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Dose-response functions for historic paper

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Abstract

Paper degradation has been studied extensively over the past few decades from both the conservation and the material science perspectives. This review focuses on the quantifiable impacts of the environment and material composition, from the viewpoint of long-term storage of historic paper-based collections. Therefore, temperature, relative humidity and their variation, and pollution are of major interest while photoinitiated processes are covered only briefly.

New experiments comparing the effects of the most abundant indoor pollutants (NO_2, acetic acid and formaldehyde) and the effects of fluctuating temperature and relative humidity are also presented as part of the discussion. This work highlights the need for revision of the existing dose-response (damage) functions for paper and their further development.

Keywords

Historic paper; hydrolysis; oxidation; viscometry; colorimetry; heritage science

1 Historic paper

Despite the ubiquity of electronic media, paper is still the most generally readable carrier of information. In heritage institutions, collections of documents of the past are being preserved for posterity. It has been estimated that in a typical Western repository, 70-80% of these documents [1] are likely to be acidic and therefore prone to rapid deterioration, their useful lifetime being about a century, a couple at best. This is in a stark contrast to paper produced before ca. 1850, the lifetime of which may be longer for at least a factor of 10 [1]. For curators of these collections, interventive conservation is an option, although the throughput of even mass treatments [2] is not sufficient to address the scale of the problem and the resources are too limited.

In many cases, preventive conservation is therefore the preferred option. However, environmental managers may struggle with the abundance of literature available on environmental effects on paper degradation and the surprisingly scarce data that is well quantified and relevant not only to the scientist but to the user as well. Unlike a recent comprehensive review of the basic mechanistic and thermodynamic concepts [3], the focus of the present review is to provide an overview of dose response functions, based on which environmental management in paper-based collections could be optimised to minimise degradation while optimising resource use.

The main structural component of paper is cellulose. As a linear homopolymer, it is composed of identical monomers and scission of inter-monomer bonds leads to its degradation [4]. It is well known that apart from temperature, water (humidity) and acidity in paper are important factors in its degradation [5-7]. Acid-catalysed hydrolysis is a major cause of paper strength loss [5,7], although other mechanisms may take place as well, such as oxidation and thermal degradation [7,8], depending on the experimental conditions. The effect of oxygen on the hydrolytic pathway should not be neglected, as differences between accelerated ageing in argon and air [8] and nitrogen and air have been observed [9]. Paper degradation should be regarded as a complex process, in which hydrolysis may be the fastest degradation mechanism [10], but not the only relevant one.

For the end user the most important properties of paper are those related to its usability, such as mechanical strength, and its visual appearance, related to text readability or image contrast. This dictates the choice of analytical techniques to measure changes in paper properties.

Mechanical properties are assessed by tensile strength and zero-span tensile strength measurements, tearing resistance, bursting strength, and folding endurance [11-14] and are affected by fibre strength and interfibre bonding, or both. The relationship between zero-span tensile strength and degree of polymerization, determined by Zou *et. al.* [7] implies that the average chain length of cellulose is one of the key factors for this mechanical property. Conversely, a process that is affected mainly by intermolecular bonding is creep of paper, which occurs when paper is under stress and deforms with time [15].

The scission of intramolecular bonds leads to a decrease in average molecular weight of cellulose, which represents the number of monomers in a cellulose polymer (i.e. DP – degree of polymerisation). It can be measured in several ways, most commonly used are viscometry to obtain the viscometric average DP or the more instrumentally demanding size-exclusion chromatography (SEC) to obtain a distribution of molar masses, number-average and mass-average molar mass [16,17].

To determine the colour of paper the CIE L*a*b* system [18] is mostly used, which takes into account the “standard human eye response”. As yellowing often accompanies paper ageing, b* is often used to evaluate changes in colour.

Among the many agents of deterioration, temperature and relative humidity [15,19-27], light [20,28-32], pollution [20,32-37], biogenic agents [34,38,39] and paper composition [5-7,20,33,34,40-43] have been researched most. Of these, temperature, humidity and pollution are the most important ones for storage in the dark, and are reviewed here.

2 Temperature and Relative Humidity

In this section, a brief review of the most common concepts used to describe the kinetics and thermodynamics of cellulose degradation are described. In-depth reviews of degradation mechanisms have been published elsewhere [3,44]. The most commonly used approach to studying paper degradation kinetics was established by Ekenstam in 1936 [45]. He derived:

$$kt = \frac{1}{DP} - \frac{1}{DP^0}\ , \tag{1}$$

where DP represents the number of monomers in a chain at time t and DP^0 at the beginning of the experiment. The temperature dependence of degradation rate constants is described by the Arrhenius equation:

$$k = Ae^{-\frac{E}{RT}}, \tag{2}$$

where A is the frequency factor, E is activation energy, R is the gas constant and T is the absolute temperature [5,43]. The activation energy represents a measure of sensitivity of the degradation rate to temperature changes, while the constant A represents all other experimental parameters, such as humidity, acidity, exposure to pollutants and light, and physical structure of paper [6,43]. It should be noted, thus, that the pre-exponential factor may depend on a number of environmental parameters and material properties.

Calvini and Gorassini [6] suggest including LODP (levelling-off degree of polymerisation), rather than glucose, as the asymptotic limit in kinetic equations:

$$\frac{DP^0}{DP} - 1 = \left(\frac{DP^0}{LODP} - 1\right)\left(1 - e^{-kt}\right), \tag{3}$$

and always performing accelerated degradation experiments at least until LODP is reached [6]. This approach might not be practical for historic documents, as the LODP is lower than the DP value of paper at which it can still be safely used, usually assumed to be 250-400 [17,46].

The remaining lifetime of paper is a concept involving the decision as to when paper reaches the end of useful lifetime. The relative lifetime was first defined by Shahani *et al.* as the time required for fold endurance to decrease to an eighth of the initial value [19]. Another possibility proposed was to calculate the ‘time to 50% property loss’ ($PL_{50\%}$) [43]. Both give little idea of the actual lifetime, as they are defined relative to the initial paper properties. Lifetime could however be calculated from the Ekenstam equation as the time needed for the DP to decrease to some value, regarded as the lower limit of usability (typically 250-300) [17,47]. This was also defined for iron gall ink containing documents [48], where one can calculate the time needed for an ink line to become fragile. The point of risk of failure for ink lines was determined at $DP_i = 400$, where the index i indicates the DP of paper with ink application.

A very well received attempt to describe the relative useful life expectancy of paper-based collections was introduced by Sebera [21]. The isoperm method quantifies the effect of temperature and relative humidity upon the anticipated useful life expectancy of paper-based collections in relative terms (relative to paper permanence at 20 °C, 50% RH) and substitutes rates of deterioration with relative permanence, which is the inverse of the ration of deterioration rates [21].

Sebera suggested a linear relationship between the rate of degradation and RH, while it is in fact known that the proportionality is exponential for acidic papers and hyperbolic for alkaline papers with the maximum rate at about 60% RH [49]. Sebera describes temperature dependence using the Arrhenius equation and employing relative permanence:

$$\frac{P_2}{P_1} = \frac{r_1}{r_2} = \frac{RH_1}{RH_2}\,\frac{T_1}{T_2}\;e^{\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}\,. \qquad (4)$$

where *P* represents permanence and *r* deterioration rate, *E* is the energy of activation in J/mol, *R* is the gas constant and *T* is in K.

The isoperm is constructed so that points at which the permanence of paper is equal are linked: if RH is increased, the *T* needs to be reduced by exactly the right amount to keep the deterioration rate constant. A line of constant permanence ('isopermanence') is defined as the isoperm [21]. According to the author the concept is not supposed to be applied to extreme conditions, such as sub-zero temperatures [21], and it is equally not valid at the extremes of RH, i.e. above 80% and below 20%.

Isoperms were recently revised by Strang and Grattan [22], arguing that it is the concentration of water in the cell wall rather than the concentration of water vapour in the atmosphere (the RH), which has a direct effect on the rate of degradation of paper. To account for the non-linear relationship between RH and moisture content they introduced the Guggenheim-Anderson-deBoer equation (GAB), which describes paper moisture sorption.

However, other research shows an exponential dependence of the rate of degradation on relative humidity, at least at elevated temperatures [49]. Additionally, there is evidence that the degradation of acidic papers depends on pH and possibly RH differently to alkaline papers. If this is so, then isoperms are in need of revision and need to reflect differences in paper composition.

Moisture in paper not only represents a reactant, but also the reaction medium for hydrolysis and is also an additional source of radicals (e.g. $OH^{\bullet}$) [20], so the degradation is generally slower in dry environments [50]. Unfortunately, low moisture content of paper leads to decreased flexibility which can lead to physical damage during handling, as brittleness is increased [23,24]. The reason is that water forms intermolecular H-bonds with cellulose and acts as a plasticizer, which increases material flexibility [51]. Stiffening of the polymer structure due to drying or water removal is referred to as 'hornification' [52]. Hornification has frequently been associated with the formation of irreversible intra-fibre hydrogen bonding [52], but has recently been described as the particular case of lactone bridge formation in lignocellulosic materials [52]. On the other hand, paper loses elasticity under high humidity conditions (stiffness index is inversely proportional to the moisture content, reaching zero at around 20% [54]), and a rule of thumb is that its strength decreases by 5-10% for each unit percentage increase in the moisture content in paper [55].

2.1 Temperature and relative humidity fluctuation

While most literature discusses degradation at constant *T* and RH, there is much speculation on the effects of fluctuations in temperature and relative humidity and opinions on the subject are not unanimous. A brief overview of the research on fluctuating environmental conditions is given in

Table 1. The changes in properties after exposure to cyclic conditions are given, relative to changes after exposure to static median conditions.

Table 1: Overview of research on the effects of fluctuating environmental conditions on paper degradation, comparisons are made relative to median conditions (LS – loose sheets, S – stacks, R – reflectance, MSF – mechano-sorptive factor). *^{1} – 50 days cyclic RH / 60 days cyclic T, *^{2} – 80 days cyclic RH, *^{3} – 600 days cyclic RH / 300 days cyclic T (only the results, where the most effect was observed, are shown in the table), *^{4} – non-acid treated / acid treated (20 days),

Reference	Experimental conditions	Samples	Measured properties	Comparison with the outcome at median conditions
Shahani *et al.* [19]	11 h at 40% RH, 1 h ramp up, 11 h at 60% RH, 1 h ramp down, T = 90 °C 46 days	Loose sheets or 100 sheet piles of bleached Kraft wood pulp waterleaf (pH = 6.1) and bleached Kraft paper (pH = 4.5)	Brightness, cold-extraction pH, MIT fold endurance	+55% / +40% ΔR (LS) +33% / +29% ΔR (S) +57% / +100% ΔpH (LS) +18% / -25% ΔpH (S) -40% / -34% rel. life (LS) -18% / -5% rel. life (S)
Bigourdan and Reilly [25]	40% - 80% RH, one week at each, T = 90 °C 60 °C - 80 °C, one day at each, RH = 50% up to a few years	Stacks of acid-processed cotton, acid-processed groundwood and buffered groundwood	folding endurance, tensile strength, brightness (sheet from the middle of stack)	up to -34% / -76% fold. end. retention*^{1} -20% ten. abs. energy*^{2} +72% / +100% Δb* *^{3}
Bogaard and Whitmore [26]	25% - 75% RH, 2 h at each T_{room} 52 weeks	Pure cellulose filter paper (Whatman No. 42) (pH = 4.9)	DP, cold-extraction pH, carbonyl group concentration, brightness of paper, zero-span tensile strength	+127% ΔDP -33% ΔpH +797% Δc(carb. gr.) +188% ΔR +330% Δz-s tens. str.
Sandy *et al.* [23,41]	3.5 h at 30%, 0.5 h ramp up, 3.5 h 80%, 0.5 h ramp down, T = 80 °C 9 or 20 days	Pure cellulose (Whatman No. 1 Chromatography paper), some subjected to acid treatment (1M hydrochloric acid)	tensile energy absorption, crystallinity	+9% / -78% TEA*^{4} +75% ΔCI (acid treated)
Panek *et al.* [15]	50% - 90% RH, 7 h per cycle, T_{room} 10 cycles	Commercial papers: kraftliner, testliner, corrugating medium (virgin and recycled)	Creep (creep stiffness)	+350% MSF(cyc) = 0.28 MSF(const.)
Alfthan [27]	70% - 80% or 60% - 80% or 40% - 80%, 6 h per cycle, T = 20 °C 4 cycles	Isotropic hand sheets (unbleached softwood sulfate pulp)	Creep	No comparison to median RH.

DeMaio and Patterson [56]	1 h at 25%, 5 min ramp up, 1 h at 75%, 5 min ramp down, T = 23 °C 10 cycles	Hand sheets, prepared from softwood bleached kraft pulp	Creep	No comparison to median RH.
This work	84.2 °C - 95 °C, 64.8 h per cycle or 6.5 h per cycle, RH = 65% 55% - 75%, 60 h per cycle or 6 h per cycle, T = 90 °C 4 slow cycles and 40 fast cycles	3 standard papers (Sa, C and Whatman) and 5 real samples (pH = 4.5, pH = 5, pH = 6.1, pH = 7.1, pH = 9.2)	DP	k(cyc.) ≈ k(const.)

One of the first studies on the effect of a fluctuating environment on paper degradation was carried out by Shahani *et al.* [57]. The authors discovered that loose sheets degrade at least as fast under cyclic conditions as under a constant relative humidity of 60%, which was the upper limit of the cycle. This effect was not observed for stacks of sheets (mock book), as the rate of degradation was between those at median RH and at the high RH [57]. The same was observed by Bigourdan and Reilly [58], who also studied stacks of paper under fluctuating temperature or relative humidity, and stated that the phenomenon could easily be explained by thermodynamics.

During cycling, time spent at the worst conditions (higher *T* and RH) has a more substantial effect than the time spent at the best conditions (lower *T* and RH), and cyclic conditions do not provoke a new mechanism of degradation or accelerate it any more than it would be expected [58]. Shahani *et al.* [57], however, drew the conclusion that cellulose exposed to cyclic conditions becomes more accessible to chemical reactants and therefore degrades faster, possibly because a flux of water in and out of the fibres facilitates hydrolysis of acids and increases their mobility, therefore increasing the probability of their interaction with cellulose.

Water transport through paper is a complex process, especially under changing humidity conditions. Moisture is transported through sheets by diffusion of water vapour through pores (more pronounced at low moisture contents) and in condensed form through or along the fibre cell walls (important at moisture contents, higher than 13% in the material, which corresponds to RH > 75%) [59]. A flux of water as assumed by Shahani *et al.*, is only feasible when the difference between equilibrium moisture content and ambient humidity is large and if the relative humidity is higher than 75% [59].

Vittadini *et. al.*[51] suggest that at 1% moisture content only 3% of water is in a liquid-like state, at 5% moisture content the percentage rises to 15% and at moisture contents, higher than 12% only the liquid-like state can be observed, which is in quite good agreement with the conclusions made by Bandyopadhyay [55,59]. As equilibration times, needed for paper to reach a steady state moisture content, are long (up to several 100 min) [55,59], the flux must be slow, so it might not have a significant effect on the mobility of ions.

The effect of cycling humidity was also studied by Bogaard *et al.* [60]. In 10 weeks, DP of pure cellulose decreased by almost a third of the initial value, following which degradation continued at a slower rate until week 30, when DP approached the ‘levelling-off’ point that approximately represents the size of cellulose crystallites (between 250 and 280). The case of zero-span tensile strength was similar. From the approximately equal number of scissions and increase in carbonyl groups, the authors conclude that the degradation observed is predominantly of hydrolytic nature [26]. The authors argue that the suddenness of the humidity change could cause local stresses, as exterior portions of fibres react quickly to new conditions while interiors are slower to respond. This is said to cause high tensile forces as physical loads become concentrated in small areas, weakening chemical bonds in cellulose and potentially breaking them [26].

Bigourdan and Reilly [25] exposed stacks of three types of papers to cycling RH and *T*, but different cycling times for *T* and RH were chosen since thermal equilibration is much faster than moisture equilibration. It was found that the rate of paper degradation under cycling conditions was faster than the rate measured at the steady median RH or temperature and slower than the rate measured at the steady upper limit of the cycle. This however can be explained, as time spent at worse conditions has a greater impact on the state of the paper than the time spent at better conditions. Therefore, the authors conclude that no evidence was found that transitions from one temperature to another (or one RH to another) provoke new mechanisms of degradation or accelerate degradation more than it would be expected. What matters in the case of cycling is the period of time spent at each condition along the way [25].

Recently, the effect of fluctuating relative humidity on tensile properties of paper was also studied by Sandy *et al*. [23,41]. They observed little difference in the case of non-acid treated samples (similar results for constant and cycled RH), however the acid treated ones behaved differently. Thermal ageing under cycling RH conditions appears to enhance the rate at which brittleness of paper increases [23]. The authors suggested the reason for the observed behaviour could be changes in relative humidity causing high local stresses that can result in chemical bond breakage, as discussed by Bogaard *et al.* [26]. Cycling RH could also promote the increase in crystallinity and it is known that paper becomes more brittle with increasing cellulose crystallinity [23]. To confirm this hypothesis the authors carried out another study, where they measured crystallite size before and after degradation experiments and they discovered that the crystallinity did in fact increase, especially if the sample was first treated with acid [41], however, it is well-known that crystallinity generally increases with degradation.

All the above described research was focused on chemical changes affected by environmental fluctuations. However, there is some disagreement between the results, as Bogaard [26], Sandy [23,41] and in the case of single sheets Shahani [19] claim fluctuations cause extra damage to paper, whereas others, e.g. Bigourdan and Reilly [25] state that this can easily be explained by thermodynamics [58].

Chemical changes however are not the only type of change occurring in paper. Fluctuations in the environment could also affect physical properties of paper, and such changes may remain undetected using chemical analytical methods, such as viscometry. However, research has been done on how physical properties are affected, as well.

A phenomenon, which is assumed to be greatly affected by RH fluctuations, is creep of paper, observed when paper deforms under stress [15,27,56,61]. It is generally accepted that creep under cycling humidity is accelerated compared to creep at constant humidity at any level, which is known as mechano-sorptive creep [27]. There is some evidence that creep is most pronounced when cycling parameters are just right, as high creep rates are not observed at cycle times much greater than sorption times (the sorption time is characteristic for a given material, paper needs 200-300 min to reach equilibrium after RH change from 15 to 90% [55]) [61]. After a certain period of time, creep leads to strain at which the paper breaks [15,27,56,61]. Mechano-sorptive creep is suggested to be a consequence of nonlinear creep of the material in combination with stresses created during changes in moisture content. The stresses are caused by inhomogeneous hygroexpansion in the material, material heterogeneities or both [27,56]. However, other theories have been put forward to explain creep under various humidity conditions, such as sorption-induced physical degradation [61]. Accelerated creep was also observed under variations in ambient temperature (between 25 °C and 50 °C) and constant RH, but the magnitude of the effect was much smaller than for fluctuating RH [62].

Creep of paper can be evaluated in different ways, for example using creep curves (strain versus time at a given stress) [15,61], creep compliance (strain divided by stress) [15], isochronous stress-strain curves (stress versus strain for a particular time) [15], lifetime curves (time to failure versus stress) [15], creep rate (change in strain divided by the change in time) [15,61], degree of accelerated creep or accelerated creep ratio (creep rate in cyclic humidity divided by the creep rate in the highest constant humidity) [15,61], or creep stiffness (stress divided by strain) [15].

Panek *et al.* [15] described an experiment of cycling relative humidity between 50 and 90% (each cycle took 7 h, which was assumed to be enough for paper to reach equilibrium moisture content), leading to release of ‘internal stress’. When paper is exposed to cyclic humidity its dimensions change but the magnitude of dimension change decreases with an increasing number of cycles, until change can no longer be detected. When comparing the stiffness of paper, they determined that paper creeps about 3.5 times more in a cyclic humidity environment than at constant conditions at the highest RH [15].

Creep of paper can also be influenced by inter-fibre bonding in the paper itself, as fibre deformation controls paper deformation behaviour. Intra-fibre bonding, however, does not influence accelerated creep if the paper has a fully efficient structure, meaning the load can be evenly distributed throughout paper structure. The mechanisms of creep at constant humidity and accelerated creep are the same, but the amount of strain is increased in accelerated creep. Increased strain is the consequence of uneven stress distribution resulting from moisture sorption. These uneven stress distributions cause more creep than a uniform stress distribution of the same average stress [56].

Erhardt *et al.* [24] showed that allowable RH fluctuations of different materials can be calculated using stress-strain curves if the dimensional change due to RH fluctuation and the amount a sample can be reversibly stretched are known. Even though paper was not included in this work, the concept of determining tolerable fluctuations might be applicable to paper as well. Authors argue that the rate of change of RH is not important, as long as the maximum allowable strains (corresponding to minimum and maximum RH values) are not exceeded. They claim that all of the allowable fluctuations are larger than those generally presently recommended, even more so for unrestrained materials, which can reversibly swell and shrink over much larger RH ranges [24].

Cycling RH also has an effect on iron gall ink on paper, as it causes iron(II) ions to diffuse out of ink regions, as discussed by Neevel [63,64]. In this work, samples were exposed to relative humidity cycled between 35% and 80% (3 h at each RH, 12 min ramp), and migration of the ink was observed on samples, aged for 18 days. This indicates that cycling RH could increase the rate of migration, although there is no direct comparison with samples, exposed to median conditions. However no such migration was observed in samples exposed to 50% RH.

Temperature not only affects relative humidity of the environment, but also has a distinct effect on the moisture content of paper materials stored inside an enclosure, e.g. a box [65]. It is well known that an increase in temperature causes absorbed water to be desorbed from cellulose and that reducing the temperature causes water vapour to be reabsorbed until the equilibrium is reached. Initially, the absorption and desorption to and from paper are fast and effective, but as temperature cycling continues, the amount of water that is absorbed and desorbed is reduced, so the two processes are never fully reversible [65]. Similar happens when RH is increased and decreased, as the time required for desorption is always greater than the time for absorption, which is likely to be connected to the irreversibility of the sorption process, manifested as hysteresis [66,67]. Hysteresis could occur because the response of the matrix is not instantaneous, which is due to sorption and desorption taking place to and from a solid, therefore a different physical state. It has also been attributed to conformational changes in the cellulose surface, due to OH groups in cellulose interacting with water via H-bonds [68]. The extent of hysteresis is likely to depend on crystallinity of cellulose as higher levels of hysteresis have been observed in cellulose with low levels of crystallinity [66].

Although the opinions on how fluctuations in temperature and relative humidity affect paper degradation are different, it is worth noting that mild changes in temperature and RH appear to be buffered by certain types of storage enclosures and by books being packed closely together [32]. As mentioned earlier, paper has a relatively long equilibration time [55,59], so sudden changes in moisture content, as a result of small RH changes are unlikely.

Another observation is that most research has been carried out using broad relative humidity ranges, and the ones demonstrating the most harmful effects were also the ones with the widest RH span (ΔRH = 50%) [23,26,41]. It therefore has to be considered whether these results are representative of real storage conditions, which paper-based objects might be exposed to.

2.2 Damage to paper under the conditions of moderate environmental fluctuations

In this section, two sets of experiments are described to investigate the effect of fluctuating environmental conditions, temperature and relative humidity. Different paper samples (8) were used in the experiments, ranging from pH = 4.5 to pH = 9.5; 3 mock (Sa, C and Whatman), and 5 historic paper samples from the SurveNIR historic paper reference collection (Table 2). They were exposed to cyclic temperature at a constant RH and cyclic RH at a constant temperature.

Table 2: Samples, used in the environmental cycling experiment.

sample	pH	DP
sur 372	5.0	1130
sur 381	6.1	950
sur 601	7.1	1100
sur 648	4.5	640
sur 2093	9.2	1280

The experiments were performed in a Vötsch VC 0020 climatic chamber. The temperature was cycled between 84.2 °C and 95 °C at two different frequencies, while the RH was kept constant at 65%. At lower frequency one cycle took 2.7 days (64.8 h), and four cycles were performed in total. A sample was removed after each cycle, always at 90 °C. Shorter cycles took 0.27 days (6.48 h), meaning the cycling was 10 times faster compared to the previous experiment. 40 cycles were performed, with a sample removed after every ten cycles, always at 90 °C.

Similarly to temperature the RH was cycled between 55% and 75% at two different frequencies at a constant temperature of 90 °C. The longer cycles took 2.5 days (60 h) and the shorter ones 0.25 days (6 h), and samples were removed after one or ten cycles, respectively, always at 65% RH. The same number of cycles was performed as for the experiment with cyclic temperature variations.

Reference samples were aged under stationary conditions, at 90 °C and 65% RH, which are the median conditions.

The average degree of polymerisation (DP) was determined using viscometry, according to ISO 5351:2004. From DP values the rates of degradation were calculated using the Ekenstam equation (Eq 1). The individual degradation rates, obtained under cyclic and non-cyclic conditions, were compared by the 2-sample *t*-test at 95% confidence using Minitab 15® software.

There is a relatively good agreement between the degradation rates obtained under cyclic and constant (median) conditions. When comparing the rates, obtained under different conditions, for each real paper sample we found that there is no statistically significant difference between 60% of all combinations of rates. When plotting the rates, obtained under constant temperature and RH, against those obtained under cyclic conditions, a linear relationship is obtained with the coefficient close to 1 (Figure 1).

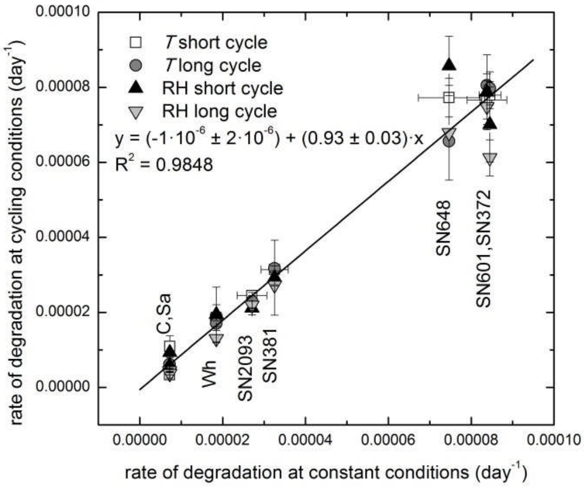

Figure 1: Degradation rates under cyclic conditions, plotted against rates under constant conditions.

This shows that the papers in our experiments degraded at the same rate under cyclic and constant conditions, meaning the cycling temperature and RH did not contribute significantly to the degradation process.

As our experiments were carried out in a limited *T* and RH interval (84.2 °C < T < 95 °C, 55% < RH < 75%), the results are difficult to compare with those obtained by other researchers in similar experiments, but investigating wider ranges of parameters. The reason behind our choice of experimental conditions was to mirror realistic conditions in library and archival repositories. As *T* and RH differences were relatively reasonable (ΔT = 10 °C, ΔRH = 20%), we assume no excessive internal stress due to changing temperature or moisture content was caused, as excessive stress was generally reported as a consequence of sudden and substantial changes in the environmental conditions.

3 Pollutants

Another factor affecting paper degradation during storage is pollution. Primary outdoor pollutants mostly originate from traffic or industrial activity and enter repositories through windows or ventilation, whereas indoor generated ones are emitted due to human activity, building materials or objects themselves [35,36]. The most common outdoor pollutants are nitrogen oxides, sulfur dioxide, ozone and particulate matter (PM) and apart from PM all have been extensively studied in relation to paper degradation [35-37]. Typical pollutant concentrations, both outdoors and in heritage institutions, summarized in [35] and [36], are listed in Table 3.

Concentrations of some of the above (particularly traffic-related pollutants) decreased significantly in the past decades due to environmental regulation; and future predictions show that their concentrations are likely to continue to decrease [69].

Table 3: Typical outdoor and indoor concentrations, summarized by Blades and Tétreault. * is < 1 with chemical filtration.

pollutant	Blades *et. al.* [35] **outdoor** (UK urban) [ppb] except particles	**indoor** [ppb] except particles	Tétreault [36] **Outdoor** [ppb] except particles	**indoor** [ppb] except particles
NO_2	10 – 40	1 - 20 *	1 - 52	1 - 47
SO_2	3 - 20	0 - 15 *	0 - 39	0 - 19
O_3	5 - 25	0 - 10 *	1 - 200	0.1 - 50
H_2S	0.1 - 0.8	0 - 0.5	0 - 7	0 - 29
$PM_{2.5}$	-	-	1 - 50 μg/m^3	1 - 30 μg/m^3
PM_{10}	20 - 30 μg/m^3	0 - 100 μg/m^3	2 - 70 μg/m^3	1 - 100 μg/m^3
CH_3COOH	negligible	< 30	0.1 - 12	16 - 40
HCOOH	negligible	< 30	0.1 - 10	0.1 - 16
HCHO	negligible	< 30	0.4 - 25	8 - 58

Indoor generated pollutants can be emitted from paper itself, and were quantified by Ramalho *et al.* [70]. After artificially degrading pure cotton linters and groundwood pulp paper the emission rates were quantified. Besides VOCs, emitted from paper, pollutants can also have other indoor sources, such as NO_2 produced during the decomposition of pyroxylin in book bindings, formaldehyde and other potentially corrosive volatiles from building and insulation materials, and volatiles and particulates from plants [71].

Air filtration can effectively reduce outdoor-generated pollutant concentrations, while there is little data available about its efficiency regarding indoor-generated pollutants. In studies of the effects of pollutants on paper most research is carried out with very exaggerated pollutant concentrations, usually around 10 ppm, which is about a thousand times higher than the typical concentrations indoors [72-75]. It is argued that the concentrations should be significantly higher than those encountered in real conditions in order to obtain results in real time, even though the extrapolation to lower concentrations might be questionable. This concern was already expressed by Williams and Grosjean [76], stating that at high concentrations SO_2 might form sulfuric acid aerosol at ambient humidity, so the observed damage might be the result of H_2SO_4 uptake rather than SO_2. Some doubts about the validity of high concentration experiments were also expressed by Adelstein *et al.*, when they concluded that observations, obtained in 50 ppm NO_2, reflect changes at much lower concentrations, but that it is not known whether the concentration multiplied by exposure time has a constant effect [74].

Generally, absorption of SO_2 and NO_2 causes acidification of paper, or leads to consumption of its alkaline reserve. This subsequently leads to loss of mechanical properties [72,74,77]. Humidity, besides other negative effects, also plays an important role in the NO_2 and SO_2 uptake, so it is sometimes recommended that papers are not stored at humidity levels, higher that 50% [75,78]. Lignin-containing papers are thought to be more susceptible to pollutant absorption, and consequently damage, especially in terms of yellowing [72,74,77]. However, to our knowledge there is no evidence of pollutants reacting with lignin selectively.

Particulate matter is another potentially harmful pollutant, as particles might create deposits on surfaces and increase corrosion processes due to their hygroscopic nature [36] and in some cases surface affinity to gaseous pollutants [79]. Atmospheric aerosols consist of many different inorganic and organic compounds such as sea salt, nitrates, sulfates, soil dust, soot, primary and secondary organic compounds, heavy metals and polyaromatic hydrocarbons (PAH) [80]. Different types of particles have different effects on artefacts, as organic particles cause deterioration of visual properties by soiling the surface and can also increase SO_2 absorption. S-rich particles, such as sulfates, can cause discolouration, which can be catalysed by Fe-rich particles [81]. Damage can be caused especially when the particles become 'wetted' and a 'liquid phase' with possibly high concentrations of compounds is formed [82]. An example of such a reaction is Fe- and Mn-catalysed oxidation of S(IV)-compounds by oxygen to sulfates or sulfuric acid, which damages paper [82].

The presence of polar functional groups, particularly carboxyl and dicarboxyl, on organic particles can increase the solubility of many organic compounds, present in aerosols, and so allows them to participate in chemical reactions [79]. Therefore organic, S-rich and Fe-rich particles are considered to be more harmful in view of heritage conservation [82]. In a study of a museum environment, carried out by Brimblecombe *et al.* [81], the most common particles smaller than 8 µm were S-rich particles. Organic particles were abundant in all particle sizes investigated (< 20 µm) and alumosilicates were present in particles larger than 2 µm. Alumosilicates originate from both natural and anthropogenic sources such as soil dust and fly ash aerosols, traffic, agriculture, deforestation etc. [80]. It was also found that organic particle concentration was generally higher indoors than outdoors, which suggests an indoor source. Similar was found by Gysels *et al.* [82], Godoi *et al.* [79] and Kontozova-Deutsch *et al.* [80]. Particles are usually classified according to their size into 0.5, 1, 2, 4, 8 and 20 µm fractions [81,82]. Indoor concentrations of particles, determined by Gysels *et al.* in the Royal Museum of Fine Arts in Antwerp, Belgium [82] ranged from $1.9 \cdot 10^5$ to $1.6 \cdot 10^6$ particles/m^3, of which fine particulate (<2.5 µm) concentration was highly variable between 0.02 and 5 µm/m^3. Similarly to the already mentioned inorganic pollutants the concentration of coarse particulates can be reduced by air-conditioning and filtration, which was shown by Godoi *et al.* [79].

Lately, indoor-generated pollutants have attracted increased interest [35-37,83], as the concentrations of volatile organic acids and aldehydes can exceed the concentration of traffic generated pollutants by a factor of 10 and more [83]. Volatile organic compounds (VOCs) cannot be removed from the atmosphere as easily as previously mentioned pollutants, as the sources are indoors. Unfortunately VOCs can also have a deteriorating effect on paper. A study was recently carried out using different types of paper (different composition and pH) and different VOCs, which were shown to have a negative effect on paper degradation during accelerated degradation experiments [9]. Papers were put into glass vessels together with VOCs and in some cases pollutant scavengers and exposed to 50 °C for one year. After the experiments, DP and molecular weight of the samples were determined, using viscometry and size exclusion chromatography respectively. It was shown that volatile acids have the most pronounced negative effect on paper degradation, although similar results were obtained with aldehydes, as well. The effects of added VOCs differ in dependence of paper type, with neutral and alkaline papers being more affected than acidic and lignin-containing papers, as the latter are net emitters of VOCs. It was also found that removal of VOCs has a significant positive effect on paper stability, whereas removal of oxygen is also beneficial, but to a smaller extent [9].

The behaviour and consequently effect of pollutants can depend greatly on relative humidity, more accurately on the moisture content of paper. Inorganic as well as organic pollutants may hydrolyse, which of course applies to water absorbed in paper as well:

$SO_2 + 2H_2O \leftrightarrow HSO_3^- + H_3O^+ \qquad pK_{a1} = 1.81$

$HSO_3^- + H_2O \leftrightarrow SO_3^{2-} + H_3O^+ \qquad pK_{a2} = 6.91$

The shift of the above equilibria depends on the pH of paper, as pH > pK_a shifts the equilibrium to the right and pH < pK_a shifts it to the left. This means that in all papers the first equilibrium will be strongly shifted to the right, producing hydronium ions (H_3O^+) causing cellulose hydrolysis. On the other hand, the second equilibrium shifts to the left for acidic and to the right for alkaline papers, only producing hydronium ions in alkaline papers and causing no extra damage to the acidic ones. In alkaline papers, especially those with a substantial alkaline reserve, this would not cause much direct damage, as hydronium ions would be neutralised by the alkaline reserve, until it is consumed.

The two reactions primarily considered for nitrous oxides are [77]:

$2\ NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + H^+ + NO_3^-$

$NO(g) + NO_2(g) + H_2O(l) \rightarrow 2\ HNO_2(aq)$

As the dissolution of NO and NO_2 in water is slow, these two reactions might not play an important role in paper. The following reaction takes place on the surface and is probably of greater importance:

$2\ NO_2(g) + H_2O(ads) \rightarrow HNO_2 + HNO_3$

and is the main source of nitrous acid (HNO_2) indoors [77].

Besides, hydrolysis pollutants can also react with each other, which affects their indoor concentrations. When ozone is present the risk increases for alkaline papers as well, as HSO_3^- can be oxidised to HSO_4^-:

$HSO_3^- + O_3 \rightarrow HSO_4^- + O_2$

HSO_4^- hydrolyses when pH of the medium is higher than 2, a condition met in all papers:

$HSO_4^- + H_2O \leftrightarrow SO_4^{2-} + H_3O^+ \qquad pK_a = 1.99$

The amount of nitrogen dioxide also depends on the presence of ozone:

$NO + O_3 \leftrightarrow NO_2 + O_2$

High ozone concentration shifts the equilibrium to the right, whereas the reverse reaction is driven by sunlight [81].The indoor pollutants acetic and formic acid also hydrolyse:

$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+ \qquad pK_a = 4.75$

$HCOOH + H_2O \leftrightarrow HCOO^- + H_3O^+ \qquad pK_a = 3.75$

In papers with pH < 4.75 dissociation of acetic acid does not occur, so no H_3O^+ ions are produced, and the presence of acetic acid will not cause additional damage. The case of neutral or alkaline papers is potentially different, as acetic acid will dissociate (the equilibrium shifts to the right), producing hydronium ions and thus accelerating paper degradation. The pH range, where formic acid dissociates, producing H_3O^+ ions, is somewhat broader than for acetic acid, as the equilibrium shifts to the right at pH > 3.75.

Some recommendations have been made with respect to safe exposure levels [35]: <4 ppb for SO_2, <5 ppb for NO_2 and <13 ppb for O_3. The recommended level for airborne particles PM_{10} is <75 μg/m^3; however no suggestions have been made about volatile organic compounds. Some standard regulations for storage and exhibition of archival documents [84] are more rigid, suggesting that the air in a repository should be "kept free of air pollution, acidic and oxidizing gases and dust". This is of course unrealistic, as it is impossible to achieve complete absence of pollutants. Tétreault [36] suggested different pollutant levels for different exposure times (1, 10 and 100 years): for a 1-year exposure <400 ppb (1000 μg/m^3) for acetic acid, <0.71 ppb (1 μg/m^3) for hydrogen sulfite, <5.2 ppb (10 μg/m^3) for nitrogen dioxide,<5.0 ppb (10 μg/m^3) for ozone, <3.8 ppb (10 μg/m^3) for sulfur dioxide and <10 μg/m^3 for fine particles ($PM_{2.5}$) are suggested.

Tétreault based his suggestions on two approaches: the no and lowest observed adverse effect levels (NOAEL and LOAEL) of an airborne pollutant surrounding an object, and the doses of a pollutant (concentration multiplied by the length of time, LOAEL · time = LOAED) [36]. He defines the adverse effect as the first visually perceptible change; a specific chemical of physical characteristic of the material (or object) usually considered undesirable. NOAEL is defined as the highest level of a pollutant that does not produce any observable adverse effect on a specific characteristic of a material. For establishing the NOAEL and LOAED the complex deterioration process is simplified to the most abundant (or harmful) pollutant having the most effect on the rate of deterioration and other parameters, such as temperature and relative humidity, being constant [36]. Therefore, these concepts should only be used in well defined and stable environmental conditions. This means that the NOAEL and LOAEL levels would have to be determined for each combination of environmental parameters, such as *T*, RH, light exposure and for various paper compositions.

In the case of pollutants emitted by the material itself, and at the same time promoting its degradation, the concepts of NOAEL or LOAED might not give realistic results.

3.1 Damage to paper due to pollutant exposure

To investigate and compare the effects of the most abundant pollutants in a repository an experiment was designed where different types of paper were exposed to acetic acid, nitrogen dioxide and formaldehyde. As mentioned earlier most experiments reported so far have been carried out with highly exaggerated pollutant concentrations, which may cause changes in the reaction mechanisms [76]. To avoid that, papers were exposed to lower and more realistic pollutant concentrations and the temperature was increased to obtain results in real time.

Papers of five different compositions (Table 4), representing typical real historic samples from the SurveNIR historic paper reference collection (A – rosin sized, N – pseudo-neutrally sized and B – $CaCO_3$-filled bleached pulp containing paper; L – lignin-containing rosin-sized paper and R – gelatine-sized rag paper), were exposed to 1000 ppb of acetic acid, nitrogen dioxide and formaldehyde at 80 ^oC and 45% RH, with the exception of the control set of samples that was degraded at 80 ^oC and 45% RH in the absence of pollutants.

Table 4: Samples, used in the pollution study.

sample	code	pH	DP^0
sur 648	A	5.3	563
sur 780	N	6.0	735
sur 2229	B	7.3	2263
sur 847	L	3.5	-
JP 427	R	5.9	1430

The experiments were carried out in a purpose-built flow-through reactor set-up, consisting of a humidity generator (Instruquest V-Gen™ Dew Point/RH generator model 1) and a pollutant generator (Vici Metronics Model 150 Dynacalibrator®), connected by PTFE tubing. A flow controller (Aalborg GFC17) was used to ensure the appropriate flow into the pollutant generator to obtain the desired concentration. After the mixing coil a trap for potential water droplets was added to avoid introducing liquid water into the flasks. The experimental setup is shown in Figure 2.

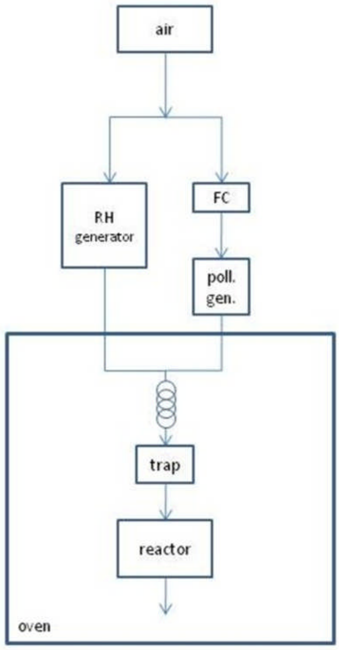

Figure 2: Scheme of the experimental setup, used for degradation of samples in dynamic polluted atmosphere (FC – flow controller).

Three 2 cm x 2 cm pieces of each sample were attached onto a stainless steel spiral and inserted into a flow-through glass reactor; four reactors for four different conditions were prepared. The reactors with samples were flushed continuously for 168 h (one week). After the experiment, the DP of all but the lignin-containing paper (L), was determined according to the BS ISO 5351:2004 standard. VIS reflectance spectra of all samples were measured using an X-Rite 530 SpectroDensitometer.

The papers, exposed to a pollutant, degraded more than the ones only exposed to elevated *T* and RH (Figure 3).

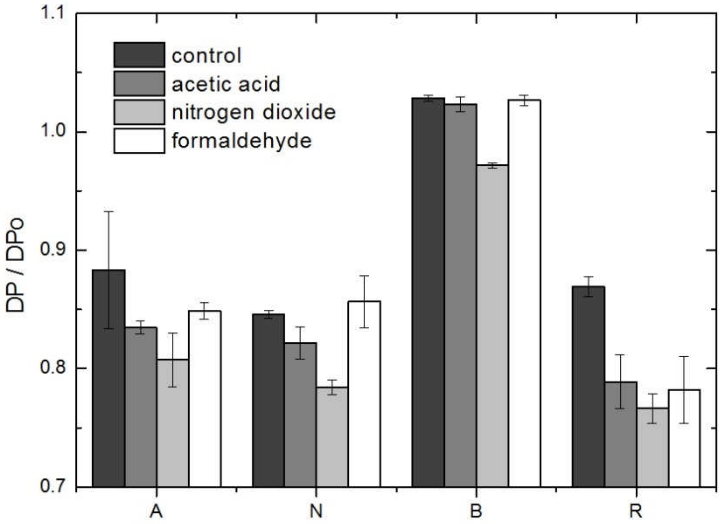

Figure 3: DP/DP^0 for different paper types (A – acidic, N – neutral, B – alkaline, R – rag), after 1 week exposure to 80 °C, 45% RH and different pollutants.

Generally, exposure to acetic acid caused more damage compared to exposure to formaldehyde, although both effects are in the same order of magnitude. Nitrogen dioxide seems to be the most harmful pollutant regardless of the paper composition. This is not entirely surprising, as NO_2 is a good oxidant and can also react with water, adsorbed to the surface of paper, which yields nitrous (HNO_2) and nitric (HNO_3) acid. pK_a of both acids are below the pH values of all papers (3.4 and -1.4 respectively), which means they hydrolyse in paper, producing H_3O^+ ions. Acetic acid has some effect on all but the alkaline sample (B), which presumably has enough alkaline reserve to not be affected by acetic acid during the duration of the experiment. Although formaldehyde is reasonably stable at room conditions it may be more prone to oxidation at the elevated temperature used during the experiment, to form formic acid, potentially having the same effect as acetic acid.

Pollutant exposure also had an appreciable effect on paper colour (Figure 4), assessed using the CIE 1976 L*a*b* system. Colour change was calculated as

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}.$$

Similarly to chemical properties, the optical properties have generally deteriorated significantly more in polluted environments. The effects of acetic acid and formaldehyde are similar, however, NO_2 generally leads to significantly more discolouration of paper of several different compositions. This could indicate that NO_2 participates in oxidation reactions leading to coloured products, in addition to hydrolysis. This is corroborated by the pronounced colour change of the lignin-containing sample, as it is known that the presence of lignin increases the sensitivity of paper to oxidation [20]. It is worth noting though that acetic acid concentrations in repositories and especially archival boxes are several times higher (typically 10x [83]) than those of nitrous oxides, while formaldehyde concentrations are the lowest of the three, which helps in prioritising the pollutant which is likely to cause most damage during long-term storage. Ozone concentration in repositories is typically even lower than that of formaldehyde, so it was not included in the experiment described above. Although extrapolation to room conditions is necessary, there is therefore indication that in a repository the effects of acetic acid and nitrogen dioxide could be comparable in terms of DP loss, while in terms of colour change, NO_2 appears to be of higher significance. The effect of formaldehyde appears to be less significant.

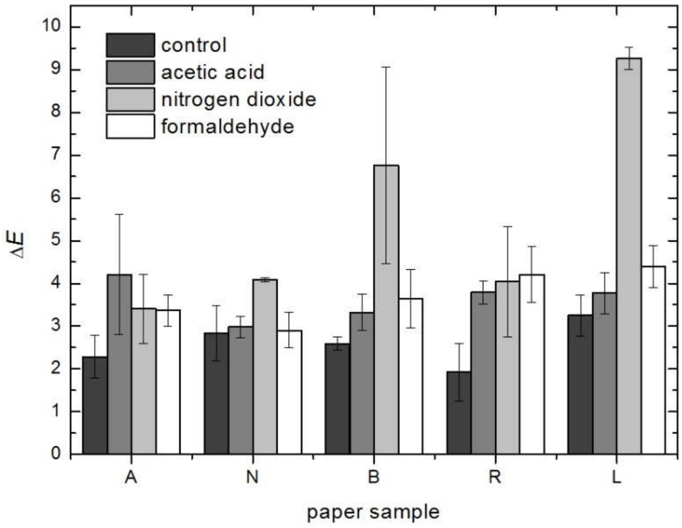

Figure 4: Δ*E* for different paper types, exposed for a week to 80 °C, 45% RH and 1000 ppb of a pollutant (A – acidic, N – neutral, B – alkaline, R – rag, L – lignin-containing)

4 Stack versus single sheet degradation

Another phenomenon that should be taken into account when discussing paper degradation, particularly in relation to indoor-generated pollutants, is stack versus single sheet degradation [43,85-87], where the rate of degradation of sheets in the middle of a stack of paper is often greater than the rate of degradation of the top and the bottom few sheets. This was shown by measuring yellowing of paper, zero-span tensile strength and cold extraction pH, which all point towards more degraded paper (more yellow and acidic, smaller tensile strength) in the middle of a stack [87]. This could be explained by volatile acids accumulating in the middle of the stack, as they are unable to escape into the environment [19,87]. However, an opposite effect is sometimes observed, where the margins of a book are more acidic and therefore more degraded compared to the middle. This could be due to past pollution exposure or lignin oxidation, as the margins are more accessible for exogenous pollutants, oxygen and light. The accumulation of degradation products, such as acids, in the pores of fibres and inter-fibre spaces creates an autocatalytic effect, resulting in enhanced degradation [33,43,85,87]. The ‘stack versus single sheet’ phenomenon should be taken into account when designing accelerated ageing experiments, however, it can probably only be addressed by a better understanding of transport phenomena, both of gases, as well as of degradation products and water, through stacks of paper.

5 Light

Most polymers are sensitive to radiation at wavelengths including natural light (λ > 280 nm). This is mainly due to the sensitivity of unsaturated groups (C=O and C=C) with absorption maxima between 200 and 400 nm. Photolysis is also enhanced by additives and impurities, which may absorb light even more efficiently than the polymer itself [88].

The consequences of long term exposure to light are increased acidity, discolouration, enhanced production of carbonyls and mechanical strength loss [28,29] and these can be observed up to the 5th sheet from the surface of a paper stack [29]. Minor or no changes in appearance do not always imply that no degradation occurred, as pronounced decrease in DP has been observed in cellulose samples (Whatman), which showed only a minor change in brightness [89]. Paper can also be affected by light even if immediately after the exposure little or no change in its visual and mechanical properties is observed [89]. The effect of light is thought to be of lower importance for paper degradation than the effect of pollutants in an average archive environment [90] and its negative effects are avoided by storage in the dark, except for papers that have been previously exhibited [28,89].

So far no dose response functions, directly linking light exposure and RH have been derived, although there is indication that at high RH photo-degradation is exacerbated [89]. Similar to pollution, more research is needed to describe the effects of paper composition and environmental parameters on photodegradation in a single multiparametric dose response function.

6 Paper composition

It has been shown that papers containing more lignin and ash are generally more sensitive to oxidation, and possibly to the overall degradation process, including oxidation, hydrolysis and peeling-off reactions [20]. There is some evidence about the connection between high lignin content and accumulation of paper acidity as a consequence of lignin degradation [91], however knowledge on the effect of lignin on paper degradation in the absence of light is still insufficient although brightness reversion during thermal degradation of lignin-containing papers has been well studied [31,91].

As mentioned above, paper degradation is affected by acidity and exposure to acidic pollutants, as acid-catalysed hydrolysis is thought to be a major cause of strength loss [5,7]. Acidity is both the consequence of accumulation of acids in paper during degradation processes and the result of acids introduced into paper during production, and it is known that acidic papers are less stable compared to neutral or alkaline ones [91,92]. Exposure to acids, especially combined with increased (or fluctuating) relative humidity, can cause increased crystallinity, which results in inferior mechanical properties [41]. Acidity is also linked to the ‘stacking effect’ described above [87].

As mentioned earlier the rate of paper degradation strongly depends on its acidity (pH). Despite this, pH has only rarely been considered in dose-response functions [5].

7 Conclusion

There are many agents affecting paper degradation during long-term storage, however they are not all equally damaging or unavoidable. Some, such as light or biodeteriogens, can be minimized or avoided relatively easily, whereas others, e.g. indoor generated pollutants or fluctuating temperature and relative humidity, are not that easy to control without major resource implications. Another issue, which has mainly been overlooked, is that some environmental factors can have synergistic effects.

An agreement has not been reached yet on whether realistic fluctuations in the environment accelerate paper degradation or not, as different results were obtained by different researchers investigating different chemical or physical properties of paper. In this work, no evidence was found for reasonably small fluctuations of temperature (10 °C) and RH (20%) having a significant effect on the most commonly measured chemical property, degree of polymerisation.

New research is also presented demonstrating that in repositories, acetic acid and NO_2 might significantly contribute to degradation, although their effect at realistic concentrations needs to be ascertained. NO_2 contributes to colour change more than other studied pollutants.

Despite the numerous studies of paper degradation, we still lack a general dose-response function taking into account the most important agents of deterioration: *T*, RH, pollutants and paper composition (acidity probably being the most important parameter). Only with such a function, we will be able to assess:

- Which environmental parameters are more important to control than others
- Which types of paper are more susceptible to particular agents of deterioration
- How the permanence (or lifetime) of paper is affected by environmental parameters other than *T*.

8 Acknowledgement

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