* (200)	*100* (40)	*13* (5)
Hydrogen sulphide	1 *(0.71)*	0.1	0.01	*2.8* (2)	*0.57* (0.4)	*0.14* (0.1)	*0.014* (0.01)
Nitrogen dioxide	10 *(5.2)*	1	0.1	*500* (260)	*50* (26)	*3.8* (2)	*0.1* (0.05)
Ozone	10 *(5.0)*	1	0.1	*150* (75)	*50* (25)	*1.0* (0.5)	*0.1* (0.05)
Sulphur dioxide	10 *(3.8)*	1	0.1	*40* (15)	*21* (8)	*1.1* (0.4)	*0.11* (0.04)
Fine particles ($PM_{2.5}$)	10	1	0.1	50	10	1	0.1
Formic acid				*290* (150)	*38* (20)	*9.6* (5)	*9.6* (5)
Formic acid‡				*500* (260)‡	*200* (104)‡	*80* (42)‡	*9.6* (5)‡
Formaldehyde				*200* (160)	*20* (16)	*12* (10)	*0.12* (0.1)
Acetaldehyde							*1.8* (1)
TVOCs				(1700)	(700)	(100)	–
RH	Keep below 60%			Keep below 60%, ideally below 50%			

*lower limit of ranges
‡limits published in ASHRAE 2007[70]
italic number: unit converted by the present author

American Society of Heating, Refrigerating and Air-Conditioning Engineers (2003–2015)

2003

The American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) is a global society advancing human well-being through sustainable technology for the built environment. Collaboration between CCI and the Getty Conservation Institute (GCI) allowed the rewriting of the 1999 chapter "Museums, Libraries, and Archives" of the ASHRAE HVAC Applications Handbook in 2003.[65] This chapter is well known for its specifications for RH and temperature, but is probably referenced less often on the topic of pollutants. Tables in the chapter presented information related to pollutant sources and effects, as well as preservation targets for six key pollutants for mixed collections that were adopted from the CCI guidelines described above.[66] The text of the 2003 ASHRAE chapter recommended the following pollutant limits: "For long-term preservation, levels of airborne pollutants should be below 0.03 $\mu g/m^3$ or less than 1 $\mu g/m^3$ for inorganic gases and fine particles and in the double- or single-digit $\mu g/m^3$ range for organic carbonyl pollutants."[67] The limit of 1 $\mu g/m^3$ for inorganic gases and fine particles matches the CCI preservation target of 10 years as indicated in **Table II** but not those for acetic acid and H_2S.

2007

Significant changes were made to the pollutant limits in the 2007 version of the ASHRAE chapter,[68] incorporating GCI data from Grzywacz[69] (**Table II**). A revised table provided recommended target levels for a larger number of pollutants for general collections and for sensitive materials, as well as high and extremely high "action limits," levels at which mitigation is necessary.[70] The 2007 table incorporated different recommendations from multiple sources. Cited references for the chapter reveal that two recommendations for "Archival Document Storage" and "Libraries, Archives and Museums" were based on the 1983 National Bureau of Standards report[37] and on NARA 1571[59] respectively. Recommendations for general collections and sensitive materials roughly follow limits based on the LOAED principle for 10 and 100 years respectively,[64] as shown in **Table II**. The two approaches differ significantly for only one limit, that for NO_2. However, the new "action limits" for high and extremely high levels of pollutants do not closely fit the notion of dose. The recommended concentration limits in these columns differ by a factor of 2 to 10.

Three indoor generated pollutants, acetaldehyde, formaldehyde and formic acid, were included in the 2007 ASHRAE recommendations table. No quantitative data or references were provided for acetaldehyde and formic acid; notes mentioned that "little damage has been directly attributed to acetaldehyde" and "very little is known about the effects of formic acid at various concentrations."[70] With respect to formaldehyde, the chapter cites a conference paper by Bradley and Thickett which concluded that there was "no significant risk with formaldehyde …" for lead and copper alloys, and that formaldehyde could be harmful to lead only at 100% RH.[71] The 2007 ASHRAE chapter, like the 2006 book by Grzywacz,[72] mentions that formaldehyde discolours organic colorants, referencing research sponsored by the GCI that concluded: “Formaldehyde … does not appear to be a major threat to colorants in museum collections.”[73] These statements suggest that the evidence to support inclusion of formaldehyde in the list of key pollutants that should be monitored is weak. Formaldehyde can, indeed, affect lead at high RH in a clean indoor environment. However, lead will also slowly tarnish in the presence of carbon dioxide and humidity. This tarnish layer can limit the attack of acetic acid.[63] Hatchfield, who reported damage to lead from formaldehyde in the mid-1980s, later clarified, in her book dedicated to pollutants, that the interior of the plywood cabinet where lead objects were affected had been varnished with an oil-modified urethane.[74] This type of coating is known to release, in addition to formaldehyde, high amounts of formic acid, acetic acid and peroxides.[75] In general, formic acid and especially acetic acid, when present in the enclosure environment, will cause more damage to lead than formaldehyde.[76]

For the preservation of sensitive materials, the maximum level of acetic acid was set at 5 ppb (13 µg/m^3) but no reference was given to support this small concentration. Grzywacz and Tennent had measured the level of acetic acid in 27 display cases and storage cabinets. They all showed a level far greater than 5 ppb.[77] The limit of 5 ppb would be very hard to achieve in enclosures without specific interventions such as high air exchange rate or the use of pollutant sorbents.

For the first time in the conservation field, there was also an interest in controlling the total volatile organic compounds (TVOCs) in museums. A maximum of 100 ppb of TVOCs (based on hexane calibration) was recommended for general collections as an indicator of overall air quality.[69,70] No reference was provided to support this number and no TVOC limit was indicated for sensitive materials. Up to this point, no correlation has been established between TVOC level and object damage. A level below 100 ppb can be relatively easily achieved in a room (possibly excluding newly built or renovated rooms), but can be a real challenge to achieve inside airtight display cases with products or objects made of organic materials such as wood, varnishes, leather and fur. TVOC levels have been measured in 42 display cases and microclimate frames and the average level found was 4800 ppb.[78,79] Only one case showed a level of below 100 ppb.[78]

The main text of the 2007 ASHRAE chapter recommended less than 1 ppb for gaseous pollutants for long term preservation,[80] a limit that does not match any specific target level proposed in the accompanying table (GCI concentration limits in **Table II**).

2011–2015

In 2011, maximum concentrations of pollutants were no longer provided in the text of the ASHRAE chapter for museums, galleries, libraries and archives.[81] The table of recommended target levels remained the same except for the removal of the concentration limit for acetaldehyde (1 ppb). The 2015 version[82] was identical to the 2011 version.

British Standards Institution – Publicly Available Specification (2012)

In 2012, the same year it released the standard document PD 5454,[52] the British Standards Institution also published a Publicly Available Specification, PAS 198, entitled *Specification for managing environmental conditions for cultural collections*.[53,83] The word “specification” was mentioned only in the title and in the foreword. This document emphasizes the best available scientific evidence on interactions between different types of objects and the indoor environment. The committee who prepared the document consisted of 16 conservation professionals who were charged with compiling information to help decision makers manage the preservation of their collections in a manner that accounted for the significance of particular collections and the need to reduce energy consumption. Quantitative data related to safe and unsafe ranges for RH, temperature, light and pollutants were listed in annexes and identified as “informative.” A list of sources of indoor pollutants and a list of pollutant-object interactions were provided, both supported by references.

The PAS 198 claimed that damage caused by pollutants was cumulative (dose-response) and no safe limit can be established. However, the use of approximate thresholds determined after long exposures or accelerated ageing research (**Table I**) was proposed. The term threshold as used by PAS 198 was similar to the term NOAEL (No Observable Adverse Effect Level) used by CCI. A table showed the approximate threshold concentration for 16 material-pollutant interactions. The interactions shown involved mainly acetic acid and reduced sulphides (such as H_2S, COS and CS_2) with materials such as soda silicate glass, ceramic, egg, paper and different metals. Unfortunately, the thresholds were not supported by references. Two tables that compiled pollutant-material interactions did cite references; however, those references usually did not provide quantitative data that could justify the thresholds (see **Appendix IV** for the case of formaldehyde and soda silicate glass). In fact, a note related to the approximate threshold table in the informative annex of PAS 198 stated: “in the absence of published threshold values, the values for paper may be used as approximate guidance.”[84] Those limits in ppb (µg/m^3) were 100 (250) for acetic acid, 1 (2.7) for SO_2 and 10 for NO_X. These were likely the pollutant limits for paper to which the 2012 PD 5454[52] referred to and proposed for the protection of a collection in general (see above). It is worth noting that the threshold concentration for interactions of reduced sulphides and some metals (including lead-based pigment) was set at 10 ppb. This level is high, in view of the fact that silver and copper will easily tarnish at lower levels in less than 1 year.[85,86] Since many institutions are concerned about protecting their metal collections from pollution, including a lower concentration limit for reduced sulphides (at least for H_2S) for the preservation of a mixed collection would have been wise.

The PAS 198 proposed different recommendations for dealing with pollutants in enclosures versus open areas. In early versions of the BSI standard documents, the focus on the airtightness (presence of vents) of enclosures was based on the level of control of RH and temperature in the room. With PAS 198, the focus was on the higher quantities of generated pollutants in enclosures. Increasing the air exchange rate was identified as one option to resolve this issue, but since each context may be different, assessing the positive and negative impacts of different mitigation options before making the final decision was recommended. The document also specified that the best way to prevent indoor generated pollutants was to carefully select products and test them if needed. Inspection every six months of objects in enclosures with emissive products was also proposed. Some advice on monitoring was provided. Firstly, review of local outdoor pollutants levels provided by government environmental agencies was suggested to determine if indoor monitoring was justified (if needed, the monitoring could be carried out seasonally). Secondly, monitoring pollutants in two phases was proposed: first, an overview of the environment using low-cost, semi-quantitative methods and then, if necessary, through more exhaustive and quantitative monitoring techniques.

SPECIFICATIONS BASED ON DOSIMETERS

Pollutant dosimeters offer an alternate approach to ensuring a suitable environment for collections. Instead of measuring pollutant levels directly, dosimeters measure the cumulative effect of pollutants on well-characterized materials, such as metals, polymers or glass, over a specific exposure time. These dosimeters provide an indication of the harmful effects of the ambient environment on a specific type of material that is often extrapolated to the collection in general. Many dosimeters are also sensitive to other environmental factors such as temperature, RH, light and UV radiation. Most dosimeters need to be sent to a specialized laboratory for analysis where the results can be compared to a dedicated scale. Each dosimeter comes with its own criteria of a suitable environment; what is considered acceptable is often defined by the developer. Aside perhaps from dosimeters based on metal coupons, the use of most dosimeters remains limited in the museum community. Four types of dosimeters are described below. Price and access remain significant limiting factors.

Metal Dosimeters

The Instrument Society of America (ISA) developed a standard test method, ANSI/ISA S71.04-1985,[87] designed to classify airborne pollutants using dosimeters based on silver and copper coupons that are exposed to the ambient environment over 30 days. Corrosion thickness is measured and correlated to a conservation environment classification from polluted to extremely pure.[88] In 1994, the Dutch National Archives adopted the class "extremely pure" as a target, which is equivalent to maximal concentrations of 1.3 (0.8), 6.7 (13) and 0.3 ppb (0.6 $\mu g/m^3$) for SO_2, NO_X and O_3, respectively.[89,90] Some companies sell the metal coupons with analysis included. Other companies sell metal coupons and the monitoring instruments necessary to measure the corrosion thickness.

Glass Dosimeter

A glass sensor made of potassium-calcium-silicate (K-Ca-silicate) glass chips was developed by the Fraunhofer Institute for Silicate Research to permit early warning of the degradation of stained glass.[91,92] The sensor is most sensitive to acetic acid, followed by formic acid. It also reacts with water vapor. This glass sensor could also indicate the harmfulness of an environment to lead objects since lead too is very vulnerable to acetic acid. As the sensor reacts with environmental agents, more water is adsorbed on the glass. An FTIR technique is employed to quantify how much water is adsorbed, a measure that is transposed to a ΔE-value. Based on three months' exposure, an environment that generates a ΔE-value of less than 0.07 is considered acceptable, while one characterized by a ΔE-value of more than 0.15 would be considered unsafe. The limit of 0.07 lacks apparent justification other than that it is a value close to the limit of detection. Based on data provided by Dahlin,[93] this corresponds to an exposure of about 300 $\mu g/m^3$ of acetic acid (RH not specified). Sensors and analysis are available through the Fraunhofer Institute.[94] It should be noted that the glass sensor has a limited shelf life.

Organic Dosimeter

The Early Warning Dosimeter for Organic Materials measures the overall impact of the environment on an organic polymer for a period of three months.[92] Change in polymer structure is measured by UV spectrophotometry. The level of degradation of the polymer had been calibrated with different parameters such as NO_2, O_3, RH, temperature and UV radiation, and converted to a scale of 1 to 5 which reflects different "acceptable – location levels" where 1 corresponds to an environment typically found in an archive storage space and 5 to an outdoor storage space with no control.[95] Level 1 corresponds to a maximum level of 1.0 and 1.15 ppb (1.9 and 2.3 $\mu g/m^3$) of NO_2 and O_3 respectively, if UV radiation levels are low. Unfortunately, this organic dosimeter is currently not commercially available.

Piezoelectric Quartz Crystal Dosimeters

A thin film of a material of interest applied on a piezoelectric quartz crystal microbalance creates a type of dosimeter that allows the direct reading of mass change in the material when exposed to the ambient environment.[92,96] Materials that can be applied include metals such as silver, copper and lead, or organic compounds such as egg tempera and mastic varnish. The reproducibility of the test is unknown. Metal coating piezoelectric dosimeters have already been commercialized but not yet those for organic materials. No acceptable levels for museums have yet been proposed by the developers.

SPECIFICATIONS BASED ON TESTING PRODUCTS

Since the 1960s, some products have been reported to be sources of pollutants, leading to recommendations that products be carefully selected for use in museums.[28,97-103] Many of the standard documents described above emphasized the need for proper selection of products without much elaboration. Many people involved in the development of specifications or guidelines for pollutants have in mind the control of pollutants at the room level and assume that most objects in display or storage enclosures will be well protected. Although usually true for protection against outdoor pollutants, there is a risk of harmful emissions from products and/or objects within enclosures. Avoiding inappropriate products is critical in enclosures where harmful emissions can accumulate and cause more damage on objects than in an open, better ventilated space. Design requirements often state that products used for construction of new display cases or new storage equipment, for example, must fulfill certain requirements or pass certain tests. Four tests for evaluating products are described below. Tests that identify the presence of specific chemical compounds, such as the azide test for sulphides or the Beilstein test for chlorine, have also been incorporated into strategies to identify potentially damaging products by the British Museum.[100,101] Given the large number of products on the market and their frequent modification by manufacturers, the need for testing never ends. As a result, many museums prefer to rely on a list of products regarded as safe.

ANSI/NISO Z39.79 (2001) and CCI guidelines (1993, 2017)

A document developed in 2001 by the National Information Standard Organization, ANSI/NISO Z39.79,[104] provided information on environmental conditions, but also about products for exhibition of library and archival materials. The appendices proposed a list of products generally recognized as safe to use for exhibition and physical support. The list of recommended products was based mainly on Tétreault and Williams.[105] A new, rewritten version of this CCI document is now available.[106] This approach is an attractive solution for clients with a limited budget for testing or monitoring. The likelihood of damage caused by the recommended products should be minimal, although their use is not without risk. The formulation of a product previously defined as safe could change with the modification of its components. For example, some rigid polyvinyl chloride (PVC) foams used to be acceptable. As a result of recent changes, they may now contain sulphur compounds which can tarnish silver.[107,108]

Oddy Test

In 1973, the British Museum developed an accelerated corrosion test – the so-called "Oddy Test" – to determine if a product in the vicinity of metals could be potentially harmful.[28,109] It is probably the best known qualitative test for pollutants in the conservation field. The product sample is placed in a jar with lead, silver and copper coupons and a source of humidity. The sealed jar is then put in an oven at 60°C for 28 days. The product passes the test if no change is observed on the metal coupons; by contrast, significant corrosion indicates the product is unsafe for use. If there is slight corrosion, the methodology suggests limited use of the product for a maximum period of six months. This aggressive test can rule out some products that could be safe for metals in ambient conditions. On the other hand, if a product did not corrode the metal coupons (and therefore passed the test), it may not necessarily be safe for any type of object. For example, polyurethane (ester) foam has passed many Oddy tests, but in museums conditions, it has caused corrosion on copper, brass, pewter and zinc[110] and crystal formation on a glazed jar and on wood.[111]

Major institutions conduct their own Oddy tests, but few offer this service to others. Institutions with no in-house testing capacity would require the services of a trusted laboratory where the test can be conducted. The methodology has varied from institution to institution.[108,112,113] Over the years, even the British Museum has updated its test procedures[114,115] and refinements continue to be proposed.[116,117] Consequently, the test result may depend on the method used.[118] A substantial list of products tested by different institutions can be found on the American Institute for Conservation website;[119] however, some test results date back over 10 years, which may lead to false confidence since formulations and manufacturing processes may change over time.

Photographic Activity Test

After the Oddy test, the second most common test for evaluating products was developed by the Image Permanence Institute (IPI) in 1988. The test, known as the Photographic Activity Test or "PAT" (ISO 18916:2007),[120] evaluates the effect of products in contact with photographic images.[121] A sample and a detector (unprocessed colloidal silver either in gelatin or on a polyester base) are squeezed in a sandwich separated by filter paper (Whatman #1) and are heated in an oven at 70°C and 86% RH for 15 days. The optical density of the detector is measured with a photographic densitometer. If the change of density of the detector is less than the acceptable limit, the product tested has passed the test. It is common to see archival institutions requesting that products to be used must pass the PAT.[122,123] The IPI and some conservation institutions can perform this test.

pH Strips

pH strips are used in an easy, semi-quantitative test to determine the acidity generated by a given product.[103] This test is fast, inexpensive, and uses pH strips that are easy to acquire. The product to be tested is placed in a jar with a pH strip (sensitive in the range 4 to 7) that has been wetted with a water-glycerol solution. After 24 hours, if the pH indicated by the strip is lower than the control (a pH strip in a jar without a sample, or a pH strip in the room), it means that the product tested released volatile acidic compounds. Similarly, the acidity of a room with collections can be compared to a room without collections. CCI defines three categories of risk in terms of pH ranges: low deterioration potential at pH from 7.0 to 5.0, moderate at pH from 5.0 to 3.5 and high at pH below 3.5. This is not a precise test, but it is accessible to many museums where money and time are issues.

An alternative test strip is the A-D strip, also an acidity indicator, developed by the Image Permanence Institute initially to detect acidity from cellulose acetate film.[124] The A-D strips have been placed in a tightly sealed container with the product of interest, like pH strips,[125] or set inside storage or transit cases.[126] Hackney describes the use of a reflectance spectrophotometer to record colour of the A-D strips, and thus relative pH, more accurately.[126] Both strips have been used as a quick test prior to the Oddy test.[108,125]

Bewertung von Emission aus Materialien für Museumsausstattungen

Since 2012, the German Materials Research Institute BAM (Bundesantalt für Materialforschung und -prüfung) has been involved in quantifying concentrations of some volatile compounds emitted by products used in enclosures for objects through their BEMMA program (Bewertung von Emission aus Materialien für Museumsausstattungen: Assessment of emissions from materials for museum equipment).[127] The Institute also proposes acceptance criteria based on the limit of detection of the specific analytical technique used to measure each specific compound. The maximum concentrations allowed are 2, 25 and 50 $\mu g/m^3$ for formaldehyde, formic acid and acetic acid respectively. Some limits have also been established for volatile organic compounds (VOCs) such as 100 $\mu g/m^3$ for very volatile organic compounds and 500 $\mu g/m^3$ for total VOCs. No information has been provided to justify these criteria. It is too early to be able to assess the impact of these specifications in the heritage community. Since the analysis of different gases for each product or display case tested is costly, these specifications may only be adhered to by major display case makers and/or clients who need to meet the highest standards for display of very significant and vulnerable objects.

FROM THOMSON TO PAS 198

Over the last 40 years, the ongoing enthusiasm for filtration and monitoring technologies, improved knowledge of some micro-scale material-pollutant interactions, and the desire for better preservation of collections has put pressure on heritage institutions to request lower pollutant concentration limits. In terms of the HVAC system and display case markets, some sellers and buyers prefer a zero pollutant policy.

In the early 1990s, Brimblecombe[9] and Tétreault[103] underlined the lack of knowledge and quantitative data on the effect of pollutants on materials in the indoor environment. In the late 2010s, it remains the greatest challenge. Studies made with a single pollutant in a test chamber at a fixed RH provide some degradation trends, but this simplistic laboratory approach may not reflect real impact on the collection of multiple pollutants together. Some researchers have shown that the prediction of degradation trends is less reliable in the presence of multiple volatile compounds commonly found in museums. The presence of some compounds can reduce or increase the degradation reactions that occur.[76,128-131] Moreover, change in a material detected at the microscopic level may indicate the formation of a protective layer rather than something that will cause damage. Compounds deposited on the material's surface prior to pollutant exposure can also interfere. The word "uncertainty" should be present in our mind during these assessments.

Bradley, of the British Museum, described an alternative to specifying pollutant concentration limits: examining the object and determining the real concerns through discussion with conservators and curators.[132] This approach works for preventing short- to medium-term problems, such as the contamination of objects, incorrect use of products, or an unacceptable dust deposition rate. Detection or prediction of small changes that occur over the long term will be more difficult with this approach and time consuming, especially if the history of the object and its environment are not well documented.

Many standard documents advise on pollutant control strategies, but many conservation professionals focus on and report the concentration limits shown in summary tables. The most recent specifications document, PAS 198,[53] comes with a strong emphasis on control strategies for collections in enclosed storage or display, in open areas and in transit, but the committee was reluctant to use threshold pollutant levels. The committee advocated instead for an "evaluate – monitor – mitigate approach." However, a lack of clear indications for "what to do" was a common complaint, based on feedback received about PAS 198.[83] At the same time, Di Pietro et al., who evaluated the need to maintain gas filtration in four European national heritage institutions, strongly recommended a revision of pollutant maximum limits for archives (with the goal of loosening constraints) after consultation with other conservation scientists and with a cost-benefit perspective in mind.[133] Balancing the goal of optimal preservation with the need for evidence-based, sustainable monitoring and control remains a challenge to keep in mind as the next generation of guidelines for the control of pollutants in museums and archives are developed.

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APPENDIX I. PUBLISHED POLLUTANT SPECIFICATIONS REVIEWED IN THIS PAPER

American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE)

2003[65] 2007[68] 2011[81] 2015[82]	"Museums, Galleries, Archives, and Libraries," in: *ASHRAE Handbook: Heating, Ventilating, and Air-Conditioning Applications*, SI edition (Atlanta: ASHRAE)

British Standards Institution (BSI)

1977[47] 1989[48] 2000[49]	BS 5454, *Recommendations for the Storage and Exhibition of Archival Documents* (London: British Standards Institution)
2012[52]	PD 5454, *Guide for the Storage and Exhibition of Archival Materials* (London: British Standards Institution)
2012[53]	PAS 198, *Specification for Managing Environmental Conditions for Cultural Collections* (London: British Standards Institution)

Canadian Conservation Institute (CCI)

2003[61]	Tétreault, Jean, *Airborne Pollutants in Museums, Galleries and Archives: Risk Assessment, Control Strategies and Preservation Management* (Ottawa: CCI)

Getty Conservation Institute (GCI)

2006[69]	Grzywacz, Cecily M., *Monitoring for Gaseous Pollutants in Museum Environments* (Los Angeles: GCI)

National Archives, USA

1983 NBS[33]	Johnson, W.B., W.P. Lull, C.A. Madson et al., *Environmental Control for Archival Record Storage* (Washington, DC: National Bureau of Standards)
1983 NBS[34]	Mathey R.G., T.K. Faison, S. Silberstein et al., *Air Quality Criteria for Storage of Paper-Based Archival Records* (Washington, DC: National Bureau of Standards)
1986 NRC[42]	National Research Council, *Preservation of Historical Records* (Washington, DC: National Academy Press)
2002 NARA[59]	NARA 1571, *Archival Storage Standards* (Washington, DC: National Archives and Records Administration)

National Information Standards Organization (NISO)

1995[50]	NISO TR01, *Environmental Guidelines for the Storage of Paper Records* (Bethesda: National Information Standards Organization Press)

Thomson

1978[25] 1986[30]	Thomson, Garry, *The Museum Environment* (London: Butterworths)

United Nations Educational, Scientific and Cultural Organization (UNESCO)

1998[50]	Boston, G. (ed.), *Safeguarding the Documentary Heritage: A Guide to Standards, Recommended Practices, and Reference Literature Related to the Preservation of Documents of All Kinds* (Milton Keynes, UK: UNESCO)

APPENDIX II. DOCUMENTS FROM THE BRITISH STANDARDS INSTITUTION

All standards from the British Standards Institution have the same basic purpose: to set out agreed principles or criteria so that users can make reliable assumptions about a particular practice.[134] Specifications for environmental control in museums and archives have been published over the years in three different types of documents. The British Standard (BS) is a document that fulfills BS 0, a standard for standards. To create this type of document, a committee is formed that must consult and reach a consensus. A Publicly Available Specification (PAS) document is similar to a BS but is developed with the help of an external sponsor which permits faster publication. A Published Document (PD) is a document that does not require a high level of consultation or consensus and is subject to further development. These include private standards for a single institution or for a group of institutions. The credibility of a given PD document may very likely rely on the reputation of the authoring institution.

APPENDIX III. CONCEPT OF LOAED AND NOAEL

The Canadian Conservation Institute used concepts of dose-respond relationship such as LOAED (Lowest Observable Adverse Effect Dose) and NOAEL (No Observable Adverse Effect Level) to assess the vulnerability of a collection to pollutants. Data was compiled from a literature review of quantitative interactions of pollutants on materials.[62] CCI identified six key airborne pollutants likely to affect the long-term preservation of most objects with their respective concentration limits based on LOAED (see **Table II**).

Assuming reciprocity, it was possible to extrapolate from LOAED the exposure period needed to reach "critical damage" (or observable adverse effect) on a material for a given pollutant concentration in specific environmental conditions. The definition of "critical damage" varies in the literature, depending on the nature of the materials studied and the quantification technique used. Often, a change in material properties (i.e., colour, strength, or thickness of corrosion) of approximately 5% is used as a marker for critical damage.[135] The lower the pollutant concentration, the longer it would take for critical damage to occur and be observed. For example, as shown in **Table II**, no damage is expected on a general collection for 1 year if the concentration of NO_2 remains below 10 $\mu g/m^3$. If the collection is to be similarly protected from damage for 10 years, the NO_2 concentration should be maintained below 1 $\mu g/m^3$, assuming reciprocity. Although further limiting the pollutant concentration is expected to extend the period of protection, it must be kept in mind that reciprocity may not be valid for an extended concentration range. Data obtained from short-term, severe conditions may not be easily extrapolated with confidence for long-term, mild conditions.

Most of the available LOAED and NOAEL data come from laboratory experiments using only one pollutant in the exposure chamber. In reality, a material will be exposed to multiple pollutants from the outside environment (e.g., NO_2, SO_2, O_3 and H_2S) or from enclosure materials (e.g., organic acids, aldehydes, sulphur compounds). Some of the gases present could have synergetic effects, while others could have antagonistic effects. For example, the interaction of formaldehyde and formic acid has been found to have an antagonistic effect, reducing the level of deterioration by formic acid in lead,[76] cellulose[131] and possibly soda glass.[136] SO_2 has a similar reduction effect on the tarnishing of silver by H_2S.[137] The concept of LOAED has also been used to predict light fading[138] and to predict the degradation of cellulose acetate film or photographic dyes by moisture.[139,140] Limited experimental data can lead to high uncertainties in the determination of LOAED and NOAEL.

Water vapour was included as a key pollutant in **Table II** for two reasons. Water vapour often influences the degradation rates of different pollutants. It can also be a reactant, such as the direct action of water (hydrolysis) on cellulose-based materials.[141,142] An RH limit of 60% was proposed since most rooms in museums contain mixed collections. Even though an RH level lower than 60% would be beneficial for the preservation of metals, paper and many dyes, a lower general RH level could not be justified without specific assessment of a given collection.

APPENDIX IV. REFERENCES ON FORMALDEHYDE-GLASS INTERACTION, PAS 198

The four references on the effect of formaldehyde and formic acid on soda silicate glass in the 2012 PAS 198 Table G.2 were examined to determine the source of the 300 ppb formaldehyde threshold shown in PAS Table G.4.[53] As demonstrated below, information that supports the formaldehyde threshold determination is not obvious from those references.

The first reference, Cumming, Lanford and Feldmann,[143] dealt with the effect of SO_2 and NO_2 on glasses but did not deal with formaldehyde or formic acid.

In the second reference, Nockert and Wadsten reported the formation of sodium formate on glass plates enclosed for about 40 years in a cardboard box with archaeological textile (silk), paper and some adhesive.[144] They assumed, with reference to a 1974 paper by Kohlbeck,[145] that the formaldehyde released by acidic paper was transformed into formic acid, and that this acid reacted with the sodium of the glass. Kohlbeck had supposed a conversion of formaldehyde to formic acid with the help of peroxide also contained in acidic paper, but provided no data to support this interpretation. In a 2010 paper, Strlič et al. observed the presence of reactive oxygen species in paper documents with iron gall ink.[146] Those species were assumed to be hydrogen peroxide. Without iron gall ink, their presence was limited. The limited presence of peroxides in paper could not justify the amount of formic acid available to react with glass. However, Dupont et al. demonstrated in 2009 that different types of paper can release formic acid.[147] It is thus possible that formic acid directly emitted by acidic paper or another organic material reacted with the glass plate.

The third and fourth references cited are the 2004 and 2007 papers by Robinet et al.[148,149] In their 2004 paper, the effect on glass of formaldehyde at 5 and 150 ppm (parts per million) was not conclusive. They referred instead to the 1992 work of Schmidt.[150] Schmidt observed damage from an atmosphere generated from a 35% formaldehyde solution, an exposure condition that can be considered far more severe than a normal enclosure environment. The 2007 paper[149] did not study the effect of formaldehyde on glass. In a 2005 paper, however, Robinet et al. exposed soda glass samples to formaldehyde, formic acid and acetic acid at concentrations of 100-150 ppm.[151] They observed no significant damage on glass exposed to formaldehyde and also noted that water vapor alone can alter soda silicate glass. They concluded: "The organic acids have more effect than formaldehyde, which should therefore not be considered as the main danger for museum glasses."[152]

As such, the four references cited provide little justification for the establishment by PAS 198 (2012) of a threshold of 300 ppb for formaldehyde-soda glass interaction.

In the indoor or enclosure environment, the conversion of formaldehyde into formic acid does not occur easily. It needs a catalyst or a strong oxidant.[76,150,153] This conversion happens in the presence of fresh paint formed by oxidative polymerization such as oil-based or alkyd paint. During the formation of the paint film, aldehydes, organic acids and peroxide compounds are released. These peroxide compounds can convert aldehydes into organic acids. This type of paint is not recommended in museums and, due to current VOC regulations, is now difficult to get from a vendor.[75] Since the late 1980s and through the 1990s, there was a focus on the harmfulness of formaldehyde on museum objects. Many conservation professionals did not consider or monitor the presence of formic acid released by many products. Much damage associated directly or indirectly to the action of formaldehyde was most likely caused by formic acid directly released by products used in museums and archives. The measurement of aldehydes and organic acids in museums became popular after a conference paper from Grzywacz and Tennent in 1994.[77]

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