ORIGINAL PAPER

Effects of NO$_2$ and acetic acid on the stability of historic paper

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Abstract This research investigates degradation of historic paper in polluted environments during long-term dark storage. In an innovative experiment, degradation rates at realistic pollution levels are compared with degradation rates in the absence of pollution, using a set of real historic papers. The most abundant pollutants in repositories in post-industrial environments are taken into account: acetic acid and nitrogen dioxide. Their action was assessed in terms of reduction of 'handling' (as defined by decrease in degree of polymerisation) and 'display' (as defined by discolouration) lifetimes. Extrapolations to room conditions enabled lifetime predictions in conditions that are comparable to a real archival or library repository environments while prediction uncertainties were analytically evaluated to assess the significance of conclusions. While 10 ppb of NO$_2$ does reduce the handling lifetime of almost all types of paper, their predicted lifetimes were still assessed to be several millennia, with the exception of acidic paper. Acetic acid at concentrations that are typical for archival and library repositories (<100 ppb) has significantly less effect than NO$_2$ while it does not affect display lifetimes. From a conservation management perspective, it needs to be addressed whether the predicted reductions in otherwise significant handling lifetimes are of real concern and whether air filtration in archival and library repositories is justified.

Keywords Paper degradation · Cellulose · Hydrolysis, oxidation · Pollution · Cultural heritage

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Introduction

Historic paper degradation can be affected by many environmental factors, temperature and relative humidity being possibly the most important during storage in the dark (Zervos 2010). In the late nineteenth century, pollution emerged as a possible factor of concern causing additional deterioration of library objects. Outdoor generated pollutants mostly originate from traffic and industry, or are formed in secondary atmospheric processes, and enter repositories storage areas through ventilation. The most common are nitrogen oxides, sulfur dioxide (although less so in post-industrial environments), ozone and particulate matter and they all generally have a negative effect on paper (Blades et al. 2000; Hatchfield 2002; Tétreault 2003; Grau-Bové et al. 2014). Pollutants such as SO$_2$

and NO_2 increase the acidity of paper, which subsequently leads to loss in mechanical properties (Bégin et al. 1999; Johansson 2000; Adelstein et al. 2003). Lignin-containing papers are more susceptible to pollutant absorption, and consequently damage, especially in terms of discolouration (Bégin et al. 1999; Johansson 2000; Adelstein et al. 2003). The detailed reactions of pollutants are described in more details, and reviewed, elsewhere (Bégin et al. 1999; Johansson 2000; Adelstein et al. 2003; Menart et al. 2011a). Their monitoring is prescribed by collection care guidance documents (BSI PAS198) and 'acceptable' (i.e. allowable, despite promoting degradation) concentrations have been proposed for long-term storage.

In the recent past (mid twentieth century), concentrations of outdoor generated pollutants were significant, which raised concerns about their effect on degradation of paper-based objects. The main pollutant of concern was SO_2, with outdoor concentrations in London, UK, of up to 200 ppb in the 1950s and 1960s (Brimblecombe 2006; Brimblecombe and Grossi 2010) and consequently, a lot of research was done on the effects of SO_2 on paper (Johansson et al. 1998; Bégin et al. 1999; Adelstein et al. 2003). The concentration of sulfur dioxide however decreased significantly over the past few decades and will continue to decrease in the future (Brimblecombe and Grossi 2009, 2010), which means it is may no longer represent a significant risk to historic paper in post-industrial environments, but may still be a concern elsewhere (Agbota et al. 2013).

The decrease in the concentrations of 'traditional' pollutants (NO_x, O_3, SO_2) along with more knowledge of paper degradation led to a shift in interest from outdoor- to indoor-generated pollutants. Indoor-generated pollutants are mainly organic compounds, introduced into the environment by emission from building and furnishing materials (Brimblecombe and Cashmore 2004) and can also be emitted from collection materials (Ramalho et al. 2009). In order to cause degradation in materials pollutants have to deposit to their surface, which means they have to be polar, such as organic acids or other short-chain carbonyls, or reactive, such as ozone (Brimblecombe and Cashmore 2004). The concentrations of volatile organic acids and aldehydes in archival repositories can exceed the concentrations of traffic generated pollutants by a factor of 10 (Fenech et al. 2010). In a study, carried out in The National Archives (UK), total volatile organic compounds

(excluding formaldehyde and acetic acid) and acetic acid concentrations were determined, 20–30 ppb of each was found in the repository and approximately 70 ppb of each in archival boxes. The concentrations of NO_x were approximately 25 and 10 ppb in the repository and archival boxes respectively, whereas SO_2 and O_3 concentrations were well below 5 ppb (Fenech et al. 2010). In addition to this study, air pollution measurements were conducted in the National Archives of the Netherlands, confirming that the 'traditional' outdoor-generated pollutants are present in repositories in very low concentrations compared to pollution levels in the past (Grossi and Brimblecombe 2007; Brimblecombe and Grossi 2010), SO_2 even below the limit of detection (0.5 ppb). In a repository without air filtration 10 ppb of NO_2 was measured, while the concentrations in archival boxes and a repository with air filtration were below 4 ppb for NO_2, SO_2 and O_3 (Menart et al. 2011b).

Indoor concentrations of O_3 were found to be well below 5 ppb both in The National Archives (UK) and the National Archives of the Netherlands, making O_3 significantly less abundant in a typical repository than NO_2 (Fenech et al. 2010; Menart et al. 2011b). This is also consistent with the results of a study, carried out at the National Archives of the Netherlands a decade earlier (Havermans and Steemers 2005).

The two Archives in the UK and the Netherlands are situated in quite different environments. The location of the former is in a reasonably unpolluted suburban area of London and the latter is located in the city centre of The Hague, between the central train and bus station. The concentrations of traffic-generated pollutants indoors were found to be similar in both, which could mean that the values are representative of an archival repository in a post-industrial economy (although O_3 concentrations are likely to be higher in geographic areas with more intensive insolation).

In recent years acetic acid has also raised concerns, as it can be present in repositories in concentrations much higher than NO_2 and as an acid is thought to contribute to acid-catalysed hydrolysis of cellulose (Menart et al. 2011a). A recent survey of the environment in several archives and libraries showed that acetic acid concentrations were between 20 and 150 ppb in repositories, containing paper-based collections (Gibson et al. 2012).

To investigate the effects of pollutants on historic paper, a variety of approaches has been employed by

different researchers. Most research was carried out with highly exaggerated pollutant concentrations (in the ppm range at room T), which is several orders of magnitude higher than the typical concentrations indoors (Bégin et al. 1999; Dupont and Tétreault 2000; Adelstein et al. 2003). The argument is that experimental concentrations should be significantly increased to obtain measurable results in a reasonable time, even though the extrapolation to lower concentrations is uncertain. The assumption of linearity in this extrapolation has already been questioned by Williams and Grosjean (1992), stating that at high concentrations SO_2 might form sulfuric acid aerosol at ambient humidity, so the observed degradation might be the result of H_2SO_4 uptake rather than SO_2. Doubts about the validity of high concentration experiments were also expressed by Adelstein et al. (2003), when they concluded that observations, obtained in 50 ppm NO_2, reflect changes at much lower concentrations, but it is not known whether the concentration multiplied by exposure time has a constant effect. Their observation was that life expectancy of paper also depends on temperature and relative humidity and that the behaviour of paper is not possible to predict using a single test condition.

Multiplying concentration by time is used to define a pollutant dose, which is thought to have a proportional effect on paper degradation (Tétreault 2003). Based on this principle a concentration of 100 ppb in 10 years would lead to the same extent of degradation as a concentration of 10 ppb in 100 years. The problem with this approach is that it neglects all other factors of degradation, the main ones being T and RH, the effect of which could be comparable or possibly more important than that of the pollutant. The concept might be valid for some material/pollutant interactions, where T and RH do not play an important role in comparison (such as silver tarnishing). However, the applicability of the concept of dose to paper degradation is not as clear, as factors other than pollutants are likely to contribute significantly to paper degradation during long-term storage.

In this study experiments were designed to investigate the contribution of pollution to degradation rates and quantify pollutant effects at close-to-real concentrations, exaggerated by only one or two orders of magnitude. Experiments were carried out at elevated temperatures, however care was taken to perform them below the glass transition temperature of cellulose

(approximately 100 °C) to ensure the processes were as similar to room conditions as possible. Relevance to lower (room) temperature degradation was also provided by using three temperatures instead of only one. Experiments at three temperatures allowed for extrapolation to lower temperatures and a quantitative comparison of the effects of pollutants with the effects of T and RH, which should allow library and archival collection managers to prioritise environmental management options.

Experimental

Experiments were carried out to investigate the effect of the most abundant pollutants in repositories on paper. Acetic acid and nitrogen dioxide were selected as the most harmful pollutants based on previous work by the authors (Menart et al. 2011a, 2011b), and recent monitoring at the National Archives (UK) (Fenech et al. 2010). Although formic acid has recently been proposed as a potential threat to paper (Tétreault et al. 2013) it has not been selected for this study, as it is found in concentrations significantly lower compared to acetic acid (at least an order of magnitude) even in archival boxes.

Paper samples were cut into 2×2 cm squares and attached to a stainless steel spiral. The samples were then placed in 1-L glass flasks (GL 45, Schott Duran®, Wertheim/Main), which were closed with PP/PTFE caps, fitted with an inlet and outlet (GL14, Schott Duran®, Wertheim/Main). PTFE tubing (Bola, Grünsfeld) was inserted into the inlet/outlet nozzles, which enabled continuous (dynamic) flushing with humidified air (control experiment) or humidified air enriched with NO_2 or acetic acid (AcOH). Three sample sets were prepared and exposed to 43 % RH and 1,000 ppb of a pollutant (or none) at three temperatures (80, 70 and 60 °C) to enable extrapolation of the results to lower temperatures. RH conditions were selected to be in a range typical for an archival repository (Menart et al. 2011b).

To obtain the desired humidity conditions, humidity generators were used (InstruQuest V-Gen™ Dew Point/RH generator model 1, InstruQuest, Coconut Creek, FL) and pollutant generators with pollutant permeation devices (acetic acid permeation tube and NO_2 permeation wafer, Vici, Poulsbo, WA), were used to obtain the desired concentrations of pollutants

Table 1 Samples, used for the experiments (year of production in brackets when applicable) and the initial values of pH and DP (* fibre composition and rosin content data obtained from the SurveNIR database, where "cellulose" is bleached wood pulp and "wood" is groundwood pulp)

Code	SurveNIR code	PH	DP_0	Year or time of production	Fibre composition*			Rosin content* (mg/g)
					Wood	Cellulose	Cotton	
A1	Sur 648	5.3	555	1910		1		2.57
A2	Sur 780	5.6	684	1936		0.1	0.8	2.33
B	Sur 2229	7.4	2330	1997		1		0
R	JP 427	5.4	1852	19th C			1	0
L	Sur 847	5.2	–	1939	0.9	0.1		1.16
W	Whatman	5.4	2533	2008			1	0

(Vici Metronics Model 150 Dynacalibrator®, Vici, Poulsbo, WA). The generators were connected to form a purpose-built set-up, using PTFE tubing and flow controllers (Aalborg mass flow controller GFC17, Aalborg, Orangeburg, NY) to obtain air with appropriate pollutant concentrations and relative humidity.

The samples were flushed continuously with a combined flow of 250 mL/min to ensure a constant pollutant concentration and RH. The experiments took between 21 and 135 days depending on the temperature. Every sample set contained six pieces of each paper, which were individually removed from the flask in equal time intervals. The samples were analysed using viscometry to determine the degree of polymerisation (BS ISO 5451:2004). DP was calculated from intrinsic viscosity, using the Mark-Houwink-Sakurada equation (Evans and Wallis 1987):

$$DP^{0.85} = 1.1[\eta]$$

Vis diffuse reflectance spectrophotometry using the CIEDE2000 system was also used to analyse samples. Vis reflectance spectra were measured using an X-Rite 530 SpectroDensitometer (X-Rite, Grand Rapids, Michigan) and overall colour change was calculated according to the ΔE_{00} formula (Luo et al. 2001).

Experiments were carried out with 6 different paper types, 5 real historic papers (2 acidic–A1, A2, 1 alkaline–B, 1 lignin-containing–L, and 1 made of rags–R) and purified cotton linters cellulose (Whatman filter paper No. 1, Maidstone). Samples from the SurveNIR[1] historic paper reference collection were used (Trafela et al. 2007). The papers differed in their year of production, initial degree of polymerisation

(DP_0) and to some extent pH (Table 1). DP measurements cannot be carried out on lignin-containing paper, as lignin is insoluble in cupri-ethylenediamine, the solvent used in viscometric determination of DP, therefore no DP value is given.

$L*a*b*$ values of samples before the degradation experiment are given in Table 2.

Cellulose chain scission rates for individual paper types were determined by plotting $(1/DP–1/DP_0)$ versus time, according to the Ekenstam equation (Ekenstam 1936):

$$kt = \frac{1}{DP} - \frac{1}{DP_0}$$

where k is the chain scission rate, t time, DP_0 initial degree of polymerisation and DP degree of polymerisation measured after the degradation experiment. Linear regression analysis was carried out using OriginPro 8.6 (Northampton, MA) software.

The rate of colour change was determined in a similar way, by plotting ΔE_{00} against time. As the plots were linear at all three temperatures the rate, k, was determined from the line slope. As an example, colour change of lignin-containing paper at 70 °C is shown in Fig. 1.

Table 2 Initial $L*a*b*$ values for all paper samples

Sample	$L*$	$a*$	$b*$
A1	85.5	3.6	17.5
A2	91.4	0.7	11.5
B	94.1	2.1	−8.0
R	90.2	0.3	10.6
L	85.3	2.8	15.5
W	96.4	−0.1	1.0
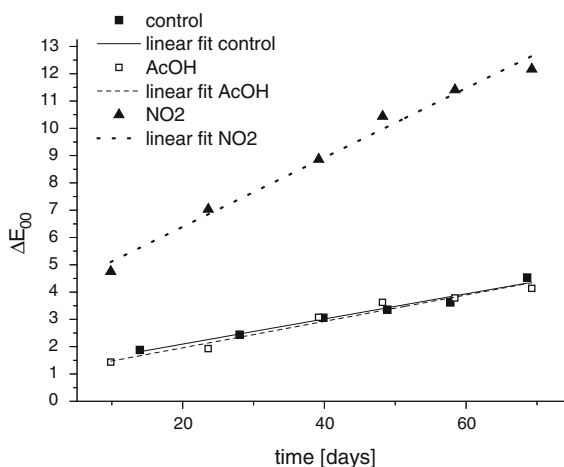
Fig. 1 Total colour change of lignin-containing paper at 70 °C

The rates described above were used to extrapolate degradation rates (i.e. chain scission and colour change rates) to lower temperatures. This was done by calculating linear regression according to the linearised form of the Arrhenius equation:

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

Logarithmic values of the degradation rates are plotted against the inverse of the temperatures, at which the rates were obtained. The slope of the line obtained is the negative of the activation energy E_a, divided by the gas constant R, and the intercept is a logarithmic value of the pre-exponential factor A. Regression lines were drawn using linear fit with errors as weights, using OriginPro 8.6 software, with direct weighting. Line slopes and intercepts with standard errors were obtained to calculate the activation energy, E_a, and the pre-exponential factor, A, in the Arrhenius equation, and used for further calculations. Temperature monitoring, carried out in the National Archives of the Netherlands (Menart et al. 2011b) and in The National Archives (UK) (Hong et al. 2012), showed the average temperature was 18 and 19 °C, respectively. Degradation rates, obtained from the experiments reported here, were therefore extrapolated to 18 °C.

The pH of papers was determined using the cold extraction method, where deionised water was added to a paper sample and left for 24 h. The pH of the solution was then measured using a micro electrode. The pH meter used was SevenGo Pro™ Portable pH/

Ion Meter SG8 and the electrode was InLab® Micro pH combination electrode (both Mettler Toledo International Inc).

Results and discussion

To evaluate the differences between the effects of different pollutant conditions on paper, remaining useful lifetimes were calculated. These were defined as the period of time it takes for paper to be no longer usable (fit) for a particular purpose. This enables us to distinguish between different purposes of objects where either DP or colour matter. Although for archival material DP is generally the more important property as it defines when a document can be safely handled (which is the primary use of archival documents), colour could play an important role if for example some of the archival material should go on display, and a document, which can no longer be handled safely due to brittleness, could still be displayed. 'Handling lifetime', $t_{handling}$, is defined here as the time needed for paper to reach the safe handling threshold DP, DP = 300 (Smith 2004). With a known starting DP and degradation rate, extrapolated from the experiments, this can be calculated using the Ekenstam equation:

$$k_{DP}t_{handling} = \frac{1}{300} - \frac{1}{DP_0}$$

The 'display lifetime', $t_{display}$, is defined here as the value of ΔE_{00}, which is perceived as unacceptable in a museum context (Ashley-Smith et al. 2002). Although this might not seem as relevant to archival documents, the colour should not be neglected entirely, as archival collections (or parts of it) are often displayed as well, which, at least temporarily brings them closer to the museum context. Unacceptable colour change amounts to 10 perceptible changes (PCs), where one PC equals $\Delta E_{00} = 1.5$.

$$k_{\Delta E}t_{display} = 15$$

When discussing display lifetimes it should be noted that light-induced degradation was not included in the experiments, discussed here. Although light is known to be an important factor in paper degradation (Bukovský 2000; Zervos 2010), it does not contribute significantly to paper degradation in an archival environment, where documents are stored in the dark,

and investigating effects in an archival setting was the main objective of this study. Display lifetimes are therefore calculated excluding light-induced degradation, which means that papers would only actually reach them if they were mainly kept in the dark and photodegradation was negligible.

Handling and display lifetimes are likely to be quite different for some paper types, e.g. contemporary alkaline paper containing optical brighteners is prone to colour change, however, it is known to be quite stable in terms of DP (Strlic et al. 2005a).

Criticism might arise from the fact that the predicted lifetimes depend on DP_0. The choice of samples in our research was guided by representativity: the samples were chosen from a historical reference collection as the most representative examples of what historic archives and libraries might have in storage today, with rag papers typically having DP of 1,500–1,800 (Strlič et al. 2010), acidic papers 500–1,000, and bleached pulp papers about 2,500 (Strlic et al. 2005b), so generalisations on the basis of the reported results are possible.

The approach also allows us to calculate the lifetimes with any given starting DP; however, as we shall see, the critical paper types are acidic papers, where the rate of degradation is mostly affected by acidity, as the rate of chain scission exponentially increases with lower pH (at least for some paper types) (Zou et al. 1996).

Activation energies, determined from the linearised Arrhenius plots, are shown in Table 3.

Activation energies are mainly within the values, reported in the extensive literature review by Zervos (2010). He reports values between 84 and 126 kJ/mol, which were obtained in a diverse range of experiments on different paper types. Activation energies for B and R, determined in this study, were higher compared to the reported ones, if samples were only exposed to T and RH. A1, exposed to NO_2, on the other hand gave a lower E_a value. The values, obtained for samples, exposed to NO_2, are consistently significantly lower compared to those obtained for samples, exposed to AcOH or T and RH only. This was the case for both DP loss (*handling*) and ΔE_{00} (*display*). Acetic acid had some effect on ΔE_{00} E_a of most samples, except for the most acidic (A1) and alkaline sample (B), but only had some effect on the DP loss E_a of A2 and R samples. As activation energy reflects the mechanism of the reaction it is possible to assume that another

Table 3 Activation energies (E_a) for DP change (*handling*) and ΔE_{00} (*display*) with the respective uncertainties, as calculated for the 6 sample papers at three experimental conditions

Sample	Conditions	E_a(*handling*) (kJ/mol)	E_a(*display*) (kJ/mol)
A1	Control	107 ± 31	133 ± 15
A1	1,000 ppb AcOH	140 ± 16	136 ± 20
A1	1,000 ppb NO_2	58 ± 16	101 ± 24
A2	Control	126 ± 28	138 ± 10
A2	1,000 ppb AcOH	111 ± 3	114 ± 5
A2	1,000 ppb NO_2	88 ± 9	81 ± 11
B	Control	135	85 ± 29
B	1,000 ppb AcOH	132 ± 8	90 ± 52
B	1,000 ppb NO_2	104 ± 12	99 ± 32
R	Control	157 ± 17	166 ± 22
R	1,000 ppb AcOH	107 ± 15	84 ± 28
R	1,000 ppb NO_2	49 ± 31	94 ± 38
L	Control	–	130 ± 19
L	1,000 ppb AcOH	–	81 ± 26
L	1,000 ppb NO_2	–	96 ± 13
W	Control	116 ± 27	109 ± 7
W	1,000 ppb AcOH	125 ± 19	98 ± 21
W	1,000 ppb NO_2	83 ± 15	90 ± 14

degradation mechanism (possibly involving radical oxidation) took place in the presence of NO_2. Typically, lower activation energies are observed for oxidation reactions and higher for hydrolysis, which suggests a significant contribution of oxidation to the chain scission process. Interestingly this was observed for all paper types, not only neutral/alkaline as previously reported (Strlic et al. 2005a). Since degradation in the presence of NO_2 proceeds at a faster rate it is possible to assume that the reaction involving NO_2, is the rate determining step in the degradation process.

The lifetimes differ greatly depending on paper type (Table 4), which is unsurprising, as papers of different composition are known to differ in stability (Zervos 2010). In terms of DP and safe handling acidic paper A1 has the shortest predicted lifetime. A2, which had somewhat higher initial DP and pH value, has a much longer predicted lifetime in comparison, very similar to Whatman cellulose. Alkaline and rag papers are very stable, with predicted handling lifetimes of several thousand years.

Table 4 Handling lifetime predictions at 1,000, 100 and 10 ppb of acetic acid or nitrogen dioxide

Sample	$t_{handling}$ (year)			
	$c_{poll} = 1{,}000$ ppb	$c_{poll} = 100$ ppb	$c_{poll} = 10$ ppb	$c_{poll} = 0$ ppb
A1 control	–	–	–	520
A1 AcOH	3,283	568	525	–
A1 NO$_2$	9	74	**325**	–
A2 control	–	–	–	**2,590**
A2 AcOH	1,006	**2,238**	2,550	–
A2 NO$_2$	79	619	**1,965**	–
B control	–	–	–	**45,848**
B AcOH	62,693	**47,114**	45,972	–
B NO$_2$	2,145	15,092	**38,086**	–
R control	–	–	–	**61,759**
R AcOH	3,589	**23,566**	53,146	–
R NO$_2$	28	277	**2,660**	–
W control	–	–	–	**1,785**
W AcOH	5,846	**1,918**	1,797	–
W NO$_2$	67	502	**1,422**	–

The results are not rounded up, the associated uncertainties are discussed in the next section

Figures in bold represent lifetimes at the realistic concentration of the respective pollutant. Predictions for 18 °C and 43 % RH

The situation is quite different when display lifetimes are considered (Table 5). Display lifetimes are shorter for papers, which where white at the start of the ageing process, such as contemporary alkaline and Whatman paper. Display lifetimes for the two are significantly shorter than their respective handling lifetimes, which shows that significant colour change (predominantly yellowing, b^*, although the other colour coordinates changed as well) of paper does not necessarily indicate significant degradation in terms of cellulose chain scission. The situation can however be opposite as well, when a significantly degraded paper changes colour to a very small extent. This is the case for acidic paper, which has a display lifetime of several thousand years, but a handling lifetime of an order of magnitude shorter. This also shows that paper degradation cannot be assessed only by following colour change, as it would seem that development of chromophores is a faster process than chain scission and different paper types change colour to a different extent during a comparable DP change.

A difference between the calculated lifetimes for samples degraded in the absence of pollutants and those exposed to NO$_2$ and AcOH can be appreciated, especially for NO$_2$ exposure. A small positive effect of acetic acid has even been calculated (as already evidenced in the higher E_a in Table 3), which is questionable considering the known mechanisms of acid catalysed degradation; therefore, this result is thought to be due to uncertainties, which will be discussed later in the text. The effect of NO$_2$ on colour change is similar to its effect on chain scission, as most lifetimes would be shortened to approximately a century or less if papers were exposed to 1,000 ppb of NO$_2$ (i.e. the experimental conditions).

However, the concentrations used in the experiment are about two orders of magnitude higher than what would be realistically found in an archival repository (depending on the pollutant), as discussed at the beginning of this section. This is why linear interpolations were made to the lower, realistic concentrations. A linear dependence of the degradation rate on the concentration of a pollutant was assumed and the degradation rate of the control samples (exposed to the same T and RH, but no pollutants) was taken as the reference point. Assumptions made here are different to the ones used for interpolation, described in the Introduction (Tétreault 2003). The main difference between the two approaches is that the previously described one uses no degradation as the reference point, whereas the degradation rate with no pollutants was used as the reference point here. This takes into account the assumption that paper will degrade even in the absence of pollutants. Degradation rates at lower concentrations were therefore calculated from the equation, describing the line, connecting degradation rates of the control sample and the sample exposed to 1,000 ppb.

Table 5 Display lifetime predictions at 1,000, 100 and 10 ppb of acetic acid or nitrogen dioxide

Sample	$t_{display}$ (year)			
	$c_{poll} = 1{,}000$ ppb	$c_{poll} = 100$ ppb	$c_{poll} = 10$ ppb	$c_{poll} = 0$ ppb
A1 control	–	–	–	**5,581**
A1 AcOH	8,646	**5,786**	5,601	–
A1 NO$_2$	316	2,092	**4,783**	–
A2 control	–	–	–	**6,808**
A2 AcOH	2,018	**5,502**	6,650	–
A2 NO$_2$	108	945	**4,202**	–
B control	–	–	–	**262**
B AcOH	566	**277**	264	–
B NO$_2$	128	237	**260**	–
R control	–	–	–	**48,878**
R AcOH	424	**3,934**	22,814	–
R NO$_2$	209	2,009	**14,666**	–
L control	–	–	–	**4,155**
L AcOH	193	**1,363**	3,449	–
L NO$_2$	156	1,167	**3,308**	–
W control	–	–	–	**1,181**
W AcOH	732	**1,113**	1,174	–
W NO$_2$	112	605	**1,078**	–

The results are not rounded up, the associated uncertainties are discussed in the next section

Figures in bold represent lifetimes at the realistic concentration of the respective pollutant. Predictions for 18 °C and 43 % RH

As pollutant concentrations decrease the corresponding lifetimes approach the lifetime determined for the control experiment. 100 ppb of acetic acid seems not to cause any additional degradation in most paper types, except rag paper, where the predicted lifetime of the control is already significantly long and even the predicted lifetime in a polluted environment is still measured in millennia.

At 10 ppb of NO$_2$ an apparently significant decrease compared to the control can be observed for the two acidic papers and the rag paper, although it should be pointed out here that the predicted lifetimes of samples A2 and R are over a millennium long and the significance of the decrease is therefore not as clear. As discussed at the beginning of this section, an archival repository could contain ∼100 ppb acetic acid and ∼10 ppb nitrogen dioxide (with the corresponding lifetimes in bold, in Table 4). If these are compared to the control it can be concluded that NO$_2$ and AcOH in realistic concentrations have an insignificant effect on paper degradation as manifested by chain scission for most paper types. The only paper type whose lifetime would be shortened by 10 ppb NO$_2$, is acidic paper. Contemporary alkaline paper was predicted to be very stable in terms of mechanical properties (represented here by DP, which is known to

correlate to mechanical properties, especially in the high DP range), which is also due to its alkaline reserve. Once the alkaline reserve is exhausted, paper degradation will probably continue at a faster rate, as it will become acidic. As the alkaline reserve was not consumed entirely in all the experiments, only the slower part of the degradation process is modelled here. The lifetimes would therefore realistically not be quite as long (e.g. approximately 40000 years, see Table 4, sample B).

Similarly to the handling lifetimes pollutant effects get progressively smaller as their concentrations decrease. At realistic conditions of 100 ppb AcOH and 10 ppb NO$_2$ no effect can be observed for alkaline and Whatman paper. 100 ppb of AcOH would equally have no effect on acidic paper. AcOH has the most effect on lignin containing and rag paper, significantly shortening their predicted lifetime. Some effect can also be observed for A2 paper. However, all these paper types would still reach display lifetimes of at least 1000 years despite acetic acid exposure.

The case of 10 ppb of NO$_2$ is very similar. Despite it having some effect on both acidic papers, rag and lignin-containing paper even at extrapolated low concentrations, the papers would still reach lifetimes of several millennia. Shorter lifetimes are only

predicted for alkaline and Whatman paper, however these would be approximately 300 and 1000 years, respectively, regardless of whether the pollutants are present or not.

As mentioned earlier, colour change and cellulose chain scission do not necessarily proceed at the same rate, which is understandable as colour change could be the consequence of degradation of not only cellulose, but also lignin or other paper components. The most striking is the difference between predicted handling and display lifetimes of modern alkaline paper. Contemporary paper often contains optical brighteners (Wilson 2006), which upon degradation cause colour reversion. The presence of an optical brightener can usually be observed in spectrocolorimetry as a fluorescence peak between 450 and 495 nm. This however was not found for the sample used in this study.

Acetic acid had little effect on the colour of alkaline paper, in contrast to NO_2. At 1,000 ppb of NO_2, significant colour change was observed for all paper types. Oxidative properties of NO_2 play an important role, as colour change is likely caused by nitration. Considering that discolouration is strong even in paper made of pure cellulose (W), reactions leading to chromophore formation with either cellulose or its degradation products must take place. Increased colour change due to NO_x exposure was also observed in a real-time study (Havermans and Steemers 2005), where different types of historic and model paper were kept in two repositories with different pollutant levels (one with and one without air filtration). Yellowness measurements, taken over the course of 8 years, showed a negative effect of pollutant presence, especially for model groundwood containing paper with high lignin content.

Very obvious differences between predicted handling and display lifetimes can also be observed for acidic paper. There are two reasons for this, the first being a fairly short handling lifetime due to poor mechanical properties, represented by a low DP, and the second being its initial strong colouration.

Considering their age at the start of the experiment and the starting DP, the acidic papers are already in an advanced stage of degradation, which could mean that the available reaction sites for chromophore formation have depleted.

On the other hand, lignin-containing papers are fairly sensitive to colour change despite their starting colour, which in this case was similar to that of acidic paper. It has been shown previously that brightness of lignin-containing paper decreases faster compared to lignin-free papers during accelerated degradation in the dark (Bégin et al. 1998) and it is known that lignin-containing papers are generally less stable in terms of optical properties due to oxidation (Bird 1999). Chromophores are formed during the process, for example quinones, thought to be responsible for darkening of lignin (Heitner et al. 2010).

Increased sensitivity of lignin-containing paper was confirmed in this study, with lignin-containing paper having a comparable or shorter predicted display lifetime compared to the other paper types in the absence of pollutants. Exaggerated concentrations of acetic acid have some effect on the colour change of lignin paper, but the effects are small at 10 ppb. However, NO_2 contributes more to discolouration, which is partly due to the oxidative nature of NO_2, as pulps containing significant amounts of lignin are known to undergo reactions with NO_2 (Bégin et al. 1999).
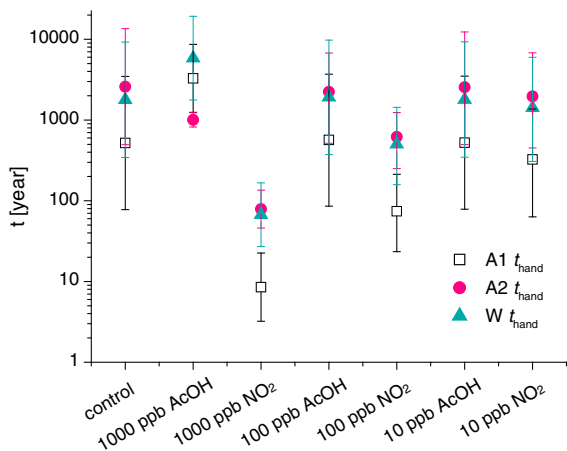
Uncertainty analysis

Significant uncertainties are inevitable when making predictions from accelerated degradation experiments, as experimental errors can originate from different sources, such as uncertainties in $L^*a^*b^*$ or DP determination, RH or T settings, and pollutant concentrations. The uncertainties were calculated for each paper type and set of conditions individually using uncertainty propagation analysis and used as uncertainty intervals for data points, used to calculate linear regression according to the linearised form of the Arrhenius equation as described in Experimental. The main contribution to uncertainties therefore arises from the uncertainty of the Arrhenius slopes, used to determine activation energies. The substantial uncertainty intervals were expected and have previously been reported in the literature (Porck 2000; Bégin and Kaminska 2002), however the robust approach to determining uncertainty intervals applied here allows for at least indicative comparison of different environmental conditions and paper types.

When the uncertainty intervals for expected lifetimes are calculated in years, the uncertainty intervals are asymmetrical, which is a consequence of
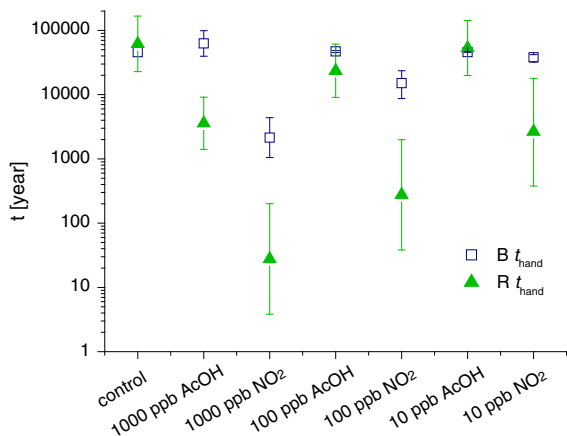
recalculating the symmetrical intervals of a logarithmic quantity into non-logarithmic values, following the Arrhenius equation. Because handling lifetimes for different paper types vary significantly they are shown in two separate graphs. The lifetimes for both acidic papers and Whatman pure cellulose with the corresponding respective uncertainty intervals are shown in Fig. 2 and lifetimes of alkaline and rag paper in Fig. 3.

Display lifetimes are divided between two graphs as well. Both acidic papers and rag paper are shown in Fig. 4 and alkaline, lignin-containing and Whatman paper in Fig. 5.

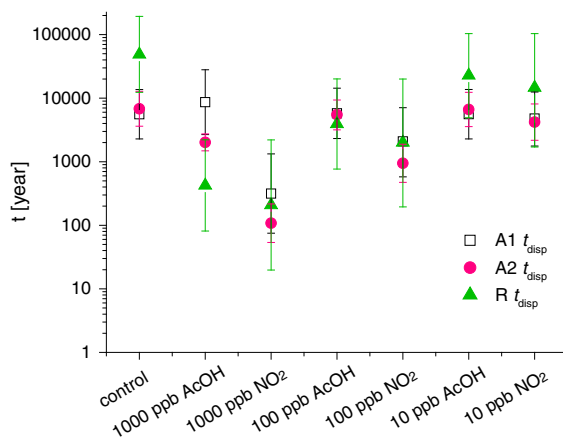The effect of 1,000 ppb NO_2 is significant even when taking into account the prediction uncertainties

both in terms of handling and display lifetime. In terms of handling lifetime a trend can be observed for 100 ppb NO_2, however there is some overlap of the uncertainty intervals. At realistic conditions of 100 ppb AcOH and 10 ppb NO_2 all differences are within prediction uncertainties of the control, so differences between the two polluted and the pollutant-free environment are not statistically significant. They can, however, still be appreciated.

The effect of 1,000 ppb AcOH and 100 ppb NO_2 on the handling lifetime of A2 sample is significant after taking into account the prediction uncertainties as well. All other predicted lifetimes are within prediction uncertainties of the control samples. The

Fig. 2 Predicted handling lifetimes for the two acidic papers and Whatman paper (A1, A2 and W), for 18 °C and 43 % RH

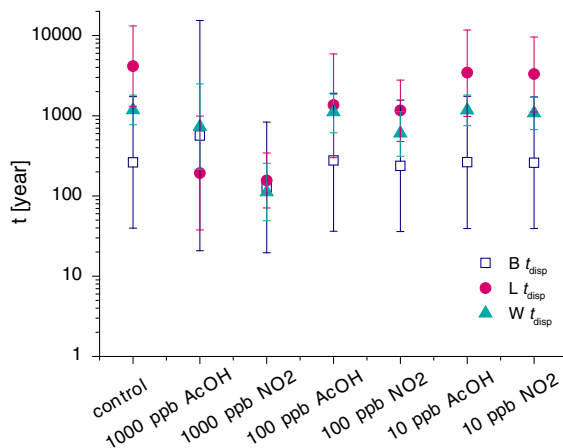**Fig. 4** Predicted display lifetimes for the two acidic papers and rag paper (A1, A2 and R), for 18 °C and 43 % RH

Fig. 3 Predicted handling lifetimes for alkaline and rag paper (R and B), for 18 °C and 43 % RH

Fig. 5 Predicted display lifetimes for alkaline, lignin-containing and Whatman paper (B, L and W), for 18 °C and 43 % RH

conclusions of this study would probably be the same even if the prediction uncertainties were significantly smaller, as the effects of NO_2 and AcOH at realistic concentrations are likely to still be insignificant.

The broad uncertainty intervals are not entirely surprising due to the number of steps in the experimental procedure where uncertainties are introduced. The Arrhenius approach, used to predict the remaining lifetimes of paper has been criticised in the past, partly due to extensive prediction errors (Ströfer-Hua 1990; Porck 2000; Bégin and Kaminska 2002). One of the arguments was that activation energies should be determined more precisely if they were to be used for predictions. This, however, is not likely, as Arrhenius studies are resource-intensive and significant uncertainties are inevitable especially when real historic materials are used and predictions are made for far ahead. However, on the basis of the observed trends and differences between investigated environmental conditions, guidance can still be given to inform decision makers, similar to other domains where despite uncertainties long-term decisions need to be made, e.g. climate change.

Long-term view of pollutants in archives and libraries

NO_2 is still present in concentrations of up to several 10 ppb, which makes it the most abundant primary pollutant. In the 1950s typical concentrations exceeded 100 ppb, however, due to environmental health regulations its concentration generally decreased in the past 30 years and will continue decreasing in the future (Brimblecombe 2006; Brimblecombe and Grossi 2009, 2010). O_3 concentrations were found to be lower compared to those of NO_2 in the two archives discussed in this work (Fenech et al. 2010; Menart et al. 2011b) and were therefore not seen as a significant risk for their paper collections.

The effects of particulate matter on paper degradation (Grau-Bové and Strlič 2013) were beyond the scope of this research. Particulate matter, however, is removed by a different filtration system than traffic generated pollutants, i.e. electrostatic filters as opposed to chemical filters, and the benefits of the former are not discussed here.

With the historically high levels of pollution, it was justified to introduce air purification in libraries and archives to improve the preservation conditions of their collections. However in the view of the results presented here, and the predicted continued decrease in the concentrations of traffic-generated pollutants, filtration might not be as necessary or beneficial as it was in the past, especially since equal benefits (at a possibly lower economic and environmental cost) could be obtained by adjusting other environmental parameters, e.g. T or RH.

As the concentrations of 'traditional' outdoor-generated pollutants keep decreasing, the interest has recently shifted towards pollutants generated indoors, such as acetic acid (Tétreault 2003). The concentration of AcOH in repositories is higher compared to outdoor-generated pollutants and this is not very likely to change in the future, as acetic acid is primarily generated by the collection itself (Ramalho et al. 2009). It is also significantly higher compared to other indoor-generated pollutants, such as formic acid, which counterbalances formic acid's higher acidity. However, the experiments showed that while pollution has a measurable effect on paper degradation (depending on the paper type), the effect in typical archival environments is limited and in some cases insignificant. This is especially the case for acetic acid, meaning VOCs in significantly lower concentrations (e.g. formic acid) are likely to have an insignificant effect.

However, it needs to be stressed that in specific environments, e.g. significantly more polluted urban environments [e.g. in rapidly developing economies (Agbota et al. 2013)], environments with significant O_3 pollution (e.g. S Europe[2]), or microenvironments with low air exchange [e.g. display cases, frames, or tightly closed books (Carter et al. 2000; Bülow et al. 2000)], the pollutant concentration (or composition), could be significantly different from the one discussed in this work. However, the presented research may still enable us to assess the effect of NO_2 and acetic acid in such cases.

Conclusions

The aim of this research was to investigate paper degradation in polluted environments at concentrations

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[2] 'PROMOTE: Air Quality Records, RIU/EURAD', http://db.eurad.uni-koeln.de/promote/riu_aqrs.php. Accessed 22 Jan 2013.

comparable to real repository environments, with real historic papers, which has not been attempted before, and compare the results with degradation in the absence of pollution, which enabled us to estimate if the presence of NO_2 and AcOH in archival repositories is likely going to lead to a significant decrease of material lifetimes in comparison to clean environments.

The effects of the most abundant pollutants in archival repositories, acetic acid and nitrogen dioxide, were assessed in terms of 'handling' (influenced by DP decrease) and 'display' (influenced by discolouration) lifetimes of paper. Experiments were carried out on different historic papers and extrapolations to room conditions were carried out to enable lifetime predictions.

- At 10 ppb NO_2 was found to reduce the handling lifetime of acidic paper. Negative effects were also observed for alkaline, rag and Whatman paper; however, their predicted lifetimes were assessed to be several millennia even in the presence of NO_2. A negative influence on display lifetimes was observed for contemporary alkaline and historic rag paper.
- Acetic acid at concentrations that are typical for archival and library repositories (<100 ppb) has even significantly less effect than NO_2. Generally, AcOH does not affect display lifetimes, and similarly to NO_2, the predicted lifetimes are significant even with the pollutant present.
- The work presented here can be used to assess the potential negative effects of NO_2 and acetic acid in significantly more polluted environments such as those currently found in some rapidly developing economies or in specific microenvironments.
- The above findings need to be assessed from a conservation management perspective, specifically to address whether minor reductions in very long predicted handling lifetimes of contemporary and rag papers (e.g. several millennia) are of real concern.

With air pollution in post-industrial economies being a much lesser risk compared to decades ago and the limited effect of pollutants on paper degradation at concentrations as currently measured in archival repositories, the need for air filtration in archival repositories needs to be reassessed.

References

Adelstein PZ, Zinn ED, Reilly JM (2003) Effect of atmospheric pollution on paper stability. J Pulp Pap Sci 29:21–28

Agbota H, Young C, Strlič M (2013) Pollution monitoring at heritage sites in developing and emerging economies. Stud Conserv 58:129–144

Ashley-Smith J, Derbyshire A, Pretzel B (2002) The continuing development of a practical lighting policy or works of art on paper and other object types at the Victoria and Albert Museum. ICOM Committee for Conservation, ICOM-CC: 13th Triennial Meeting, Rio de Janeiro, 22–27 September 2002: preprints 1:3–8

Bégin P, Kaminska E (2002) Thermal accelerated ageing test method development. Restaurator 2002:89–105

Bégin P, Deschâtelets S, Grattan D, Gurnagul N, Iraci J, Kaminska E, Woods D, Zou X (1998) The impact of lignin on paper permanence. Restaurator 19:135–154

Bégin P, Deschâtelets S, Grattan D, Gurnagul N, Iraci J, Kaminska E, Woods D, Zou X (1999) The effect of air pollutants on paper stability. Restaurator 20:1–21

Bird AJ (1999) Addressing the real issues for permanent papers, brightness reversion, and lignin-containing pulps. Tappi J 82:159–164

Blades N, Oreszczyn T, Bordass B, Cassar M (2000) Guidelines on pollution control in museum buildings. Museum Practice, Museum Association, London

Brimblecombe P (2006) The clean air act after 50 years. Weather 61:311–314

Brimblecombe P, Cashmore M (2004) Indoor air pollution. J Phys IV France 121:209–221

Brimblecombe P, Grossi CM (2009) Millennium-long damage to building materials in London. Sci Total Environ 407:1354–1361

Brimblecombe P, Grossi CM (2010) Potential damage to modern building materials from 21st century air pollution. Sci World J 10:116–125

Bukovský V (2000) The influence of light on ageing of newsprint paper. Restaurator 21:55–76

Bülow A, Bégin P, Carter H, Burns T (2000) Migration of volatile compounds through stacked sheets of paper during accelerated ageing. Part II: variable tempreature studies. Restaurator 21:187–203

Carter H, Bégin P, Grattan D (2000) Migration of volatile compounds through stacked sheets of paper during accelerated ageing. Part I: acid migration at 90 C. Restaurator 21:77–84

Dupont A-L, Tétreault J (2000) Cellulose degradation in an acetic acid environment. Stud Conserv 45:201–210

Ekenstam A (1936) Über das verhalten der cellulose in mineralsäure-lösungen, II. Mitteil: kinetisches studium des abbaus der cellulose in säure-lösungen (concerning the behavior of cellulose in mineral acid solutions, communication II: kinetic investigation). Ber Dtsch Chem Ges 69:553–559

Evans R, Wallis A (1987) Comparison of cellulose molecular weights determined by high performance size exclusion chromatography and viscometry. Proc Fourth Intern Symp Wood Chem, Paris

Fenech A, Strlič M, Kralj-Cigić I, Levart A, Gibson LT, de Bruin G, Ntanos K, Kolar J, Cassar M (2010) Volatile aldehydes in libraries and archives. Atmospheric Environ 44:2067–2073

Gibson LT, Ewlad-Ahmed A, Knight B, Horie V, Mitchell G, Robertson CJ (2012) Measurement of volatile organic compounds emitted in libraries and archives: an inferential indicator of paper decay? Chem Cent J 6:42

Grau-Bové J, Strlič M (2013) Fine particulate matter in indoor cultural heritage: a literature review. Herit Sci 1(8):1–17

Grau-Bové J, Budič B, Thickett D, Strlič M (2014) The effect of particulate matter on paper degradation. 11th International conference indoor air quality in heritage and historic environments, 13–16 April 2014. Prague, Czech Republic

Grossi CM, Brimblecombe P (2007) Effect of long-term changes in air pollution and climate on the decay and blackening of european stone buildings. In: Prikryl R, Smith BJ (eds). Building stone decay: from diagnosis to conservation. Geological society, London, Special Publications 271:117–130

Hatchfield PB (2002) Pollutants in the museum environment. Archetype Publications Ltd, London

Havermans JBGA, Steemers TAG (2005) Air pollution and its prevention. In: Strlič M, Kolar J (eds) Ageing and stabilisation of paper. Narodna in univerzitetna knjižnica, Ljubljana, Slovenia

Heitner C, Dimmel DR, Schmidt JA (eds) (2010) Lignin and Lignans: advances in chemistry. CRC Press, Boca Raton

Hong SH, Strlič M, Ridley I, Ntanos K, Bell N, Cassar M (2012) Climate change mitigation strategies for mechanically controlled repositories: the case of the National archives, kew. Atmospheric Environ 49:163–170

Johansson A (2000) Air pollution and paper deterioration-Causes and remedies (PhD thesis). Department of Chemistry, Göteburg University, Göteburg, Sweden

Johansson A, Kolseth P, Lindqvist O (1998) Uptake of air pollutants by paper. Report No. 8, FoU-projektet for papperkonservering, Stockholm

Luo MR, Cui G, Rigg B (2001) The development of the CIE 2000 colour difference formula: CIEDE2000. Color Res Appl 26:340–350

Menart E, de Bruin G, Strlič M (2011a) Dose-response functions for historic paper. Polym Degrad Stab 96:2029–2039

Menart E, de Bruin G, Strlič M (2011b) The effect of environment on long-term storage of historic paper—A preliminary study, 5th European Weathering Symposium, 21–23 September 2011. CEEES Publication No. 15, Lisbon, Portugal

Porck H (2000) The rate of paper degradation: the predictive value of artificial aging tests, ECPA

Ramalho O, Dupont A-L, Egasse C, Lattuati-Derieux A (2009) Emission rates of volatile organic compounds from paper. e-PS 6:53–59

Smith RD (2004) Paper stability and collection risk: a perspective and choices. Restaurator 25:199–210

Strlič M, Kolar J, Kočar D, Rychlý J (2005a) Thermo-oxidative degradation. In: Strlič M, Kolar J (eds) Ageing and stabilisation of paper. Narodna in univerzitetna knjižnica, Ljubljana, Slovenia

Strlič M, Kolar J, Scholten S (2005b) Paper and durability. In: Strlič M, Kolar J (eds) Ageing and stabilisation of paper. Narodna in univerzitetna knjižnica, Ljubljana, Slovenia

Strlič M, Cséfalvayová L, Kolar J, Menart E, Kosek J, Berry C, Higgitt C, Cassar M (2010) Non-destructive characterisation of iron all ink drawings: not such a galling problem. Talanta 81:412–417

Ströfer-Hua E (1990) Experimental measurement: interpreting extrapolation and prediction by accelerated aging. Restaurator 11:254–266

Tétreault J (2003) Airborne pollutants in museums, galleries and archives: risk assessment, control strategies, and preservation management. Minister of Public Works and Government services, Canada

Tétreault J, Dupont A-L, Bégin P, Paris S (2013) The impact of volatile compounds released by paper on cellulose degradation in ambient hygrothermal conditions. Polym Degrad Stab 98:1827–1837

Trafela T, Strlič M, Kolar J, Lichtblau DA, Anders M, Mencigar DP, Pihlar B (2007) Nondestructive analysis and dating of historical paper based on IR spectroscopy and chemometric data evaluation. Anal Chem 79:6319–6323

Williams EL, Grosjean D (1992) Exposure of deacidified and untreated paper to ambient levels of sulfur dioxide and nitrogen dioxide: nature and yields of reaction products. J Am Inst Conserv 31:199–212

Wilson I (2006) Filler and coating pigments for papermakers. In Kogel JE, Trivedi NC, Barker JM, Krukowski ST (eds) industrial minerals & rocks: commodities, markets, and uses, 7th Edition. Society for mining, metallurgy, and exploration, Inc., Littleton, Colorado, USA

Zervos S (2010) Natural and accelerated ageing of cellulose and paper: a literature review. In: Lejeune A, Deprez T (eds) Cellulose: structure and properties, derivatives and industrial uses. Nova Science Publishers Inc, Hauppauge, NY

Zou X, Uesaka T, Gurnagul N (1996) Prediction of paper permanence by accelerated aging I. Kinetic analysis of the aging process. Cellulose 3:243–267