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Doctoral Thesis

Indoor pollution in archival collections in the context of a changing environment

By

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I, Eva Menart, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Eva Menart

Abstract

Paper degradation is an unavoidable series of processes and the most important factors causing paper degradation in long-term archival storage are temperature, relative humidity, pollutants and the paper properties, mainly acidity. To study these effects, experiments were performed to determine degradation rates on sacrificial historic papers, with a reference to Nationaal Archief (The Netherlands).

Handling and display lifetimes were defined and calculated for each paper type and shown to differ significantly according to paper type and purpose of use. The lifetimes were significantly affected by concentrations of NO_2 resembling actual concentrations in archival repositories, whereas the effect of AcOH was limited.

A new approach to defining pollutant doses was introduced, which also takes into account degradation resulting from *T* and RH. At realistic pollutant concentrations, *T* and RH, and paper properties contribute significantly to the overall degradation process during long-term storage, and should therefore be included in a comparative assessment of preservation options.

A new concept of pollutant thresholds was also introduced. Using this concept, the determined thresholds are in the concentration range found in an archival repository or above for NO_2, but depend significantly on paper type for AcOH.

A method for estimating paper lifetime was proposed. As both handling and display lifetimes of the most sensitive parts of a typical collection were predicted to be less than 500 years, preservation measures to achieve that target were investigated using the method of lifetime prediction.

Air filtration would prolong the lifetime of the most sensitive acidic paper by approximately 150 years. The same effect could, however, be achieved by other preservation measures, such as decreasing the temperature by 4 °C.

Outcomes of the research presented here could inform the decision-making process in planning long-term preservation measures by providing a quantitative comparison of different options and the required research evidence.

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Glossary

Acidic paper – Paper produced in the late 19th and 20th century, which is prone to degradation. Its acidity is the result of acids introduced during paper production (e.g. rosin sizing) or a consequence of the degradation process.

Alkaline paper – Contemporary paper with alkaline fillers, which inhibit the degradation process.

Arrhenius study – Study carried out at different temperatures, in order to determine the activation energy and pre-exponential factor, which enable extrapolation of reaction rates to different temperatures.

Display lifetime – Time needed for paper to reach a value of ΔE_{00}, which is perceived unacceptable, $\Delta E_{00} = 15$.

Groundwood paper – Paper for which a significant amount of the pulp was obtained by grinding wood. Lignin is not removed during this process and is therefore present in this paper type.

Handling lifetime – Time needed for the paper *DP* to decrease to the safe handling threshold, *DP* = 300.

Hydrolysis – Reaction involving the breaking of a chemical bond in a molecule by the addition of water.

Interventive conservation – Actions, which intervene directly with the material or object, such as repair or deacidification (of paper).

Lignin-containing paper – Paper containing a significant amount of lignin, originating from the plant material. Lignin is an aromatic polymer, which impregnates the cellulose in plant cells.

Oxidation – Reaction in which the oxidation state of an atom or molecule is increased, i.e. loss of electrons.

Passive sampling – Type of sampling where the chemicals are allowed to diffuse (e.g. from the atmosphere) onto an adsorbent without the use of a pump.

Polysaccharide – Carbohydrate molecules composed of a chain of monosaccharides, liked together by glycosidic bonds.

Preventive conservation – Actions taken to decelerate or prevent the degradation process.

Rag paper – High quality paper made of cotton rags, usually gelatine sized.

Repository – Location where the collection is stored (e.g. archival repository).

Whatman paper – Paper made of pure cellulose linters, commonly used as a model paper in degradation experiments.

Abbreviations, symbols, and formulas

A1 – acidic paper 1

A2 – acidic paper 2

A – pre-exponential factor in the Arrhenius equation

AcOH – acetic acid, CH_3COOH

B – alkaline paper

c – concentration

C_1 – carbon atom on position 1 in a glucose molecule

C_4 – carbon atom on position 4 in a glucose molecule

$^1C_4$ – chair conformation the glucose molecules adopt, where C_1 is above and C_4 below the reference plane of the chair

Ca – calcium

CED – cupriethylenediamine solution, used in viscometry measurements

CIE L*a*b* – colour space, where *L** ranges from 0 to 100 (black to white), *a** represents red (positive) and green (negative) and *b** represents yellow (positive) and blue (negative)

CIEDE2000 – method of calculating colour difference (ΔE_{00})

DP – degree of polymerisation

ΔE_{00} – colour change, calculated according to the CIEDE2000 formula

E_a – activation energy

Fe – iron

HCHO – formaldehyde

HCOOH – formic acid

HNO_2 – nitrous acid

HNO_3 – nitric acid

H_2S – hydrogen sulfide

H_2SO_4 – sulfuric acid

H_3O^+ – hydronium ion

k – reaction (degradation) rate

L – lignin-containing paper

L.O.D. – limit of detection

LOAED – lowest observed adverse effect dose

LOAEL – lowest observed adverse effect level

LODP – levelling-off degree of polymerisation

***m* –** factor describing the degradation rate dependence on pollutant concentration

M – molecular weight

Mn – manganese

NO – nitrogen oxide

NO_2 – nitrogen dioxide

NO_x – nitrogen oxides

NOAEL – no observed adverse effect level

O_3 – ozone

P – permanence

PAH – poly-aromatic hydrocarbons

pH – negative logarithm of hydrogen ion activity, commonly simplified to negative logarithm of H_3O^+ concentration

pK_a – negative logarithm of the acid dissociation constant, K_a

PM$_{2.5}$ – particulate matter less than 2.5 µm in diameter

PM$_{10}$ – particulate matter less than 10 µm in diameter

ppb – parts per billion

R – rag paper

R – gas constant, 8.314 J/mol K

RH – relative humidity

S – sulfur

SEC – size-exclusion chromatography

SO_2 – sulfur dioxide

t – time

T – temperature

TS – tensile strength

VOC – volatile organic compounds

W – Whatman paper

λ – wavelength

1. Introduction

1.1. Scope of work

Despite the current digital age, paper still retains its role as the main information carrier, especially when historic information is considered. Throughout history, records of important events, newly obtained knowledge and even everyday life have been written down, in the past millennium mostly on paper. This has resulted in archival collections, composed of hundreds of kilometres of materials, which should be preserved for future generations.

Although that sounds like a simple task, this may not always be the case. Paper degradation is an inevitable series of processes, however by increasing the understanding of these processes, efforts can be made to decrease their rate and preserve paper-based collections for longer.

It is estimated that 70-80% of documents in a typical Western repository are acidic and therefore even more prone to degradation, which means they might not last longer than a couple of centuries [1]. These papers were produced in the late 19th and early 20th century, when the paper production increased significantly due to a rapid increase in demand, which resulted in a significant decrease in paper quality. The paper produced before that, on the other hand, might outlive them by centuries, if not millennia. The reason lies in the raw material, used in paper manufacturing, which changed from high-quality fibres, obtained from cotton or linen rags, to lower-quality wood fibres [1]. In the early 20th century the recycled cotton and linen were no longer a sufficient source of cellulose fibres to meet the increasing demand and paper production was forced to move to other sources. Over 90% of cellulose, used for making paper, is nowadays derived from wood, and the rest originates from other plant material and to a lesser degree rags [2].

Different approaches to paper preservation can be taken to try to prolong the lifetime of documents. Interventive conservation is one of the options [3], although it might not meet the requirements, based on the scale of the issue. Preventive conservation in terms of environmental control might therefore be the preferred option, as the storage environment affects the whole collection simultaneously.

Many different factors affect paper degradation, such as heat (the measure of which is temperature), humidity, radiation, pollution and paper composition [4]. This thesis, however, is focused on archival storage, where the collections are mainly kept in the dark. The focus is therefore on environmental parameters which can be controlled in order to achieve better preservation of the collection. Those are temperature (*T*), humidity (RH) and pollution.

The research was carried out in collaboration with the Nationaal Archief (the National Archives of the Netherlands), which holds over 100 km of paper-based objects. Temperature and relative humidity in their archival repositories are controlled and air filtration is employed to minimise concentrations of traffic-generated pollutants in order to preserve the collection for posterity. All these measures, however, have not yet been quantitatively assessed in combination and in terms of the effect of realistic conditions on real paper.

The main aim of this research was to assess and compare different environmental effects on the lifetimes of paper [5] and using that to determine, which preservation measures would be most beneficial for the collection and would ensure the longest lifetimes. As some of the most accurate analytical methods for following paper degradation are destructive, this was done through a series of accelerated degradation experiments on sacrificial materials. These were real historic papers, selected to represent different types of paper in an archival or library collection. The aim was also to generalise the findings to a typical archival collection and provide a method of assessing the combined effects of the environment, which could be used by institutions to assess the future behaviour of their own collections. This thesis represents research, investigating the combined effects of exogenous and endogenous factors on chemical degradation of real paper, and using the results predicting paper lifetimes under different environmental conditions, which had not been carried out previously.

1.2. Thesis outline

This thesis is divided into ten chapters. The first outlines the topic of the research and its justification and gives a brief structure of the thesis itself. The literature review is given in Chapters 2 and 3. Chapter 2 describes the structure of paper, its change during the degradation process and how this is measured using analytical techniques. The mechanisms of paper degradation and the degradation kinetics are presented, as well as how lifetime and permanence have been defined in the literature. Different effects on paper degradation are described in Chapter 3, such as biodeterioration, pollution, radiation, temperature and relative humidity fluctuations and paper composition including acidity. Among these, those most important for long-term archival storage are identified.

The research questions in relation to the preservation of collections at Nationaal Archief are presented in Chapter 4. The building and the collection are described briefly and environmental monitoring, where T, RH and pollutant concentrations were measured over the course of one year, is presented and discussed.

Methodology is presented in Chapter 5. The samples are described and the experimental setup and analytical methods, used throughout this research to follow paper degradation, are discussed as well. Steady-state and dynamic experiments are presented and calculations used to analyse results are shown as well. Uncertainty analysis is discussed and definitions of handling and display lifetimes, used in this work, are given.

Chapter 6 describes the steady-state experiments. This first set of experiments was carried out under stationary conditions under the assumption that intermittent introduction of polluted and humidified air into sample reactors was sufficient to ensure a constant environment. Preliminary experiments and their conclusions are presented. Assumptions made about the pollutant conditions in this experimental setup turned out to be false, these difficulties are discussed.

Chapter 7 starts with a description of why the experimental setup and design were adapted. Another set of preliminary experiments with the changed setup is presented, followed by the Arrhenius study at three temperatures. The Arrhenius study at different temperatures enabled degradation rate extrapolations to lower temperatures, according to the Arrhenius equation, commonly used in accelerated degradation studies. Chain scission, colour change and pH measurements for individual paper types are shown and the degradation rates are discussed. This is followed by the Arrhenius regressions and determination of activation energies and degradation rate uncertainties. Extrapolations of degradation rates to room conditions are also presented here.

The overall results are discussed in Chapter 8, where remaining lifetimes are calculated for individual paper types. The concept of pollutant doses and thresholds is also discussed and applied to the experimental results. The effects of different environmental options on the predicted lifetimes of individual paper types are calculated and compared. The chapter is concluded with a proposed method for assessing environmental effects on paper-based collections.

The discussion continues with recommendations for archival storage in Chapter 9. The method, proposed in Chapter 8, is applied to a typical archival collection and used to assess possible preservation measures and future conditions. The same is also done for the collection, held in the Nationaal Archief.

Chapter 10 summarizes the conclusions, derived from this research. Further work on this subject is also suggested.

2. Paper degradation

As paper is still the most widespread and generally readable carrier of information, its degradation is unwanted, but unfortunately also unavoidable. Understanding degradation and what affects it may, however, help decrease the rate of the process.

2.1. Paper, its structure and its change during ageing

2.1.1. Structure of paper

The main structural component of paper is cellulose. Cellulose fibres in paper form interlocking networks, which are ordered in an approximately layered structure, usually between 30 and 300 µm thick. An individual fibre is approximately 10 to 50 µm wide, which means a sheet of paper of 100 µm is approximately 5 to 10 cellulose fibres in thickness [2].

The main structural component in paper is cellulose. Cellulose exists in four polymorphic forms, generally known as cellulose I, II, III and IV. Cellulose I is the only form occurring naturally, despite the fact that it is not the most stable one. It is a natural polymer of cellobiose, which consists of two glucose molecules (D-glucopyranose), joined by C_1-C_4 glycosidic oxygen linkage. The second glucose unit is inverted relative to the first, but both adopt a stable $^1C_4$ chair conformation (Figure 2.1). One glucose unit is treated as a monomer, which will be used further on in calculations, although the repeating unit is one dimer.

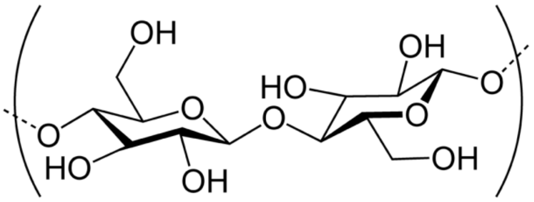

Figure 2.1: Cellulose dimer, the repeating unit in a cellulose chain, composed of two glucose units.

Linear arrangement of the polymer chain is maintained by hydrogen (H-) bonding. H-bonds are formed between oxygen and hydrogen atoms in hydroxyl groups and also the oxygen atom in the glucose ring. Cellulose fibrils are formed by hydrogen bonds within and between chains, which hold the polymer flat and therefore enable the cellulose ribbons to stack (Figure 2.2) [6].

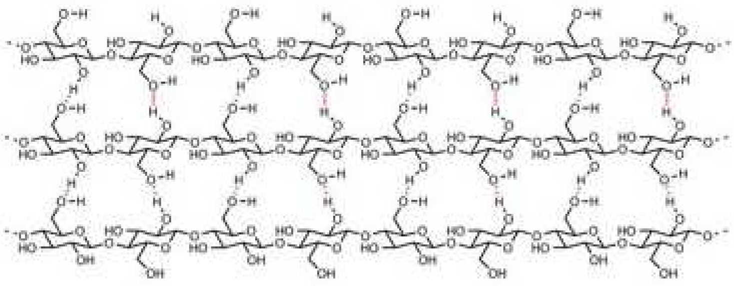

Figure 2.2: H-bonds between cellulose chains [7].

Cellulose is never found in a completely crystalline form, it always partly consists of an amorphous phase. The degree of crystallinity varies between 50 and 90% and depends on the cellulose source, as cotton cellulose tends to be highly crystalline and wood cellulose generally less so (upper and lower part of the crystallinity range, respectively) [2].

Besides cellulose, which is the main structural polysaccharide, wood-fibre paper can also consist of other components, such as lignin and hemicelluloses. Lignin is a complex aromatic polymer, which impregnates the cellulose in plant cells and is found in secondary cell walls of plants, and its amount increases with the age of the plant. It is composed of up to three phenyl propane monomers: coniferyl alcohol, coumaryl alcohol and sinapyl alcohol, which can be bonded in different patterns, depending on plant species (Figure 2.3) [2,8].

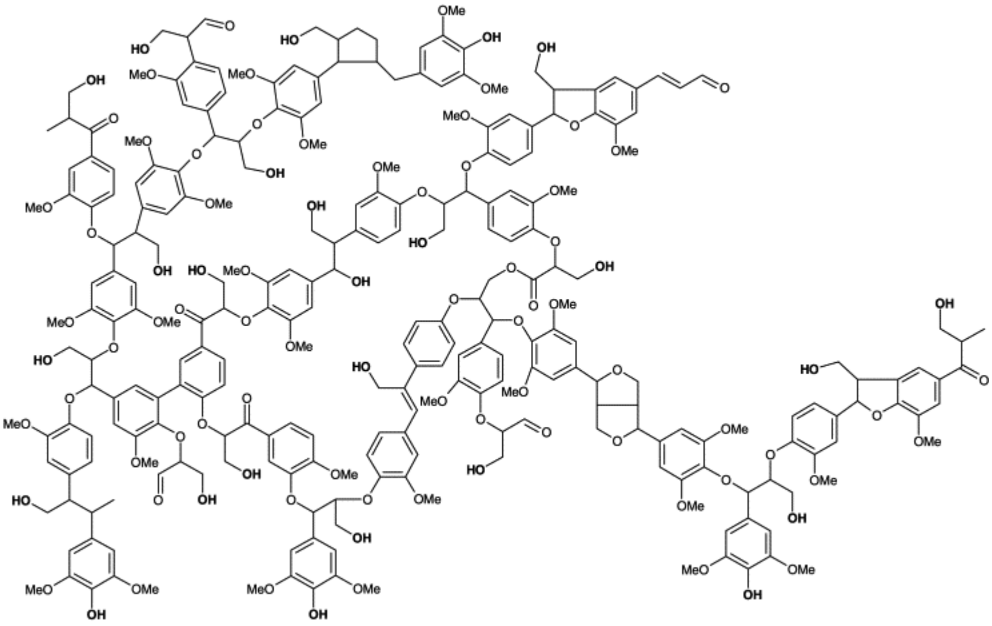

Figure 2.3: Hardwood lignin structure [9].

Hemicelluloses are non-structural polysaccharides with a much lower molecular weight compared to cellulose, however they are not biosynthetic precursors of cellulose, as the name might suggest. Besides glucose monomers, hemicelluloses can also include xylose, mannose, galactose and other sugars, depending on the source. Hemicellulose polymers are much shorter compared to cellulose and unlike cellulose are also branched (Figure 2.4) [2,10].

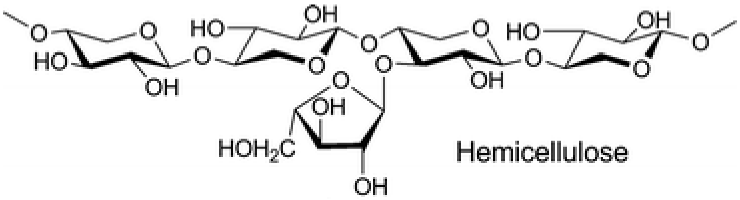

Figure 2.4: The structure of hemicelluloses .

Lignin and hemicelluloses are not only typical of wood, but can also be found in other plant material, such as grasses [11].

Cellulose degradation occurs by breakage of covalent bonds within and between monomer units in the chain and loss of inter- and intra-chain hydrogen bonds [6,12]. It is speculated that random chain scission, which is considered the standard degradation reaction, is preceded by a rapid reaction, where so called ‘weak links’ in the chains are broken [6].

2.1.2. Change due to ageing and analytical techniques to detect it

As the main use of paper, at least in the heritage or archival context, is to transmit information, its most important properties are mechanical strength, closely related to safe handling of documents, and its visual appearance, related to text readability or image contrast. This dictates the choice of analytical techniques to measure changes in paper properties.

The scission of intramolecular (inter-monomer) bonds shortens the long cellulose chains and therefore leads to a decrease in the average molecular weight of cellulose. In linear homopolymers the molecular weight of the polymer equals the molecular weight of a monomer, multiplied by the number of monomer units. The average molecular weight therefore 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* and the more instrumentally demanding size-exclusion chromatography (SEC) to obtain a distribution of molar masses, number-average and mass-average molar mass [13,14]. The latter can also be used to follow changes in the distribution of molecular weight, which can be useful for studying degradation kinetics [6].

Mechanical properties of paper are assessed by measuring tensile strength and zero-span tensile strength, tearing resistance, bursting strength, and folding endurance. Tensile strength is the maximum tensile force per unit width that paper will withstand before breaking and is measured using a testing instrument, that holds a piece of paper in two clamps and pulls it apart [15]. For zero-span tensile strength the two clamps are positioned right next to each other. Both zero-span tensile strength and tensile strength are highly dependent on the fibre strength, while tensile strength is also influenced by interfibre bonding [2,16]. Tearing resistance is assessed by determining the mean force required to continue the tearing started by an initial cut in a single sheet of paper and it is measured by an Elmendorf-type tear tester [17]. It not only depends on the fibre strength, but also on fibre length and interfibre bonding [16]. Bursting strength is the maximum pressure developed by a hydraulic system forcing an elastic diaphragm through a circular area of paper when pressure is applied [18]. Folding endurance is the decadic logarithm of the number of double folds required to cause rupture to a test piece when tested under standard stress conditions and it is measured by a fold tester [19]. As mentioned earlier, all these properties are manifestations of fibre and interfibre bonding. Another process, affected by intermolecular bonding is creep of paper, which occurs when paper is under stress and deforms with time [20].

The relationship between zero-span tensile strength and degree of polymerisation, determined by Zou et al. [21], shows that the average chain length of cellulose is one of the key factors for its mechanical properties. However, mechanical properties of paper depend both on cellulose macromolecular chain length and intermolecular and interfibre bonding [14]. It should also be noted that the work of Zou et al. [21] was carried out on pulp sheets without fillers or sizing, which would also have an effect on the strength of real paper.

Since a correlation between mechanical properties and the degree of polymerisation has been established [21], determination of cellulose molecular weight is often used to understand the deterioration of mechanical properties. However since not only intramolecular, but also intermolecular bonding affects mechanical properties, the relationship between the two may be different for different pulps and papers [22]. Determination of *DP* instead of a physical property is also more favourable from the viewpoint of sample consumption (only approximately 20 mg of paper is needed for *DP* determination [13]) and from the viewpoint of modelling, as the smaller uncertainty of *DP* determinations increases the quality of any extrapolation [14].

Beside the mechanical properties, the appearance of paper is also of great importance, as changes in the colour of paper may also be undesired. Paper colour is a consequence of interactions of light with the material, especially light absorption/reflection, and fluorescence. During cellulose degradation all can change simultaneously [14]. To determine the colour of paper the CIE $L^*a^*b^*$ system is mostly used, which takes into account the “standard human eye response”. The values for L^* range from 0 to 100 (black to white), whereas a^* and b^* have no limits. a^* represents red (positive) and green (negative); b^* represents yellow (positive) and blue (negative).

As yellowing often accompanies paper ageing, b^* is often used to evaluate changes in colour (yellowness). For overall colour change ΔE, which can be calculated from

*L**, *a** and *b**, is used. Different ways of calculating ΔE have been proposed in the past 4 decades [23], the latest one being CIEDE2000 (ΔE_{00}), which represents the colour space most realistically.

2.2. Degradation mechanisms and kinetics

2.2.1. Degradation mechanisms

The major cause of loss of paper strength is acid-catalysed hydrolysis of the glycosidic bonds between glucose monomers (Figure 2.1) and molecular mass distribution studies have shown, that the chain scission occurs at random positions [21,24]. Other mechanisms may take place as well, such as oxidation, cross-linking and thermolysis [4,21,25], depending on the experimental conditions and the pH of paper.

Zou et al. [21] showed that filter paper with acidic pH does not degrade substantially in dry air and high temperature (90 °C), whereas the presence of moisture significantly accelerates degradation. Experiments carried out in an oxygen free environment also suggested that oxidation was not an important factor and that acid-catalysed hydrolysis was the predominant mechanism [21,22]. However it should be pointed out that all of Zou’s experiments were carried out on acidic paper samples, with pH ranging from 4 to 6.5, so the conclusion on the effect of oxygen was not surprising, as acid-catalysed hydrolysis is the prevalent degradation mechanism leading to *DP* decrease in acidic samples and its relative importance decreases as the pH of paper is increased [26,27]. Oxidation is more likely to occur at the ends of cellulose chains, contributing to the formation of low-molecular weight organic acids. Studies by Barański [25] suggest that the effect of oxygen should not be entirely neglected, as differences in *DP* after accelerated ageing in argon or air were observed even for acidic papers. Similarly, anoxia was recently shown to have a positive effect even on the stability of acidic papers [28]. Experiments on acidic softwood cellulose have shown that degradation of cellulose (in terms of *DP* loss) is more advanced in the presence of oxygen, therefore it should be regarded as a complex process, in which hydrolysis is not the only possible mechanism of degradation [29], but possibly the main mechanism leading to chain scission.

Zou et al. [22] suggested a mechanism, which consists of three stages: rapid protonation of the glycosidic oxygen atom, slow transfer of the positive charge to C_1 (the carbon atom, also forming the glycosidic bond) with consequent formation of carbonium ion and fission of the glycosidic bond, and the reformation of hydroxonium. They also found a linear relationship between the degradation rate constant and hydrogen ion concentration in cellulose. In fact the effects of moisture and acidity are coupled, so when the moisture content is high, the effect of acidity is magnified.

Acid hydrolysis of cellulose has been studied for decades, and a concept, involving different reaction stages of the degradation process, had already been applied in the late 1950s [30]. It was generally assumed that during the early stages of hydrolysis, removal of the non-crystalline or water-sensitive material takes place simultaneously with chain scission and crystallisation of cellulose. Further hydrolysis under milder conditions leads to a decrease of degree of polymerisation in all types of cellulosic materials [30].

As mentioned earlier, the fact that cellulose degradation depends on moisture does not prove that acid-catalysed hydrolysis is the only degradation mechanism, taking place in paper, although it may be the predominant one, since other mechanisms might be humidity-dependent as well. It has been shown that the rate of bond scission during oxidation of alkaline samples increases as the relative humidity increases from 20% to 65%, and decreases again above RH of 65%. A possible explanation for the latter may be that a completely hydrated cellulose fibre is less susceptible to oxidation simply due to the fact that the solubility of oxygen in water is low [26,27].

Oxidation is not thought to be negligible especially for neutral and alkaline papers. Pure cellulose paper is less susceptible to oxidation than paper containing lignin, hemicelluloses or various additives [4].

During accelerated degradation, oxidation is caused by oxygen, acting as a non-specific oxidising agent. The autoxidation scheme, shown in Figure 2.2, is thought to adequately describe the process of oxidation of organic polymers, including cellulose. A direct reaction between cellulose and an oxygen molecule in unlikely, as it is a spin-forbidden[1] process. The more reactive oxygen species are superoxide anion ($O_2^{\bullet -}$), hydroperoxyl radical ($HOO^{\bullet}$), hydrogen peroxide (H_2O_2) and hydroxyl radical ($HO^{\bullet}$), but their direct reactions with cellulose may not be thermodynamically favourable due to high reduction potentials, except for hydroxyl radicals. The most reactive part of a cellulose macromolecule is the aldehyde group at the end of the chain, and it was shown that the content of peroxides, which influence the rate of degradation, after a pre-oxidation treatment depends on the initial content of aldehyde groups [26,31].

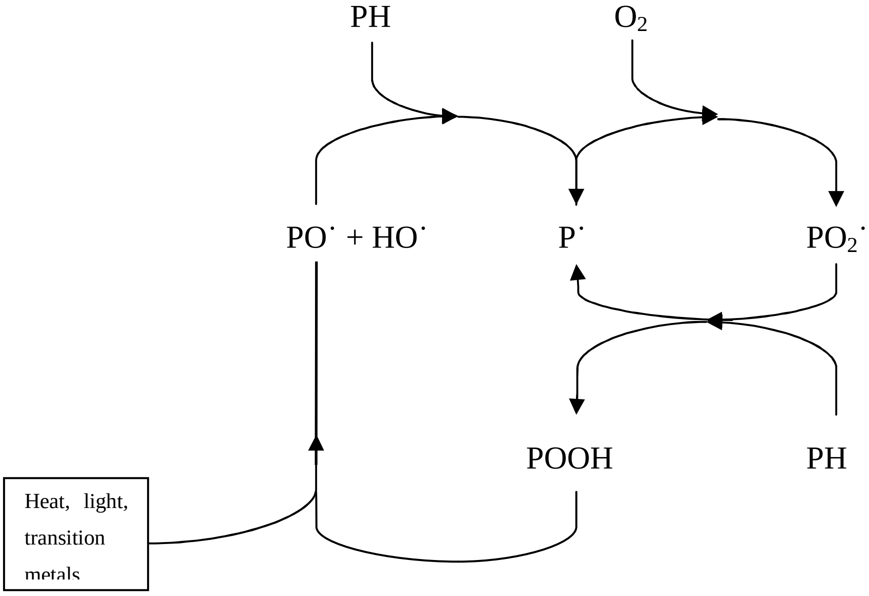

Figure 2.5: The Bolland-Gee autoxidation scheme, where the native cellulose polymer is denoted as PH [26].

Transition metal ions can reduce oxygen to superoxide and produce radicals via the Fenton reaction, therefore contributing to the oxidation process. Lignin and hemicelluloses may initiate the production of reactive oxygen species and peroxides as well [4].

Cross-linking of cellulose can also occur during accelerated degradation at elevated temperatures, resulting in increased wet-strength, restricted swelling by water sorption and increased brittleness of paper. An increase in wet-strength was observed over a wide range of elevated temperatures (70-350 °C) [32]. Cross-linking is speculated to also occur during natural ageing and has been shown to occur during

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[1] Spin forbidden processes are those, where electronic transition would occur within a set of p or d orbitals.

photodegradation [33]. Similar to hydrolysis, this process is catalysed by acidity and metal ions with a high redox potential. Cross-linking and chain scission are competing processes and cross-linking can cause an increase in tensile strength in the early stage of thermal ageing, which is then followed by a decline due to chain scission [4].

A phenomenon, which is supposed to be common for both hydrolytic and oxidative degradation of cellulose, is rapid degradation occurring at the start of the experiment, before linearity is established [6]. This two stage kinetics theory is supported by several authors [34-38].

2.2.2. Degradation kinetics

The most commonly used approach to studying cellulose chain scission was established by Ekenstam in 1936 [39], when he studied the behaviour of cellulose in mineral acids. Although the reaction medium is very different to realistic conditions, the glycosidic bond breakage, responsible for cellulose chain scission, follows similar kinetic principles, which makes this approach a suitable approximation.

Ekenstam defined the number of inter-monomer bonds still present at time *t* as:

$$(P - y - 1), \tag{1}$$

where P is the number of breakable bonds at the beginning of the experiment and is defined as $P = \frac{M}{m}$, (2)

where M is the average molecular weight of cellulose at the beginning of the experiment, and m is the average molecular weight of cellulose at the end of degradation. y is the number of broken bonds after time *t* and is defined as:

$$y = \frac{M}{x} - 1 \tag{3}$$

In this equation, x is the average molecular weight of cellulose after time *t*. The number of broken bonds in a unit of time is:

$$\frac{dy}{dt} = k(P - y - 1) = k\left(\frac{M}{m} - \frac{M}{x}\right), \tag{4}$$

where *k* is a constant. By deriving Equation 3 we obtain:

$$\frac{dy}{dt} = -\frac{M}{x^2}\frac{dx}{dt}, \tag{5}$$

so Equation 4 becomes:

$$-\frac{M}{x^2}\frac{dx}{dt} = k\left(\frac{M}{m} - \frac{M}{x}\right) \qquad \text{and} \qquad \frac{dx}{dt} = -\frac{k}{m}(x^2 - mx). \tag{6}$$

By integration, Ekenstam obtained the equation (*x* in the above equations is substituted for M_t, molecular weight at time *t*):

$$k = \frac{1}{t} ln \frac{\left(1-\frac{m}{M}\right)}{\left(1-\frac{m}{M_t}\right)}, \tag{7}$$

which, when developed into a Taylor series, yields:

$$k = \frac{1}{t}\frac{m(M - M_t)}{MM_t} + \frac{1}{t}\frac{m^2(M^2 - M_t^2)}{2M^2M_t^2} + \ ... \tag{8}$$

Since all the terms from the second one onwards are very small compared to the first one, they can be neglected, which gives:

$$kt = \frac{m(M - M_t)}{MM_t}. \qquad [39] \tag{9}$$

By substituting $\frac{M_t}{m}$ with *DP* and $\frac{M}{m}$ with DP_0, the very well-known Ekenstam equation is obtained:

$$kt = \frac{1}{DP} - \frac{1}{DP_0}\ , \tag{10}$$

where *DP* represents the number of monomers in a chain at time *t* and DP_0 at the beginning of the experiment.

This approach can only be used if the polymer chain is linear and of high molecular weight, the polymer is monodisperse and the products of scission are long chains themselves, there is a low degree of chain end-chopping and there is no loss of monomer units during scission. Although this idealized approach does not fully apply to cellulose, it is used extensively as a simple tool for kinetic analysis and was shown to be applicable to a wide range of experimental data [6].

The Ekenstam equation is a derivation of the rate law of chemical reaction kinetics:

$$reaction\,rate\ = \frac{dc}{dt} = -kc^{n}, \tag{11}$$

where c is normally reactant concentration, n is reaction order, t is time and k is the rate constant. In paper ageing kinetics, c can be replaced by paper properties, like tensile strength, brightness, fold endurance [22]. Molecular weight distributions show that the depolymerisation of cellulose proceeds in a random fashion and follows first order reaction kinetics [21]. In the early stages, however, it can be approximated (simplified) to a pseudo zero order reaction [4].

The temperature dependence of degradation rate constants is described by the Arrhenius equation:

$$k\ =\ Ae^{-\frac{E_a}{RT}}, \tag{12}$$

where A is the frequency factor, E_a is activation energy, R is the gas constant and T is absolute temperature [22,40]. The activation energy depends mainly on the mechanism of the reaction and represents a measure of sensitivity of the degradation rate of the studied property to temperature changes (the higher the E_a, the more temperature-dependent the reaction). The factor A represents all other experimental parameters, such as humidity, pollutants and light and paper properties, such as acidity, fibre source and morphology, additives in paper etc. [40,41]. It should be noted, however, that the pre-exponential factor is not necessarily a constant and can depend on a number of environmental parameters and material properties.

The Arrhenius equation was developed to describe single chemical reaction systems and for a valid Arrhenius model a straight line is obtained when plotting the logarithm of the reaction rate against reciprocal values of temperatures. Reaction rates at different temperatures are therefore obtained from the line slope and intercept, and this approach is commonly used to predict degradation rates at e.g. room temperature. However, paper degradation can involve multiple reactions [40], which raised doubts about the applicability of the equation. Nevertheless, Zou et al. [22] demonstrated that paper degradation follows the Arrhenius law even if activation energies of individual reactions are considerably different. To do so one should apply A_a and E_a as the frequency factor and apparent activation energy of a multiple reaction system, respectively.

According to Barański et al. [25,42] the multiple reaction system or mixed-control mechanism should be solved with two Arrhenius plots, as there are two separate rate constants (k_h – hydrolysis and k_{ox} – oxidation). Ekenstam equation should be replaced by a 'mixed-control' equation, however the equation itself has not yet been suggested. The experiments by Barański et al. [42] were carried out in closed vessels, so the oxygen consumption during the experiment was not taken into account, which might have a significant effect on the results.

Beside the usual extrapolation approach, based on accelerated degradation experiments at a number of temperatures using the Arrhenius equation, the time-temperature superposition method was also applied to paper permanence prediction [43]. It was claimed to give better correlation with ageing under ambient conditions and it has been assessed quantitatively against literature data. It does however have a drawback, which is that it has only been developed for thermal degradation. As such it does not take into account the effects of relative humidity, acidity etc. [43].

As mentioned earlier, the degree of polymerisation (*DP*) is one of the most widespread properties used to follow paper degradation. The number-average *DP* is the ratio between the number of monomers (*M*) and the number of macromolecules (m):

$$DP_0 = \frac{M}{m}, \tag{13}$$

and each scission (*S*) decreases the amount of inter-monomer bonds and increases the number of chains [44]:

$$DP = \frac{M}{(m + S)}. \tag{14}$$

As the number-average *DP* cannot be determined in a simple way, it is replaced by the viscosity-average *DP*, calculated from the viscosity of the cellulose solution. Due to a simple mathematical relation between the number of cellulose chain scissions and the degree of polymerisation (*DP*) the latter became the most commonly used parameter to assess the rate of paper degradation. It should not, however, be used without caution [41,44]. When employing viscometric *DP* determination it has to be considered that during the dissolution of a sample in the alkaline cupriethylenediamine solvent, chain scission will take place at a certain rate wherever an oxidised group has been introduced into a monomer. The measured *DP* (and therefore the number of scissions, obtained by *DP*) is therefore the sum of both the actual (hydrolytic and oxidative) and potential (oxidative) degradation [41,45].

The number of scissions is not a measurable property, but found useful in determining degradation kinetics. It is generally given by:

$$S = \frac{1}{DP} - \frac{1}{DP_0}, \qquad (15)$$

where DP_0 is the initial degree of polymerisation . Since the equation consists of two reciprocal values of *DP*, the experimental uncertainties of the actual *DP* values are propagated in the uncertainty of determination of the number of scissions.

Assuming that paper degradation is a pseudo-zero order reaction, Equation 15 equals Equation 10, i.e. the Ekenstam equation:

$$S = \frac{1}{DP} - \frac{1}{DP_0} = kt, \qquad (16)$$

where *k* is rate constant and *t* is time [21,22,25,39,46]. However there are some strong arguments against the pseudo-zero order assumption, particularly the non-linear multi-stage degradation model, consisting of at least two consecutive stages of degradation: a faster one and a slower one. This does not necessarily mean that the Ekenstam equation cannot be applied; it does however mean that two or more different rates (*k*) might be needed to describe the different stages of degradation. There are different theories about the stages; some suggest the weaker links being attacked in the faster stage, and the reactions taking place in the amorphous region in the slower stage, and others suggest fast acid-catalysed hydrolysis in the amorphous phase and slower hydrolysis in the crystalline phase [34-38,41]. The suggested ‘weak links’ occur approximately every 500 monomer units and may be created by chain ends acting as stress raisers in adjacent chains [6]. Another hypothesis is that the initial faster stage actually represents the time needed for the material to reach steady state reaction conditions at the beginning of an accelerated ageing experiment. In all historic paper some degradation already occurred before an accelerated experiment starts, so the papers already contain some partly degraded material (glucose in cellulose), which is more quickly consumed as the temperature is initially increased. This is in agreement with the fact that the addition of glucose to paper accelerates degradation considerably [26]. This initial stage, before the pro-degrading effect of the accumulated degraded material is over, and the material reaches a steady state at a higher temperature, could therefore also represent a fast initial degradation stage.

Calvini and Gorassini [41] suggest including *LODP* (levelling-off degree of polymerisation) rather than glucose as the asymptotic limit in kinetic equations:

$$\frac{DP_0}{DP} - 1 = \left(\frac{DP_0}{LODP} - 1\right)(1 - e^{-kt}), \qquad (17)$$

and always performing accelerated ageing experiments at least until *LODP* is reached [41]. 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 200-300 (400 for ink lines) units [6,14,38,47].

Ding and Wang [38] however argue that the chain scission number (CSN) concept, introduced by Calvini and Gorassini [41,44] is only suitable when the initial degree of polymerisation of all cellulose samples studied is the same. It is unsuitable for characterising the frequency of cellulose chain scission, since the number of scissions at a high *DP* is greater than that at a low *DP* of cellulose, while the chain scission activity of cellulose remains the same [38].

To avoid using the number of scissions as a parameter, Ding and Wang [38] introduced a new continuous scalar variable δ and defined it as ‘percentage retention of *DP*’:

$$\delta = \frac{DP}{DP_0}. \qquad (18)$$

They also defined the degradation variable of cellulose:

$$\omega_{DP} = 1 - \delta = 1 - \frac{DP}{DP_0}, \qquad (19)$$

where ω_{DP} is the accumulated *DP* loss of cellulose. $\omega_{DP} = 0$ corresponds to undamaged cellulose, whereas $\omega_{DP} = 1$ represents total failure of cellulose. As ω_{DP} physically represents the extent of progression of cellulose degradation towards a maximum value before losing all its mechanical strength, the authors believe it to be more mathematically convenient and also accurate than using the number of scissions [38].

As mentioned earlier, Ding and Wang [38] introduced a number of scissile bonds, available for degradation, when degradation time equals zero, described as:

$$\frac{dN}{dt} = k(N_T - N), \tag{20}$$

where $N(t = 0) = 0$ and N_T is the number of scissile bonds. The term can be normalised:

$$n(t) = \frac{N(t)}{N_F}, \tag{21}$$

where N_F is chain scission concentration in polymers at the point of failure and is approximately a constant. Introducing this into the previous equation yields:

$$\frac{dn}{dt} = k(n^* - n), \tag{22}$$

where $n(t = 0) = 0$ and n^* represents the ‘capacity of the chain scission reservoir’. For a constant reaction rate *k*, the equation is:

$$n = n^*(1 - e^{-kt}). \tag{23}$$

As the two degradation state variables, *n* at a molecular level and ω_{DP} at a macroscopic level (concerning cellulose, composed of numerous molecules), are very similar in their nature, the authors assume the same equations can be applied to ω_{DP} as well:

$$\frac{d\omega_{DP}}{dx} = k_{DP}(\omega_{DP}^* - \omega_{DP}), \tag{24}$$

where ω_{DP} (t = 0) = 0. For a constant reaction rate the equation becomes:

$$\omega_{DP} = 1 - \frac{DP}{DP_0} = \omega_{DP}^*(1 - e^{-k_{DP}t}), \tag{25}$$

which was claimed to be a new degradation evolution equation for cellulose, with ω_{DP} representing the ‘capacity of the *DP* degradation reservoir’ [38]. According to the authors cellulose degradation is best described by degree of polymerisation and tensile strength loss, so they applied the same equations to tensile strength (*TS*) loss as well:

$$\omega_{TS} = 1 - \frac{TS}{TS_0} , \tag{26}$$

and

$$\omega_{TS} = 1 - \frac{TS}{TS^0} = \omega^*_{TS}(1 - e^{-k_{TS}t}) , \tag{27}$$

where k_{TS} is the *TS* degradation rate constant and ω^*_{TS} is the ‘capacity of the *TS* degradation reservoir’. ω^*_{TS} can be determined by introducing the condition: $\omega_{TS}(t = t_f) = 1$, t_f being the time to failure, where time to failure represents the time before cellulose loses all its mechanical strength and $\omega_{TS} = 1$ [38]. It has to be noted here that degree of polymerisation and tensile strength are not entirely comparable, as the latter also depends on intermolecular, as well as intramolecular bonding, so the application of this equation might be questionable.

2.2.3. Accelerated degradation experiments

In practice the Arrhenius principle is used in accelerated degradation experiments, which are used for the purpose of studying chemical changes in paper during ageing, based on the assumption that the rate of most chemical reactions increases when the temperature is increased [22]. An assumption is made that no change in mechanism of the degradation reactions takes place between the experimental and ambient temperature. More reliable extrapolation is therefore obtained at smaller temperature extrapolation intervals, so some authors suggest performing accelerated degradation experiments at temperatures as close to room temperature as possible [25,48].

According to some researchers [41,48] Arrhenius equation should not be used to state exactly the rate of paper degradation at room temperature and therefore to predict life expectancy, as the plot might not hold outside the range of temperatures, for which it was obtained. Such extrapolation assumes the activation energy E_a is independent of temperature, which is not always the case, especially if a phase change takes place in the interval of extrapolation [40]. This could simply be avoided by performing accelerated degradation experiments below the glass transition temperature. The glass transition of cellulose, however, is very poorly defined [26] and might stretch over a large interval around 100 °C (some suggest temperatures over 200 °C for dry samples [49], which is decreased by water absorption [50]). If experiments are therefore preformed at temperatures lower than 100 °C, the glass transition temperature might not have any effect.

There have been other objections to accelerated degradation experiments at elevated temperatures due to the complexity of paper as the studied material and the degradation process, which can involve multiple reactions. Generally the question is whether accelerated degradation produces the same effects as natural ageing (only at a faster rate), or if it perhaps promotes chemical reactions which would not occur during the natural process [4,40,48]. Extrapolation can however be very useful to identify the factors that increase the pre-exponential factor A (such as acidity and RH) and decrease activation energy E_a, and by doing so, promote paper degradation [40,41].

To provide an experimental proof of the assumed correlation between accelerated degradation and natural ageing, Zou et al. [46] measured DP, α-cellulose (pure cellulose with a high degree of polymerisation) content and cold extraction pH of bleached Kraft pulps (all samples were acidic), naturally aged for 22 years, and compared them to predictions, obtained from a previously constructed model. When extrapolating results obtained from accelerated degradation to natural ageing conditions, statistical errors associated with original data are inevitably high. It is therefore important to examine the statistical error of prediction. Similar to previous accelerated ageing studies the authors found that the degradation rate strongly depends on sample acidity, as DP values decreased much more significantly for samples with a lower pH. Unlike DP, α-cellulose content did not change much. Bansa and Hofer [51] on the other hand found no correlation between natural and accelerated ageing and claim that the chemical processes are temperature specific. Experimental results should therefore only be used in a relative way (e.g. to compare paper types), not to draw absolute conclusions. They carried out experiments on naturally aged commercially produced paper rather than model paper and measured

DP and tearing resistance during dry or moist degradation. They concluded that paper composition (i.e. type) plays a very important role in how representative accelerated ageing is as well. If accelerated degradation must be employed after all (e.g. to determine whether a change in the paper production process or a conservation treatment has a positive or negative effect on the degradation of a specific paper), they suggested experiments at 80 °C and 65% RH.

Another factor to be taken into account is the way in which paper is exposed to accelerated degradation and there is some evidence that degradation in sealed tubes resembles natural ageing most [4]. The reason being that they maintain a steady moisture content of paper and retain degradation products, which could further promote the degradation process.

Although planning accelerated degradation experiments, which would provide useful results, indicative of processes taking place during natural ageing, might not be very straight-forward and a general consensus on the applicability of the Arrhenius principle has not been reached yet, this model is still the best available temperature-dependent function, describing cellulose chain scission.

2.3. Lifetime and permanence

The remaining lifetime of paper is difficult to predict because it involves the decision as to when paper reaches the end of useful lifetime. The relative lifetime was first defined by Shahani et al. [52] as time required for fold endurance to decrease to an eighth of the initial value. Another possibility proposed was to calculate the ‘time to 50% property loss’ ($PL_{50\%}$) [40], which unfortunately gives little idea of the actual lifetime. 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 200-300) [6,14,47].

Lifetime of paper, used for insulation in transformers, was defined using the Ekenstam equation:

$$\frac{1}{DP_{final}} - \frac{1}{DP_{initial}} = k\ (life). \tag{28}$$

DP_{final} was set at 200 and $DP_{initial}$ at 1000. Degradation rate was calculated using the Arrhenius equation and experimentally determined pre-exponential factor and activation energy [6].

This was also defined for ink lines [53], where the time needed for an ink line to become fragile under conditions, similar to storage conditions until the present time, can be calculated. The point of risk of failure for ink lines was determined as $DP_i = 400$, where the index i indicates the DP of paper with an ink line. The Ekenstam equation, used in this example, is:

$$t_{400} = \frac{1}{k_i}\left(\frac{1}{400} - \frac{1}{DPi}\right). \tag{29}$$

A very well received attempt to describe the relative useful life expectancy of paper-based collections in relative terms was introduced by Sebera [54]. As a part of his preservation strategy Sebera proposed isoperms as a quantitative tool for predicting the ‘preservation outcome’ [54,55]. The method employs relative rather than absolute lifetimes and substitutes rates of deterioration with relative permanence, which is the inverse of the deterioration rate ratio:

$$\frac{P_2}{P_1} = \frac{1}{\frac{k_2}{k_1}} = \frac{k_1}{k_2} \tag{30}$$

where P represents permanence and k deterioration rate [54].

The isoperm method quantifies in relative terms (relative to paper permanence at 20 ^{o}C, 50% RH) the effect of temperature and relative humidity upon the anticipated useful life expectancy of paper-based collections [54].

Sebera described the effect of RH as follows: the greater the % RH of the environment, the greater the moisture content of paper, the higher the moisture content of paper, the greater the hydrolysis deterioration rate of paper, the faster the paper deterioration, the shorter the life expectancy (permanence) of the paper, which can be summarized as:

$$\frac{k_2}{k_1} = \frac{c(H_2O)_2}{c(H_2O)_1} = \frac{RH_2}{RH_1} = \frac{P_1}{P_2} \tag{31}$$

where RH_1 and RH_2 are percent relative humidity in the environment in equilibrium with the paper and $c(H_2O)_1$ and $c(H_2O)_2$ are moisture contents of the paper [54]. It was therefore assumed that the rate of degradation is linearly proportional to RH, which does not necessarily hold for all paper types. There is some indication that the proportionality is exponential for model acidic papers and hyperbolic for model alkaline papers with a maximum rate at about 60% RH [27], indicating that RH dependence differs according to paper type, especially pH. A power law relationship between the degradation rate and RH was suggested by Michalski [56], when he found fibre strength loss to be proportional to $RH^{1.3}$. Generally an agreement on RH dependence has not yet been reached, which indicates more research on the subject is needed.

Sebera described the effect of temperature change using the Eyring equation [54]:

$$\frac{k_2}{k_1} = \frac{T_2}{T_1} e^{\frac{\Delta^{\ddagger} H^{o}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}, \tag{32}$$

where $\Delta^{\ddagger}H^{0}$ is the standard enthalpy of activation in J/mol, R is the gas constant 8.314 J/molK and T_1 and T_2 are temperatures in K. Sebera combined the two effects of T and RH as:

$$\frac{r_2}{r_1} = \frac{RH_2}{RH_1} \frac{T_2}{T_1} e^{\frac{\Delta^{\ddagger} H^{o}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} . \tag{33}$$

Employing relative permanence the equation becomes:

$$\frac{P_2}{P_1} = \frac{RH_1}{RH_2} \frac{T_1}{T_2} e^{\frac{\Delta^{\ddagger} H^{o}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} . \tag{34}$$

The isoperm is constructed so that points, at which the permanence of paper is equal, are linked: if RH is increased, the temperature is reduced by exactly the right amount to decrease the deterioration rate. A line of constant permanence (isopermanence) was defined as the isoperm [54]. Different isoperms represent different deterioration rate ratios and are calculated from the combined-effect Equation 33 (product of T and RH). The isoperms were constructed to enable simple assessment of the impact of storage conditions, and according to the author they are not supposed to be applied to extreme conditions, such as sub-zero temperatures [54]. From the thermodynamic point of view there is no reason why they should not be used, however, definition of relative humidity at such temperatures is somewhat more complicated [57].

Isoperms were recently revised by Strang and Grattan [55], arguing that it is the concentration of water in the cell wall rather than the concentration of water vapour in the atmosphere (as expressed by the RH), which has a direct impact on the rate of degradation of paper. Sebera's assumption was claimed not to be consistent with the moisture sorption isotherm for paper, because it describes a linear relationship between RH and moisture content in paper, whereas the relationship is actually a sigmoidal curve, with only approximate linearity in the middle of the moisture sorption isotherms [55]. The authors argued that there is significant non-linearity at the dry and damp ends, which is where the greatest protection and deterioration occur, which Sebera acknowledged by stating his method is to be used in the non-extreme conditions, commonly encountered in practice (30-65% RH) [54].

To account for the non-linear relationship between RH and moisture content, Strang and Grattan used the Guggenheim-Anderson-deBoer equation (GAB) [55], initially suggested by Parker et al. [58] after reviewing different moisture sorption models, which describes paper moisture sorption:

$$\frac{P_2}{P_1} = \frac{GAB_1}{GAB_2} \times \frac{k_1}{k_2}, \tag{35}$$

where *GAB* represents moisture content. It is given by the equation:

$$M = \frac{M_0 K C A_w}{(1 - KA_w)(1 - KA_w + CKA_w)} , \tag{36}$$

and *k* is given by the Arrhenius equation:

$$k = A\, e^{-\frac{E_a}{RT}} , \tag{12}$$

where E_a is the activation energy (J/mol), *A* is the pre-exponential or frequency factor, *R* is the gas constant (8.314 J/molK), *M* is the equilibrium moisture content, M_0 is the mono-layer moisture content, *K* is the difference in state between pure liquid and upper layers, *C* is the difference between the monolayer and the upper layers and A_w is the water activity, which is temperature dependent [55].

As Zou et al. described previously, it is the moisture content, not relative humidity, that is linearly related to a first order rate constant for the acid-catalysed hydrolysis [22], and taking this into account the isoperms should be, according to Strang and Grattan [55], calculated as follows:

$$\frac{P_2}{P_1} = \frac{\frac{M_{01}K_1C_1A_{w1}}{(1-K_1A_{w1})(1-K_1A_{w1}+C_1K_1A_{w1})}}{\frac{M_{02}K_2C_2A_{w2}}{(1-K_2A_{w2})(1-K_2A_{w2}+C_2K_2A_{w2})}} \times e^{\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}, \tag{37}$$

where subscript 1 represents initial or reference state and subscript 2 represents a proposed state for comparison [55].

However, other research shows an exponential or power dependence of the rate of degradation on relative humidity, at least for model papers at elevated temperatures [27,56]. Additionally, there is indication that the degradation of acidic papers depends on RH differently to alkaline papers. If this is so, then the isoperms are in need of revision and need to reflect differences in paper composition. Alternatively, comparisons using isoperms should only be made within the same paper type or group of papers with similar sensitivity or response to RH.

2.4. Conclusion

The main component of paper is cellulose, which unfortunately degrades during ageing. The main degradation mechanism is acid-catalyses hydrolysis, although other mechanisms might play a role as well, such as oxidation or cross-linking. Cellulose degradation can be followed using different analytical methods, depending on the purpose of the paper-based material in question. Determining degree of polymerisation (*DP*) and following colour change, however, are generally very common approaches. If the degradation process is simplified to a pseudo zero order reaction, degradation rates can be calculated using the Ekenstam equation. Different ways of describing the remaining useful lifetime, both absolute and relative, have been introduced so far, including the well-known and accepted isoperm approach.

3. Agents of paper degradation

The degradation processes, described in the previous Chapter, are affected by different factors. Among the many agents of degradation, temperature (*T*) and relative humidity (RH) [20,52,54,55,59-64], light [59,65-69], pollution [59,69-74], biogenic agents [71,75,76] and paper composition [21,22,40,41,59,70,71,77,78] have been researched the most. While *T* and RH have been discussed in the previous chapter, only their fluctuations will be addressed in this section.

3.1. Biogenic agents

Biodegradation is caused by organisms which have the ability of using substrates to sustain their growth and reproduction. Microbial activity affects not only the appearance of objects, but often consists of modification of their chemical and physical structure. Different types of paper sizing were associated with very different types of microbiologically induced stains and damage [75,76]. Biodegradation is also the only degradation process that leads to changes in the paper's elemental composition, especially calcium content, whereas trace elements heavier than Ca are not affected [71]. A decrease in Ca concentration is due to *C. cellulolyticum*, an anaerobic bacterium which produces enzymes, which bind Ca. However, microbial activity on paper is only possible in the presence of unbound water in the substrate which is available for mould growth. This requirement is especially easily fulfilled at RH levels higher than 65% and temperatures above 20 °C, when moisture content of paper reaches 8-10% [75]. Another form of biodegradation is degradation by fungi. The organic components of paper can be decomposed by saprotrophic fungi [75,79]. Formation of calcium oxalates during fungal growth is a well known phenomenon on marbles and other inorganic materials, but it has been shown recently that inorganic components in paper can also be subjected to biodegradation [80]. Pinzari et al. [80] studied biogenic formation of calcium oxalate crystals on paper samples and found that papers containing carbonates (such as contemporary alkaline, where carbonates can be used as alkaline reserve) were significantly affected by the growth of *A. terreus*, while acidic papers, containing clay and alum, remained unaffected. Calcium is often present in modern and ancient paper as filling material and can play an important role in substrate exploitation by the fungus. Some bacteria are capable of degrading plant material using cellulose and starch hydrolysing enzymes, and could therefore cause damage to materials containing cellulose. It was also shown that airborne bacteria, which could also be harmful to paper-based objects, are more abundant in the summer than in winter [81]. Luckily however most mould and fungal degradation can be avoided by RH and temperature control, by maintaining RH below 65% and *T* below 20 °C.

3.2. Pollution

Another factor affecting paper degradation is pollution, generated both outdoors and indoors. Outdoor pollutants mostly originate from traffic and industry and enter repositories through windows or ventilation, whereas indoor generated ones are emitted by building and furnishing materials and also paper-based objects themselves [72,73]. The most common outdoor pollutants are nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone (O_3), hydrogen sulfide (H_2S) and particulate matter (PM) and they all have negative effects on degradation of paper [72-74].

Typical pollutant concentrations, summarized in [72] and [73], are listed in Table 3.1.

Table 3.1: Typical outdoor and indoor concentrations, summarized by Blades and Tétreault.

	Blades et al. [72]		Tétreault [73]	
pollutant	**outdoor** (UK urban) /ppb except particles	**indoor** /ppb except particles	**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

*** is < 1 with chemical filtration.**

The concentration of SO_2 has decreased significantly in the 20th century, initially due to dilution as cities expanded and then due to changes in legislation, which led to somewhat ‘cleaner’ industry. In parallel the decline was partly caused by the reduction in coal consumption due to the wide use of electricity in households [82]. The 20th century was marked by increasing emissions of nitrogen oxides and volatile organic compounds (VOC), which resulted in the evolution of photochemically polluted urban air. In such conditions secondary pollutants are produced by reactions in the atmosphere. An example of this is O_3 in urban air, and unlike NO_2, which has stabilised in terms of outdoor concentration, the concentrations of O_3 might slowly increase in the future [83]. However it is likely that future urban atmosphere will be dominated by organic pollutants, while the concentrations of traditional pollutants, such as SO_2 and NO_2, will continue to decrease [82-84].

Indoor generated pollutants are mainly organic compounds, introduced into the environment by emissions from building and furnishing materials. In order to cause damage to materials the pollutants have to deposit onto their surface, which means they have to be quite polar, such as organic acids or other short-chain carbonyls, or reactive with surfaces, such as O_3 [85]. Indoor generated pollutants can also be emitted from the collection itself, as was quantified by Ramalho et al. [86]. After artificially ageing pure cotton linters and groundwood pulp paper they quantified the emission rates of volatile compounds, emitted during degradation. An extensive study, where measurements of VOC concentrations were carried out in several archives and libraries in the UK and Ireland was recently carried out by Gibson et al. [87]. They compared acetic acid concentrations in locations, where paper-based collections were stored, with reference concentrations in the same building, but in a location where no paper-based material was kept. They found that acetic acid (AcOH) concentrations were significantly higher in repositories, containing paper-based materials, in all but one building. The concentrations were mainly between 50 and 100 ppb, but ranged from 20 to 150 ppb. Similarly high concentrations in low air exchange locations (such as boxes) were reported by Ryhl-Svendsen [88]. Even higher concentrations, up to 170 ppb were measured in the Library of Geneva [89].

Besides VOCs, emitted from paper, other pollutants can also have 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 [90].

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) [91]. Particulate matter is another potentially harmful pollutant, as particles might create deposits on surfaces and promote corrosion processes due to their hygroscopic nature [73] and in some cases surface affinity to gaseous pollutants [92]. Different types of particles have different effects on objects. Organic particles cause deterioration in visual properties by soiling the surface and can also increase SO_2 absorption and sulfur (S) -rich particles, such as sulfates, can cause discolouration, which can be catalysed by iron (Fe) -rich particles [81]. Damage can be caused when chemical reactions occur with the gases or other harmful compounds, which could be present in the deposited particles. This can happen especially when the particles become ‘wetted’ and a liquid phase with possibly high compound concentrations is formed. 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 [93]. The presence of polar functional groups, particularly carboxyl and dicarboxyl, on organic particles can increase the solubility of many organic compounds, present in aerosol, and so allows them to participate in chemical reactions [92]. Organic, S-rich and Fe-rich particles are therefore considered the most harmful in view of conservation [93]. 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 aluminosilicates 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. [91]. 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. [93], Godoi et al. [92] and Kontozova-Deutsch et al. [91]. Particles are usually classified and analyzed according to their size, for example 0.5, 1, 2, 4, 8 and 20 µm [81,93]. The coarse fraction of particles (> 2.5 µm) is mostly soil dust, which is related to human activity in the building, as visitors are an important source of dust particles, which are continuously resuspended [91,93]. Smaller aerosol particles are not as affected by human activity inside a building, but are more weather-dependent, as for example their concentration decreases when it rains [93]. Indoor concentrations of particles, determined by Gysels et al. in the Royal Museum of Fine

Arts in Antwerp, Belgium [93] 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 μg/m^3 (different units due to different analytical methods). Similar to already mentioned inorganic pollutants the concentration of coarse particulates can be reduced by air-conditioning (as opposed to natural ventilation) and filtration, which was shown by Godoi et al. [92], so the main concern are the fine organic particles, which might have an indoor source.

Air filtration can effectively reduce the concentrations of outdoor-generated pollutants, while there is little data available on its efficiency regarding indoor-generated pollutants. Measurements, carried out at the Swiss National Library, showed that AcOH concentration can be reduced by 20-30% if a chemical filtration unit (activated carbon filter) is installed [94], but no examples were found in the literature. Sorbent properties were studied by Grosjean and Parmar [95], when they compared removal rates of various pollutants, found in museum display cases, by activated carbon and Purafil (potassium permanganate on activated alumina). They found that activated carbon was much more efficient in removing pollutants, but also that aldehydes and chlorinated hydrocarbons (carboxylic acids were not included in the study) were more difficult (or slower) to remove compared to NO_x.

In a study, carried out in the Nationaal Archief [96], model (bleached sulfite softwood cellulose, cotton linters cellulose and groundwood containing paper) and original paper materials were stored in one repository with and one without air filtration for eight years. A measurable positive effect of air purification was noticed, as the materials, exposed to higher pollutant concentrations in the repository without air filtration, became more acidic and discoloured compared to the ones stored in the filtered environment [96].

In studies of the effects of pollutants on paper most research is carried out with very high pollutant concentrations, usually around 10 ppm, which is about a thousand times higher than the typical concentrations indoors [70,97,98,99,100]. It is argued that the concentrations should be significantly elevated from realistic conditions in order to obtain measurable results in a practical timeframe, even though the extrapolation to lower concentrations might be questionable. This concern was already expressed by Williams and Grosjean [101], arguing 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 on the validity of high concentration experiments were also expressed by Adelstein et al. [99], when they concluded that their observations, obtained in 50 ppm NO_2, reflect changes at much lower concentrations, but that they have not found whether the concentration multiplied by exposure time has a constant effect .

Generally, absorption of SO_2 and NO_2 causes acidification of paper, especially of paper types without an alkaline reserve, and NO_2 is also an oxidant. Acidification subsequently leads to loss in mechanical properties, represented by the loss of cellulose *DP* [97,99,102]. Alkaline reserve is common in contemporary paper and is created by adding bicarbonates to wood pulp during the production process. After drying this results in residual carbonates in paper, which protect it from both endogenous and exogenous acids, therefore prolonging the paper's lifetime. Although such paper is relatively resistant towards acid-catalysed hydrolysis, it can still be affected by oxidants.

Lignin-containing papers are thought to be more susceptible to pollutant absorption, and consequently damage, especially in terms of yellowing [97,99,102]. NO_x is thought to react with both lignin, causing yellowing, and cellulose, causing depolymerisation and the higher SO_2 uptake can probably be attributed to sulfonation of lignin [103,104]. Zou [104], however, suggested that lignin might provide some protection to cellulose by preferentially reacting with NO_x. NO_x would therefore be consumed for the yellowing of lignin instead of cellulose chain scission, at least in the initial stage.

Lately, indoor-generated pollutants have attracted increased interest, as the concentrations of volatile organic acids and aldehydes were found to be significant [72-74,87,105] and can exceed the concentration of traffic generated pollutants by a factor of 10 and more [105]. VOCs cannot be removed from the atmosphere as easily as previously mentioned pollutants, as their sources include the paper-based collection itself, so air filtration has little effect on their concentrations. They can, however, also have a deteriorating effect on paper. A study was 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 [106]. Papers were placed into glass vials together with VOCs and in some cases pollutant scavengers. Sealed vials were then exposed to 50 °C for one year. After the experiments, *DP* and molecular weight of the samples were determined. It was shown that volatile acids have the most pronounced negative effect on paper degradation, although similar results were obtained for aldehydes as well. The effects of added VOCs differ depending on paper type, with neutral and alkaline papers being more affected than acidic and lignin-containing papers, as the latter are net emitters of VOCs. This has been shown in a study where different paper types were degraded together in the same vial to investigate the effect they had on each other [107]. A pronounced negative effect of groundwood paper on the reference sheet was observed, indicating significant VOC emission. Rag paper, on the other hand, had no or a slight positive effect, suggesting it behaved as an absorber for VOCs, emitted from the reference sheet. 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 [106].

Another study on VOC-induced degradation was recently carried out [100], where Whatman paper was exposed to high concentrations (20 – 80 ppm) of volatile compounds, commonly released by paper (carboxylic acids, carbonyls and hydrogen peroxide). Whatman No.1 and Whatman No.40 (the latter being the more acidic of the two) were exposed to pollutants and humidity using salt solutions in desiccators at room temperature. After the exposure the samples were thermally aged as well. The experiments showed that hydrogen peroxide and formic acid were the most harmful to both papers, whereas the effect of AcOH was small and aldehydes were found to have no effect. A mixture of AcOH and NO_x, originating from the salt used to generate the appropriate humidity, however did cause significant degradation, possibly due to NO_x. Although this study indicates a significant effect of some VOCs, especially formic acid, it should be pointed out that the concentrations used in the experiments are several orders of magnitude higher that what could realistically be found in a repository.

The behaviour and consequently effect of pollutants can depend greatly on relative humidity, more accurately on the moisture content of paper. It is well known that some inorganic as well as organic pollutants hydrolyse. This process applies to absorbed water in paper as well:

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

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

The shift of the above equilibria depends on the pH of paper, as pH > pK_a[2] shifts the equilibrium to the right and pH < pK_a shifts it to the left (at pH = pK_a the concentrations of the dissociated and undissociated form are equal). 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 [102]:

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

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

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

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

This is the main source of nitrous acid (HNO_2) indoors [102].

Besides hydrolysing, pollutants can also react with each other, which affects their indoor concentrations. When O_3 is present the risk increases for all papers, as HSO_3^- can be oxidised to HSO_4^-, which has a significantly lower pK_a value and therefore dissociates much easier:

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[2] Negative logarithm of the acid dissociation constant K_a, the measure of acidity.

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

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

$HSO_4^- + H_2O \rightleftarrows SO_4^{2-} + H_3O^+$ $\quad$ $pK_a = 1.99$

The amount of NO_2 also depends on the presence of O_3:

$NO + O_3 \rightleftarrows NO_2 + O_2$

A higher O_3 concentration shifts the equilibrium to the right, whereas the reverse reaction is driven by sunlight [81].The indoor pollutants acetic and formic acid also dissociate in water:

$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$ $\quad$ $pK_a = 4.75$

$HCOOH + H_2O \rightleftarrows HCOO^- + H_3O^+$ $\quad$ $pK_a = 3.75$

In very acidic papers ($pH < 4.75$) AcOH will not dissociate easily and therefore its contribution to acidity will be small. The case of neutral or alkaline papers is potentially different, as AcOH will dissociate (the equilibrium shifts to the right), producing hydronium ions and thus accelerating paper degradation. The pH range, where formic acid dissociates fairly easily, producing H_3O^+ ions, is somewhat broader than for AcOH, as the equilibrium shifts to the right at $pH > 3.75$.

Some recommendations on the acceptable pollutant concentrations have been made and are gathered in the publication by Blades et al. [72]. They range from 0 to 4 ppb for SO_2, from 0 to 5 ppb for NO_2 and from 0 to 13 ppb for O_3. Recommended maximum exposure level for airborne particles PM_{10} is 75 $\mu g/m^3$; however no suggestions have been made about volatile organic compounds in this publication. The British Standard for storage and exhibition of archival documents BS 5454:2000 [108], in use when the research described in this thesis started, is more rigid, as it suggests 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, especially the ones with indoor sources. The suggestions were improved by the recently published Specification for managing environmental conditions for cultural collections PAS 198:2012 [5], stating that pollution related damage is cumulative, therefore no safe pollutant concentrations can be defined as they would depend on exposure time. This concept was introduced by Tétreault [73] when he suggested different pollutant levels for different exposure times (1, 10 and 100 years). This uses the hypothesis that the concentration multiplied by exposure time has a constant effect. For example a 10-year exposure allows a concentration 10 times greater than a 100-year exposure. Maximum levels suggested for 1-year exposure time for paper are 400 ppb (1000 $\mu g/m^3$) for AcOH, 0.71 ppb (1 $\mu g/m^3$) for hydrogen sulfite, 5.2 ppb (10 $\mu g/m^3$) for NO_2, 5.0 ppb (10 $\mu g/m^3$) for O_3, 3.8 ppb (10 $\mu g/m^3$) for SO_2 and 10 $\mu g/m^3$ for fine particles ($PM_{2.5}$).

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) [73]. He defined adverse effect as the first visually perceptible change; a specific chemical or 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. As minor changes in the materials are often difficult to monitor and the NOAEL concept is not applicable to some pollutant-material systems, the lowest observable adverse effect dose (LOAED) is sometimes used to quantify the exposure-effect relationship. LOAED is the cumulative dose, at which the first adverse effects appear; estimation of time required to observe an adverse effect on a material at different pollutant concentrations can be estimated due to assumed linear reciprocity. However not all pollutant-material systems follow the linear reciprocity principle, as some deterioration processes follow auto-retardant patterns and others are autocatalytic, so the LOAED concept might only be valid in a certain concentration range and for certain pollutant-material interactions [73]. In auto-retardant processes deterioration is fast at the beginning and is reduced progressively over time, whereas in autocatalytic processes formation of new products accelerates the deterioration. An example of a self destructive object is acidic paper, since its main degradation mechanism is hydrolysis, which is accelerated by the accumulation of the degradation products, VOCs emitted by the paper itself.

For establishing the NOAEL and LOAED a rather complex degradation process (e.g. paper degradation) is simplified to the most abundant (or harmful) pollutant having the most effect on the rate of degradation and the other parameters, such as temperature and relative humidity, not contributing significantly to the overall degradation process [73]. So in principle the ‘concentration multiplied by time equals a constant effect’ concept should only be used in well-defined and stable environmental conditions, where the most harmful process of degradation, in this case pollution-material interaction, can be prioritised over other degradation processes. Equally lowest-effect pollutant doses (LOAED) should be determined separately for each material (in this case paper type), as the effect could be quite different for papers of different compositions.

3.3. Light

Most polymers are sensitive to radiation at wavelengths including natural radiation (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 [109].

Radiation-induced degradation can follow two pathways, direct photolysis and photosensitised degradation. Light penetrating indoors is filtered by glass windows, so that wavelengths <340 nm are removed and direct photolysis in paper does not occur. However, absorption of radiation with λ >360 nm may induce homolytic decomposition of hydroperoxides, producing reactive hydroxyl radicals, causing subsequent photo-initiated decay of cellulose:

$H_2O_2 + h\nu \rightarrow 2HO^{\bullet}$.

Photosensitised oxidation of cellulose is believed to proceed in a similar way to oxidation, described in the previous Chapter (section 2.2.1., Figure 2.2). The initial step is therefore:

$ROOH + h\nu \rightarrow RO^{\bullet} + HO^{\bullet}$

The rate of oxidative degradation of polysaccharides during thermally accelerated degradation depends on the amount of carbonyl groups, transition metals and other impurities in the starting material, and in the case of light-induced degradation the most common oxidation initiators are ketones and hydroperoxides [110]. Exposure to radiation, filtered by glass windows (λ <340 nm), promotes oxidation reactions even in pure cellulose, but has a much greater effect on groundwood paper, affecting lignin degradation [65].

The consequences of long term exposure to light are increased acidity, discolouration, enhanced production of carbonyls and loss of mechanical strength [65,66]. These consequences can be observed up to the 5th sheet from the surface of a paper stack [66]. 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 increase of brightness [110].

Paper can be affected by light even if immediately after the exposure little or no change in its visual and mechanical properties is observed. When previously irradiated papers were subsequently thermally aged at 80 °C and the rates of degradation during this thermal treatment were compared to those of papers not previously exposed to light, the exposed papers were found to degrade up to 40% faster in terms of *DP* loss [110]. This indicates that light-induced degradation leads to accumulation of degradation products, subsequently affecting paper degradation in the dark. While light ageing could potentially be regarded as a cumulative process, it can trigger accelerated degradation processes once the object is back in the dark.

The same authors have shown that relative humidity plays an important role in light-induced paper degradation [110] and similarly to most degradation processes it is thought that light-induced degradation increases with increasing relative humidity [111]. It is therefore important to design accelerated ageing experiments with controlled relative humidity in order to distinguish between the effects and to be able to compare results from different studies.

The effect of light is thought to be of lower importance for paper degradation than the effect of pollutants in an average archive environment [96] and most of its negative effects are avoided by storage in the dark, except for papers that have been previously exhibited [65,110].

3.4. Temperature and relative humidity fluctuations

Storage conditions directly affect the moisture content of paper [54,55]. High moisture content in paper represents the reaction medium for hydrolysis and is also an additional source of radicals ($OH^\bullet$) [59], so the degradation is generally slower in dry environments [26]. Unfortunately, low moisture content of paper leads to decreased flexibility, which can lead to physical damage during handling, as brittleness is increased [60]. The reason is that water forms intermolecular H-bonds with cellulose and acts as a plasticizer, which increases material flexibility [49]. Stiffening of the polymer structure due to drying or water removal is referred to as hornification [112]. Hornification has frequently been associated with the formation of irreversible intra-fibre hydrogen bonding [113], but has recently been described as only a particular case of lactone bridge formation in lignocellulosic materials [112]. 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% [114]), and a rule of thumb is that its strength decreases by 5-10% for each unit percentage increase of the moisture content in paper [115].

Temperature has an effect on paper degradation for a different reason; it is often simplified that chemical reactions related to paper degradation are accelerated by a factor of two for each increase in temperature of 5 °C [56]. Temperature also affects relative humidity and ‘incorrect’ temperatures result in ‘incorrect’ humidity levels [69]. In terms of environmental control, it is therefore necessary to consider both RH and T setpoints, allowable fluctuations and the seasonal drift [61].

Standard recommendations from 2000 [108] suggest that storage temperature for frequently-handled materials should be held at a fixed point between 16 °C and 19 °C with 1 °C tolerance on either side, but ranging neither below the minimum nor above the maximum. For infrequently handled materials the temperature should be kept at a fixed point between 13 °C and 16 °C and the material should be allowed to acclimatize before use. Relative humidity should be between 45% and 60% with 5% tolerance on either side for frequently used materials, and infrequently used materials may be kept below 40% RH but should be acclimatized before use. According to BS 5454:2000 both temperature and relative humidity should be kept as constant as possible and rapid changes should be avoided [108]. The new recommendations in PAS 198:2012 [5] are more lenient and allow more variation and seasonal drift. According to PAS it is up to the institution (organization) to set the environmental specifications in line with their collection and the expected collection lifetime.

Much research has been done and there is much speculation in the literature on the effects of fluctuations in temperature and relative humidity on paper degradation. Despite this, opinions on the subject are not unanimous. A brief overview of the research on fluctuating environmental conditions is given in Table 3.2. The changes in properties after exposure to cyclic (fluctuating) conditions are given relative to changes after exposure to static median conditions.

Table 3.2: 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).

Reference	Experimental conditions	Samples	Measured properties	Comparison with the outcome at median conditions
Shahani et al. (1989) [52]	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% Δ R (LS) +33% / +29% Δ R (S) +57% / +100% Δ pH (LS) +18% / -25% Δ pH (S) -40% / -34% rel. life (LS) -18% / -5% rel. life (S)
Bigourdan and Reilly (2002) [62]	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% Δ b^* *[3]

Bogaard and Whitmore (2002) [63]	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% Δ *DP* -33% Δ pH +797% Δ c(carbonyl group) +188% Δ R +330% Δ z-s tens. str.
Sandy et al. (2010) [60,77]	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% Δ CI (acid treated)
Panek et al. (2004) [20]	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 (2004) [64]	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 (2006) [116]	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.

Menart et al. (2011) [117]	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*	$k(\text{cyc.}) \approx k(\text{const.})$

***^{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).**

One of the first studies on the effect of a fluctuating environment on paper degradation was carried out by Shahani et al. [52]. Loose sheets or 100-sheet stacks of bleached Kraft wood pulp waterleaf and bleached Kraft paper (Foldur Kraft) were exposed to relative humidity, alternately set to 40% and 60% for 11 h (with 1 h in between), and to constant relative humidities of 40%, 50% and 60%. The temperature was kept constant at 90 °C throughout the experiments. The samples were selected as the first represented natural cellulose and the second resembled a library book, as it was 15 years old and fairly acidic. To compare the samples after the experiments the authors measured brightness and cold-extraction pH of paper and determined MIT fold endurance. They showed that the rate of loss of fold endurance increased with increasing relative humidity. This was explained by samples having a lower moisture content at lower RH, leading to less swelling, and therefore to lower susceptibility to damage from acids and oxidants. Their results also showed that paper within a book aged faster than a loose sheet, which suggested that acidic degradation products were trapped inside a book where they accumulated and therefore created an increasingly acidic environment [52]. The same effect has been described in the literature elsewhere [25,42]. The acid build-up might be nullified by introducing a sheet containing alkaline reserve. The decrease in fold endurance generally proceeded in parallel to the decline in pH and loss in brightness [52].

The authors discovered that loose sheets degraded at least as fast if exposed to fluctuating relative humidity as under a constant relative humidity of 60%. This effect was not observed for stacks of sheets (mock book), as the rate of degradation was between those at the median RH and at the high RH [52]. The same was observed by Bigourdan and Reilly [62], who also studied stacks of paper, exposed to fluctuating temperature or relative humidity, and argued that the phenomenon could easily be explained by current thermodynamic theories. 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), so fluctuating conditions do not provoke a new mechanism of degradation or accelerate it any more than it would be expected [62]. Shahani et al. [52] 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. In fact, water transport through paper is a complex process, especially under changing humidity conditions, and therefore very difficult to analyze. 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%) [118]. A flux of water as assumed by Shahani et al., is feasible when the difference between equilibrium moisture content and ambient humidity is large and if the relative humidity is higher than 75% [118]. Vittadini et al. [49] 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 relatively good agreement with the conclusions, made by Bandyopadhyay [115,118]. As equilibration times, needed for paper to reach a steady-state moisture content, are long (up to several hundred minutes), the flux must be slow, so it might not have a significant impact on the mobility of ions.

In a study by Bogaard et al. [63] cotton filter paper (Whatman No. 42) was exposed to cycling relative humidity (RH was cycled between 25 and 75% every 2 h) at room temperature for a maximum of 52 weeks, with samples taken at different stages of the experiment. To assess the condition of paper the authors determined the degree of polymerization (*DP*), cold-extraction pH, carbonyl group content, brightness and zero-span tensile strength. In 10 weeks, *DP* values 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 crystals (between 250 and 280). The results from zero-span tensile strength measurements were similar. Consistent with the *DP* change, carbonyl content of cellulose increased, whereas the carboxyl content showed no differences. Very little or no change was also observed in pH and brightness measurements. From the approximately equal number of scissions and increase in carbonyl groups, the authors concluded that the degradation observed is predominantly of hydrolytic nature [63].

The authors argued that the suddenness of humidity change could cause very high local stresses, as exterior portions of fibres react quickly to new conditions while interiors are slower to respond. This was said to cause high tensile forces as physical loads become concentrated in small areas, weakening chemical bonds in cellulose and potentially breaking them. The cellulose chain is most likely to break at the weakest point, the carbon-oxygen bond connecting the glucose rings. In most circumstances breaking this bond results in free radicals (an unpaired electron on each carbon and oxygen atom), which can also initiate oxidative reactions [63].

Bigourdan and Reilly [62] exposed stacks of three types of papers (acid-processed cotton, acid-processed groundwood and buffered groundwood) to fluctuating RH at a constant temperature or fluctuating temperature at a constant RH. For comparison they also exposed paper to steady states, corresponding with the middle of the cycle and the upper limit of the cycle. For analyses, sheets from the middle of stacks were chosen, and folding endurance, tensile strength and brightness were determined. RH was cycled between 40 and 80% with one week at each condition and temperature was cycled between 60 and 80 °C daily. Different cycling times for *T* and RH were chosen since thermal equilibration is much faster than moisture equilibration [62].

It was found that the rate of paper degradation under fluctuating conditions was faster than the rate measured at the steady mid-range of RH or temperature cycle and slower than the rate measured at the steady upper limit of the cycle. This, however, can be thermodynamically explained, as time spent at worse conditions has a greater impact on the state of paper than the time spent at better conditions. Therefore, the authors concluded 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 amount of time spent at each condition along the way [62].

Recently, the effect of fluctuating relative humidity on tensile properties of paper was also studied by Sandy et al. [60,77]. They exposed Whatman No. 1 filter paper (pure cellulose) to different RH conditions (at 80 °C ± 2 °C); some were previously subjected to an acid treatment (1 M hydrochloric acid) to simulate paper degraded by acid hydrolysis. The accelerated ageing lasted for 9 or 20 days at constant or cycled relative humidity; constant RH was set to 65%, and the cycled RH was operated between 30% and 80% (3.5 h at each RH, 30 min linear ramp). After the experiment, tensile strength and tensile energy absorption were measured. They observed little difference in the case of non-acid treated samples (similar results for constant and cycled RH), however the treated ones behaved differently. The mean tensile energy absorption for 20 day acid-treated, relative humidity-cycled group was the lowest recorded of any of the sample groups, suggesting these samples were the most brittle. This shows that thermal ageing under cycling RH conditions appears to increase the rate at which brittleness of paper increases [60]. 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. [63]. Cycling RH could also promote the increase in crystallinity and it is known that brittleness of paper increases with increased cellulose crystallinity [60]. 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 [77].

In previous work by Menart et al. [117] eight different paper samples were exposed to RH cycles at a constant temperature and *T* cycles at a constant relative humidity, both at two different cycle frequencies. The temperature was cycled between 84.2 °C and 95 °C at two different frequencies, while the RH was kept constant at 65%. One lower frequency 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. Similar 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 in the experiment with fluctuating temperature. Reference samples were aged under stationary conditions, at 90 °C and 65% RH, which are the median conditions.

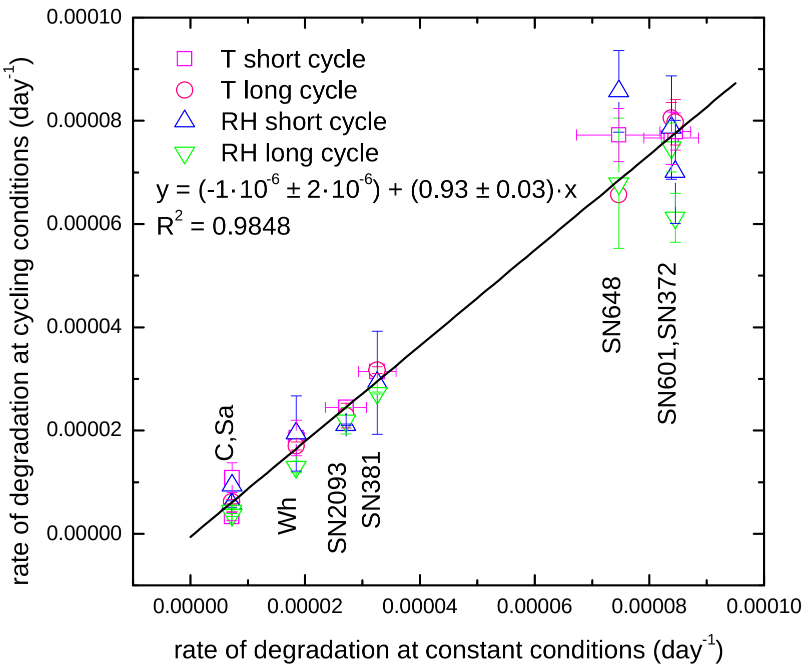


Figure 3.1: Degradation rates under fluctuating and stationary median conditions [117]. (C, Sa and Wh are model papers, the rest are real paper samples)

No increase in degradation rates for papers, exposed to fluctuating conditions, as opposed to those, exposed to median *T* and RH, was observed (Figure 3.1). As *T* and RH differences were relatively limited (ΔT = 10 °C, ΔRH = 20%), no excessive internal stress due to changing temperature or moisture content was assumed to be caused, as excessive stress was generally reported as a consequence of sudden and substantial changes in the environmental conditions.

All the research, described above, was focused on chemical changes, potentially affected by fluctuations in the environment. However, there is some disagreement between the results, as Bogaard and Whitmore [63], Sandy et al. [60,77] and in the case of single sheets Shahani et al. [52] claimed fluctuations cause extra damage to paper, whereas others, like Bigourdan and Reilly [62] argued the phenomenon could easily be explained by thermodynamics, similarly to other chemical reactions.

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 would remain undetected using chemical analytical methods, such as viscometry. However, some research has been done on how physical properties can be affected, as well.

A phenomenon, which is assumed to be greatly affected by RH fluctuations, is the creep of paper, observed when paper deforms under stress [20,64,116,119]. 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 [64]. There is some evidence that creep is most pronounced when the cycling parameters are fitting for a particular paper, as highly increased 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% [115]) [119]. After a certain period of time, creep leads to strain at which the paper breaks [20,64,116,119]. Mechano-sorptive creep was 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 [64,116]. However there have also been other theories to explain creep under various humidity conditions, such as sorption-induced physical ageing [119]. Accelerated creep of paper was also observed under variations in ambient temperature (between 25 °C and 50 °C) and a constant RH, but the magnitude of the effect was much smaller than for fluctuating RH [120].

The creep of paper can be evaluated in different ways, for example using creep curves (strain versus time at a given stress) [20,119], creep compliance (strain divided by stress) [20], isochronous stress-strain curves (stress versus strain for a particular time) [20], lifetime curves (time to failure versus stress) [20], creep rate (change in strain divided by the change in time) [20,119], degree of accelerated creep or accelerated creep ratio (creep rate in cyclic humidity divided by the creep rate in the highest constant humidity) [20,119], or creep stiffness (stress divided by strain) [20].

Panek et al. [20] described an interesting phenomenon after 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), described as release of internal stress. When paper was exposed to cycling humidity its dimensions changed, but the magnitude of dimension change decreased with an increasing number of cycles, until change could 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 [20].

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 the paper structure. The mechanisms of constant humidity creep 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 [116].

Cycling RH also has some effect on iron gall ink, as it causes iron(II) ions to diffuse out of ink regions, creating ink ‘bleeding’, as shown by Neevel [121,122]. While testing different phytate conservation treatments he exposed samples to relative humidity, cycled between 35% and 80% (3 h at each RH, 12 min ramp in between), and observed migration of the ink 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 bleeding was observed in samples exposed to 50% RH.

Temperature not only affects the RH of the environment, but also has a distinct effect on the moisture content of paper materials stored inside an enclosure, e.g. a box [123]. 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 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 decreasing, so the two processes are never fully reversible [123]. 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 [124,125]. 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 (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 [126]. 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 [124].

A recent study into equilibration times of books was carried out by Garside and Knight [127], where they inserted RH sensors into books and exposed them to changing RH at a constant temperature. When changing the RH from 40% to 80% in 5 h, they found that the internal moisture content of a book responds very slowly to changes in the environment, and the rate of change differs depending on the accessibility of a particular spot in the book. The more accessible edges of a book start responding with a roughly 2 h delay according to external changes, whereas for the centre of the book and the spine the delay is at least 8 h. The edges reached equilibrium after 10 days and the centre and spine after 20, however a very slow rise was still observed after 30 days. During a sudden drop and rise of external RH no change was observed inside the book. This shows that despite individual sheets of paper responding rapidly to external changes, books, especially when stacked together, respond very slowly to steadily changing RH and are largely insensitive to short-term fluctuations [127].

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 [69,127]. As mentioned earlier, paper has a relatively long equilibration time [115,118], so sudden changes in moisture content, as a result of small RH changes, are unlikely [127].

Another observation is that most research has been carried out employing broad relative humidity ranges, and the ones demonstrating the most harmful effects were also the ones with the widest RH span (ΔRH = 50%) [60,63,77]. It therefore has to be considered how well these results represent realistic conditions, which paper-based objects might be exposed to. Realistically the temperature fluctuations within a repository do not exceed ± 2 °C and humidity fluctuations are within ±10%, as will be shown in Chapter 4.

3.5. Paper composition and acidity

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 [59]. It has also been shown that lignin does not have a negative effect on mechanical and chemical properties of paper during ageing if the paper is buffered with calcium carbonate [16], which might confirm the connection between high lignin content and accumulation of paper acidity as a consequence of lignin degradation. Knowledge on the effect of lignin on paper degradation is, however, still insufficient and more research is needed before a general agreement can be achieved. Lignin and also hemicelluloses may play a part in the oxidation of cellulose by initiating the production of reactive oxygen species and peroxides [26]. Lignin was thought to contribute significantly to paper degradation, however it was shown that it exhibits an antioxidant effect and stabilises cellulose against ageing [4]. On the other hand it is well known that lignin-containing papers change colour from yellow to brown during thermal ageing [4,16,68]. Exposure to radiation also causes change in lignin-containing papers as lignin is a much better absorber in the 280-300 nm region compared to cellulose and is thought to be primarily responsible for photoyellowing. The three main pathways for photoyellowing have been identified as: phenol pathway, phenacyl pathway and ketyl pathway [128]. During the process lignin undergoes photochemical changes, which result in different chromophores, one of the most important yellow coloured products being *p*-quinone [129].

Crystallinity is also thought to be an important property of paper, as it affects many different paper properties. Some studies suggest that higher crystallinity causes higher resistance to depolymerisation [59], whereas others show that increases in crystallinity cause increased brittleness [60,77]. As mentioned in the previous Chapter, the degree of crystallinity also depends on the cellulose source, as cellulose, derived from cotton, usually has a higher proportion of crystalline phase compared to wood-derived cellulose [2].

As mentioned earlier paper degradation is affected by acidity and exposure to volatile acids, as acid-catalysed hydrolysis is thought to be a major cause of loss of paper strength [21,22]. Acidity is both the consequence of accumulation of acids in paper during degradation processes and the result of acids being introduced into paper during production, and it is known that acidic papers are less stable compared to neutral or alkaline ones [16,130]. Exposure to AcOH apparently causes little immediate depolymerisation, but the paper having been exposed is more likely to degrade at a higher rate in the future [70], although this has recently been disputed by the same authors [131]. This, of course, depends on the concentration of AcOH, as very low concentrations (3 mg/m^3) do not produce measurable depolymerisation, whereas the effect is very obvious at 20 mg/m^3, as shown by Dupont and Tétreault [70]. Exposure to acids, especially combined with increased (or fluctuating) relative humidity, can cause increased crystallinity, which results in inferior mechanical properties [77]. Acidity is also linked to the 'stacking effect', described in section 3.6 [132].

A very common source of acidity in paper is sizing. Potassium aluminium sulfate (alum) or zinc sulfate (white vitriol) were a common addition to gelatine sizing, and they both increase the paper's acidity [1]. Since the 19th century the most established (and therefore most common in archival papers) sizing system involves wood resin acids and aluminium sulfate (rosin and papermaker's alum) [2], which also decrease the paper's pH. Acidity is increased by metal ions forming hydrated complexes, which can donate protons to water and therefore act as weak acids.

As paper degradation is highly pH-dependant, the paper's acidity and overall composition should be taken into account when describing the degradation process using damage functions or predicting lifetimes of collections.

3.6. Stack versus single sheet degradation

Another phenomenon, which should be taken into account when discussing paper degradation, is the ’stack versus single sheet degradation’ [25,40,42,132], where the rate of degradation of the pages in the middle of a stack of paper is greater than the rate of degradation of the top and bottom sheet. 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 [132]. This could be explained by volatile acids migrating through paper and accumulating in the middle of the stack, as they are unable to escape into the environment [52,132]. However sometimes an opposite effect is 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, light and oxygen. The accumulation of degradation products, such as acids, in the pores of fibres and inter-fibre spaces has an autocatalytic effect, resulting in enhanced degradation [25,40,70,132]. The ‘stack versus single sheet’ phenomenon should be taken into account when designing accelerated ageing experiments, as results differ significantly when comparing single sheets to stacks of paper [40]. A study, carried out by Bégin and Kaminska [40], suggests that the most accurate simulation of natural ageing would be between single sheets and stacks, as single sheets might release too many volatile organic compounds (VOCs) that would otherwise accelerate the degradation of paper, whereas the stack might trap too many VOCs, which might extensively accelerate paper degradation. To account for that, they suggested degradation experiments in sealed glass tubes, as this approach was thought to simulate the natural ageing of paper best [40,59]. However, sealed tubes may not be the perfect representative of natural ageing either, as oxygen in the tube is being consumed during degradation reactions, which inevitably leads to a decrease in its concentration, so the conditions might not be stationary throughout the experiment.

3.7. Conclusion

Paper degradation can be affected by many different factors. Not all, however, are equally important in an archival setting, where the environment is usually controlled and the objects can be stored in the dark. Environmental parameters, which have the most effect in an archival repository, are temperature, relative humidity and pollution.

Pollutants can be outdoor- or indoor-generated, with the concentrations of the latter exceeding the concentrations of the former by up to an order of magnitude. The most harmful and therefore important outdoor-generated pollutants are SO_2, NO_2 and O_3. Indoor-generated pollutants are VOCs, emitted from the objects themselves, and the ones most dangerous to paper are organic acids and aldehydes. AcOH has generally become one of the main concerns in terms of pollutant-induced degradation, with reported concentrations in archival repositories of approximately 100 ppb. Pollutants can affect paper degradation in two ways, by lowering the paper’s pH and therefore promoting acid-catalysed hydrolysis (e.g. SO_2, NO_2 and organic acids) and by reacting as oxidants (e.g. NO_2 and O_3). Both processes are possibly related to RH, especially the former, since pollutants require water to dissociate and therefore increase the paper’s acidity. Experiments investigating pollutant-induced degradation should therefore be carried out at realistic RH levels.

The effects of temperature and RH were discussed thoroughly in the previous Chapter. The effect of temperature and RH fluctuations, however, is still a subject of debate, although recent research shows that mild fluctuations, commonly encountered in an archival repository, do not contribute significantly to degradation rates. This has also been acknowledged in the current recommendations for environmental control PAS 198:2012.

Another important effect, which cannot be controlled externally, is the paper composition, especially acidity. Experiments on different paper types, especially real papers, are therefore necessary to understand how different paper compositions affect degradation in real archival collections.

So far no function, linking the most important agents of paper degradation, has been derived. Experiments, described further on in this thesis (Chapter 5, results is Chapters 6 and 7), were therefore carried out in attempt to quantify these different effects and to help make decisions on how to prioritise them.

4. Environmental assessment of repositories in the Nationaal Archief

As described in Chapter 1, the main aim of the project was to quantitatively compare the effects of indoor- and outdoor-generated pollutants on paper degradation, together with other environmental parameters. In order to develop knowledge, relevant to real archival storage environments, it was necessary to assess the conditions in different types of archival repositories (e.g. with and without air filtration) by monitoring temperature and relative humidity, measuring the concentration of total volatile organic compounds (tVOC), O_3 and NO_2/SO_2 concentrations and measuring the concentrations of different sizes of particles. This provided the necessary baseline data against which the degradation experiments were performed and results were interpreted.

4.1. Introduction

The collection of the National Archives of the Netherlands (Nationaal Archief) stretches over 130 km of shelf space, 120 km of which is occupied by the paper-based collection. Besides paper the collection contains 14 million photographs and 500,000 maps and drawings. The majority of the Archives, however, is their paper collection, 42% of which dates from before 1830. 8% of the collection is acid paper, 45% groundwood and 55% rag.

The latest environmental standard for archival collections, accepted in the Netherlands, suggests maintaining the temperature in repositories at 18 °C (± 2 °C) and relative humidity at 50% (± 5%) and that the conditions should be as steady as possible to avoid the presumed negative effect of fluctuations on paper based objects [133], although they might not actually be as harmful as previously thought (Chapter 3, section 3.4.). The previously widely used but now outdated British Standard 5454:2000 suggested very similar conditions; a temperature between 16 °C and 19 °C for frequently handled material and between 13 °C and 16 °C for infrequently handled material and relative humidity between 45% and 60%. It also strongly recommended avoiding rapid changes and fluctuations in the environment [134]. The recently published Specifications for managing environmental conditions for cultural collections (PAS 198:2012) are much less rigid in terms of *T* and RH control and allow institutions to set their own environmental specifications depending on the use, significance, expected usable lifetime etc. *T* and RH should be set to enable the expected collection lifetime to be achieved and their lower and upper limits should not exceed conditions, which would cause irreversible chemical or physical change [5]. Strictly speaking this sets an unrealistic target, as paper degradation occurs at all temperatures and RH levels, it only proceeds at different rates. Unfortunately it is also irreversible.

The air conditioning system in the Nationaal Archief is set to maintain the temperature at 18 °C (± 2 °C) and relative humidity at 50% (± 5%), according to standards and legal requirements [133]. To achieve that, the outside air is first cooled to extract the water (lower the humidity) and then heated again, only then is moisture added to meet the 50% set point. Each repository is controlled individually.

All the air in a repository is exchanged twice a day, even though the standard suggests no more than one air exchange per day in order to provide more stable environmental conditions and avoid introducing large amounts of traffic generated pollutants [135]. The air inside most Nationaal Archief repositories consists of 10 – 15% outside air and 85 – 90% recirculated air. There are however a few repositories, in which the air is pumped directly into the repository with no pre-mixing. For comparison, BS 5454:2000 suggested an air infiltration rate of one to two changes per day and not less than 5% to 10% of purified fresh air [136], so air exchange in the Nationaal Archief (two per day) is consistent with these recommendations.

Outside air, coming into the repositories, first passes through EU 9 filters to remove particles. EU 9 filters are fine particle filters produced from glass fibres and most efficient for filtering particles larger than 0.1 mm as well as microbes. For most repositories it is then combined with the recirculated air and chemically purified (filtered) before entering the repositories (‘repositories with air filtration’). As mentioned before, in a few cases the air goes directly into the repository without being mixed or filtered beyond particle removal (‘repositories without air filtration’).

Each of the nine floors has its own filtration unit and the two underground floors share a common one. The filtration unit consists of three different filters: electrostatic for particles (each unit has two), chemisorbent and a carbon filter (Figure 4.1).

Chemisorbent filters work on the principle of chemisorption, which is a type of adsorption, where a chemical reaction takes place between the adsorbate and the substrate (pollutant and filtering material, respectively) and a bond is formed. Carbon filters, if they do not carry a chemisorbent impregnant, use physisorption to filter air. Physisorption does not alter the chemical structure of the adsorbate or substrate; the interactions between the two are weaker inter-molecular forces.

Some filters are changed twice a year and others (like the carbon filter) can last several years – the state of the filters is assessed after taking samples from the filters and sending them to a contractor for analysis. A decision whether to change the filter is made according to the analysis results.

Figure 4.1: Filtration units in Nationaal Archief.

In 2012 a decision to change the filtration supplier and the current system was made at the Archives. Whereas the previous contract specified the type of filters and filtration media used, the new one only specifies the air quality and it is up to the contractor to ensure the requirements are met. The new filters are shown in

Figure 4.2. The acceptable pollutant concentration thresholds, specified in the contract, are 1.3 ppb for SO_2, 6.7 ppb for NO_2 and 0.3 ppb for O_3.

Figure 4.2: The filters inside a new filtration unit (both sides of one chamber).

The Dutch standard [137] includes limit concentrations of most common outdoor (traffic generated) pollutants, which are presumed to be relatively safe for archival materials. SO_2 should be kept under 5.5 ppb, nitrogen oxides under 10 ppb and O_3 under 5 ppb (all values being annual average concentrations). To test whether the conditions in the Nationaal Archief meet these criteria, the concentrations of these pollutants were measured every 3-4 months, using 4-week long passive sampling in diffusion tubes. AcOH concentration levels were also measured once, using 3-week long passive sampling. Unlike for the other pollutants measured, the analytical method for AcOH was semi-quantitative, which will be discussed later in this Chapter.

According to the standard the maximum concentration of particles in air should not exceed 75 $\mu g/m^3$ [137]. However, the standard does not say anything about the particle size, so concentrations of different sizes of particles were measured.

Recommendations about air pollution in repositories found in the BS 5454:2000 are much more rigid and even unrealistic, as it is suggested that the air should be kept free of air pollution, acidic and oxidizing gases and dust [134], which is, of course, impossible. As mentioned in the previous Chapter (section 3.2.), this was improved to some extent by PAS 198:2012 [5], suggesting pollutant related damage depends on exposure time and concentration.

Besides measurements, taken in this project, the Nationaal Archief also have their own monitoring system, consisting of temperature and RH sensor and an OnGuard® unit. The *T* and RH measurements are taken in the middle of the room, next to the OnGuard® system (so all the measurements are taken in the same environment). OnGuard® is an ‘air quality monitor’ (Purafil, Doraville, GA) and is widely used in museums and archives. It provides real-time information on the extent of corrosion occurring due to gaseous pollutants, which is measured as the amount of corrosion forming on two metal sensors (one copper and one silver). The OnGuard® monitoring was discontinued in 2012, as the data showed very stable conditions, which meant there was no need for constant monitoring. The high financial input (approximately 3000 € per year) of having OnGuard® data loggers in all repositories was therefore no longer justifiable.

Pollutant concentrations in the Nationaal Archief repositories were measured on the following dates: 8th December 2009 – 5th January 2010, 8th – 10th March 2010, 28th – 30th June 2010 and 8th – 10th November 2010. AcOH sampling was carried out 18th December 2012 – 8th January 2013. Passive samplers were installed on the dates above and then collected 4 weeks later by a member of the Nationaal Archief staff.

4.2. Experimental

4.2.1. Locations

For monitoring two repositories were selected, one with (404) and one without air filtration (40 A). Repository 40 A is used for temporary storage of recently acquired, but not yet catalogued objects. The monitoring was also carried out outside the building, on the roof, to obtain pollutant concentrations near the air conditioning inlets (9th floor, Figure 4.3). The monitoring in all locations was carried out simultaneously or within a couple of days, when simultaneous monitoring was not possible due to instrumental limitations.

In both repositories measurements were taken in the general environment and in the boxes, where documents are stored (where possible in both open and closed boxes, to see whether VOC concentration is higher in an enclosure with a low air exchange). In the repository without air filtration some measurements were also taken next to a ventilation exhaust.

Figure 4.3: The roof terrace on the 9th floor with air coolers.

4.2.2. Measurements

Temperature and relative humidity were monitored continuously during a longer period of time; O_3 and acid gas concentrations were measured intermittently 4 times per year. The sampling for O_3 and NO_2/SO_2 was carried out using passive sampling on diffusion tubes (Gradko Environmental, Winchester) and took 4 weeks each time. Of nitrogen oxides (NO_x) only NO_2 was selected for measurements as it is more reactive and therefore harmful to paper compared to NO. As described in the previous Chapter (Section 3.2.) it is generally assumed that O_3, NO_2 and SO_2 are the main outdoor-generated pollutants, causing (or accelerating) paper degradation.

Diffusion tubes work on the principle of molecular diffusion, where compounds in air move from areas of higher concentration (i.e. the environment) to areas of lower concentration (i.e. inside of the tube). Inside the tube the pollutants are absorbed, which means the concentration in the tube does not increase, allowing diffusion to continue. The average concentration of the pollutant in the environment is then calculated from the mass of the absorbed pollutant, length of the tube, diffusion coefficient of the pollutant, cross-section area of the tube and exposure time using Fick’s law of diffusion.

AcOH sampling was also carried out using passive sampling on diffusion tubes (Gradko Environmental, Winchester) and took 3 weeks.

For temperature and relative humidity monitoring data loggers (HOBO U12 Temp/RH Data Logger, Onset, Cape Cod, MA) were used. The accuracy of the data loggers is ± 0.35 °C and ± 2.5% RH. The measurements started on 8th December 2009 at 12 pm (GMT). The data was collected every hour and downloaded every three months. The Hobo data loggers and diffusion tubes were placed next to each other to ensure similar conditions (Figure 4.4).

Figure 4.4: HOBO data logger (bottom) and four diffusion tubes in the repository without air filtration (40A), in the general environment. The top left data logger is a part of the regular monitoring, carried out at the Nationaal Archief.

Two sets of loggers and diffusion tubes were placed in the repositories; one in boxes, containing objects (each device/sampler was placed in a separate box, meaning the measurements were actually taken in five very similar boxes – 1 with a data logger, 2 with diffusion tubes for NO_2/SO_2 and 2 with diffusion tubes for O_3, Figure 4.5) and outside the boxes in the general environment (on a wall).

Figure 4.5: Five boxes, in which the measurements were taking place, in the repository without air filtration (40 A).

In addition to RH and temperature monitoring and pollutant sampling using diffusion tubes the concentrations of total VOCs (tVOC) and particles of four different sizes (>1 µm, >2.5 µm, >5 µm and >10 µm, based on the instruments available) were measured. In one of the measuring campaigns smaller particles (>0.5 µm) were also monitored. Monitoring, lasting several hours or days, was carried out when possible.

Particle concentration measurements were carried out using DC1100 air particle monitors, calibrated for different sizes (>1 µm and >5 µm, >2.5 µm and >10 µm, >0.5 µm and >2.5 µm) (Gradko Environmental, Winchester). DC1100 monitors are laser particle counters, which means laser light illuminates the particles as they pass through the instrument, and the scattered light is then detected by a photodetector. Particle sizes counted depend on the calibration of the instrument, performed by the manufacturer. The results are given in particle count (i.e. number of particles) per volume of air.

tVOC concentrations were measured with the ppbRAE 3000 instrument (RAE Systems, San Jose, CA). The instrument has a photoionisation detector (PID) and ionisation is achieved using a UV lamp. The instrument is able to detect VOCs with ionisation energies above 10.6 eV, which excludes AcOH and formaldehyde. The measurement results are shown as tVOC in ppb of the calibration gas, which was isobutylene (standard for this instrument).

The instrument was calibrated using isobutylene (a cylinder was provided with the instrument) every couple of months, but zero calibration was performed before each measurement (i.e. before starting the monitoring in each location). Zero calibration is performed by sampling air through a glass tube, filled with a VOC adsorbent, which means only clean air is supposed to reach the detector. This is then set as 0 ppb. Accuracy of the instrument was checked against the calibration standard, although unfortunately that was not possible after each zero calibration was performed, as it was not possible to travel to the Netherlands with the calibration gas cylinder.

Measurements were taken in several different locations inside the repositories, externally, and also inside boxes, of which most have holes enabling air exchange with the rest of the repository atmosphere (Figure 4.6).

Similar to the particle measurements, tVOC measurements were also carried out over several hours (preferably 24 h) when possible.

Figure 4.6: Boxes in the repository without filtration.

Results were statistically evaluated using Minitab 15 software. Two-sample t-tests were performed to compare two data series (e.g. two monitoring locations or two monitoring campaigns).

4.3. Results and discussion

4.3.1. VOC measurements

Results of the tVOC measurements, taken in the two repositories and externally in December 2009 are shown in Tables 4.1 and 4.2.

Table 4.1: Measurements, taken in the repository with air filtration (404), N – number of measurements.

location	av. c /ppb	st.dev.	RSD %	N
General environment	51	3	6	10
"Open" boxes (with a hole)	62	7	12	11
"Closed" boxes	75	8	10	10

Table 4.2: Measurements, taken in the repository without filtration (40 A) and externally (9th floor), N – number of measurements.

location	av. c /ppb	st.dev.	RSD %	N
General environment	68	4	5	8
"Open" boxes (with a hole)	76	6	8	8
Near ventilation exhaust	73	2	3	3
9th Floor - external	38	5	14	14

It was observed that the tVOC concentrations are the lowest outside and the highest in the closed boxes in the repository with air filtration and open boxes in the repository without. The concentrations are also slightly higher in the repository without air filtration. The differences between the measurements in the general environment, open and closed boxes are statistically significant (95% confidence).

Results of VOC monitoring in March are not shown, as it was suspected there was a problem with the ppbRAE 3000 instrument. Both daily profiles consisted of a slight decrease in the first measurements and then an exponential increase until the value became steadier. There was no decrease in VOC concentrations, meaning that the measured concentration at the end of the 24 h monitoring was considerably higher (even more than 100 ppb) than at the beginning. Since the time of the day was approximately the same at the start and end of measurements, the conditions should be similar.

Another attempt to monitor VOC concentrations was made during the third visit in June, but was unfortunately unsuccessful. The ppbRAE 3000 instrument measured zero concentrations regardless of the environment and only responded to very high VOC concentrations (several hundred ppb), so a problem with zero calibration was assumed. The presumed 0 ppb was set too high, which could happen if the zero calibration was performed in a VOC-rich environment. To avoid this, all following zero calibrations were carried out outside, where VOC concentrations are very low.

In the last measuring campaign in November similar results were obtained as in the second one in March. The measurements in the repository with air filtration (404) started at 40 ppb and slowly increased to almost 100 ppb, where the concentration settled and remained constant for the rest of the monitoring time. After moving the instrument to the other repository (it was switched off in the mean time) the readings started at approximately 40 ppb, but the value started increasing immediately, reaching over 140 ppb in 2 h. The instrument was briefly switched off after 2 h and when switched on again, the value dropped to about 100 ppb, but started rising immediately after. Results of the monitoring are shown in Figure 4.7.

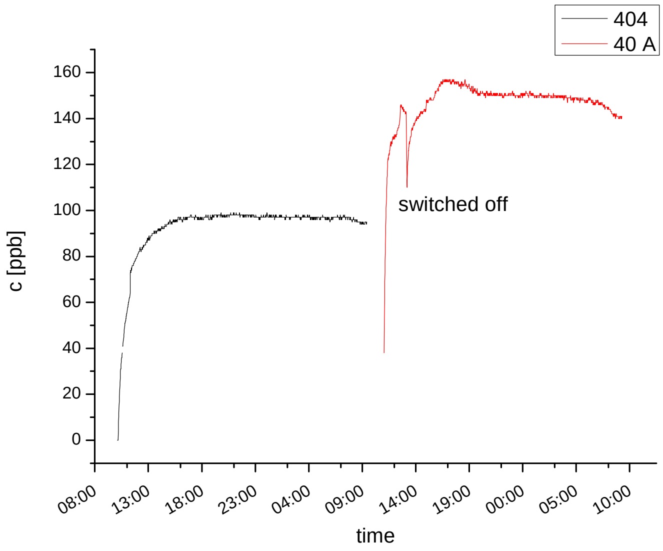


Figure 4.7: 24-hour measurements in both repositories, November 2010.

Such a VOC concentration profile seems unrealistic, especially the rapid decrease and increase when the instrument was switched off. It was therefore assumed that there was a problem with ppbRAE 3000 instrument and the measurement attempt was unsuccessful.

4.3.2. Particle measurements

Particle measurements, carried out in December, are shown in Tables 4.3 and 4.4.

Table 4.3: Particle measurements in the repository with air filtration (404), N = 5 (N – number of measurements).

particle size	average	st.dev.	RSD %
> 1 µm	1802500	554900	31
> 2.5 µm	13400	6300	47
> 5 µm	2800	3000	105
> 10 µm	700	1600	224

Table 4.4: Particle measurements in the repository without air filtration (40 A), N = 5.

particle size	average	st.dev.	RSD %
> 1 µm	652600	479800	74
> 2.5 µm	89000	20300	23
> 5 µm	19100	6900	36
> 10 µm	5700	4000	71

Particle monitors, used in this research, were laser particle counters, which meant the results were number concentrations, not mass concentrations. Unfortunately standards only provide mass concentration guidelines, which means the results could not be directly compared to environmental standards.

The average concentration of the smallest particles (>1 µm) during the first measuring campaign was higher in the repository with air filtration, but the trend changed with larger particle size. Uncertainties were relatively high in these measurements, so individual measurements may not represent the overall conditions. Since the values change with time and according to the particle monitor position, it is advisable to perform long-term monitoring, e.g. at least for a day, which enables diurnal changes to be determined. The differences between the two repositories were statistically significant for all particle sizes, except for > 10 µm, where the standard deviations were substantial. No conclusion about how filtration affects the largest particles could therefore be drawn with certainty from these measurements.

To account for the significant uncertainties of intermittent measurements, the measurements in March were carried out over the whole day. Ideally the monitoring would last for 24 h, but it was only possible to take measurements during the day, as the power supply in the repositories is switched off during the night (on Mondays at 8 pm and on Tuesdays at 10 pm). On the roof the monitoring was carried out for several hours.

Particle monitoring results are shown in Figures 4.8, 4.9 and 4.10. The monitoring was carried out on consecutive days, in similar weather.

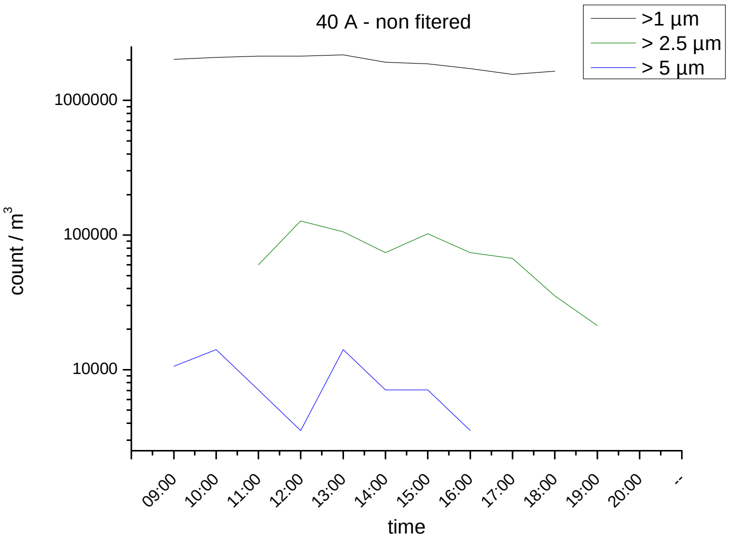


Figure 4.8: Particle concentrations in the repository without air filtration (in logarithmic scale), March 2010.

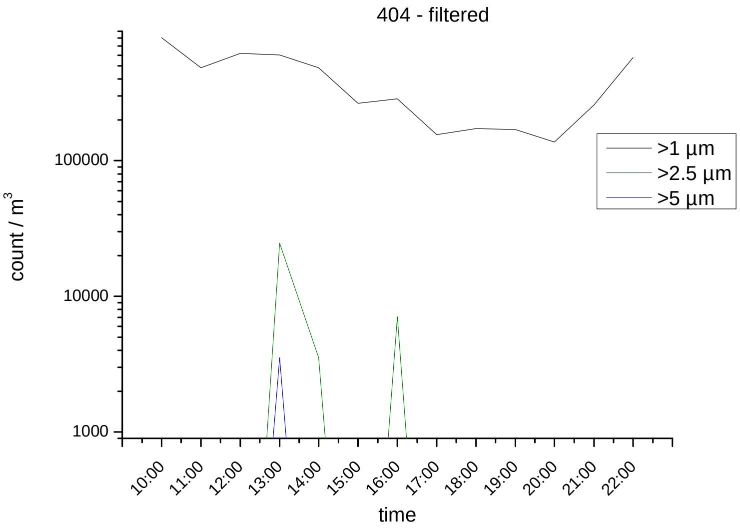


Figure 4.9: Particle concentrations in the repository with air filtration (in logarithmic scale), March 2010.

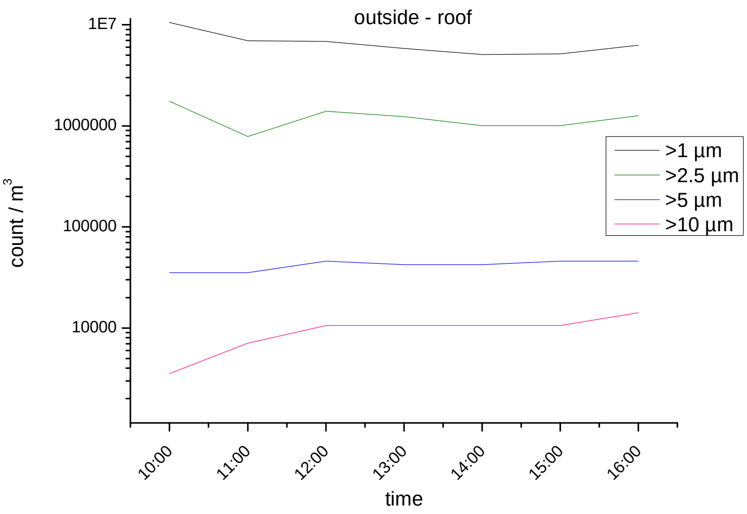


Figure 4.10: Particle concentrations on the roof (in logarithmic scale), March 2010.

Concentrations of the largest particles were almost negligible (below the detection limit) in all three locations and therefore could not be statistically evaluated. Measurable concentrations of particles, larger than 5 µm, could be found outside, whereas the smaller particles (>2.5 µm and >1 µm) could be measured in all three locations. Overall the highest concentrations of all particles could be found outside and the lowest in the repository with air filtration (Figure 4.11). The differences between the two repositories are statistically significant with 95% confidence. Indoor/outdoor ratio (I/O) for the non-filtered repository was 0.3 for the smallest particles, 0.06 for $PM_{2.5}$, 0.1 for PM_5 and 0.04 for PM_{10}. I/O values for the filtered repository were lower; 0.06 for $PM_{0.5}$ and below 0.01 for the other three particle sizes.

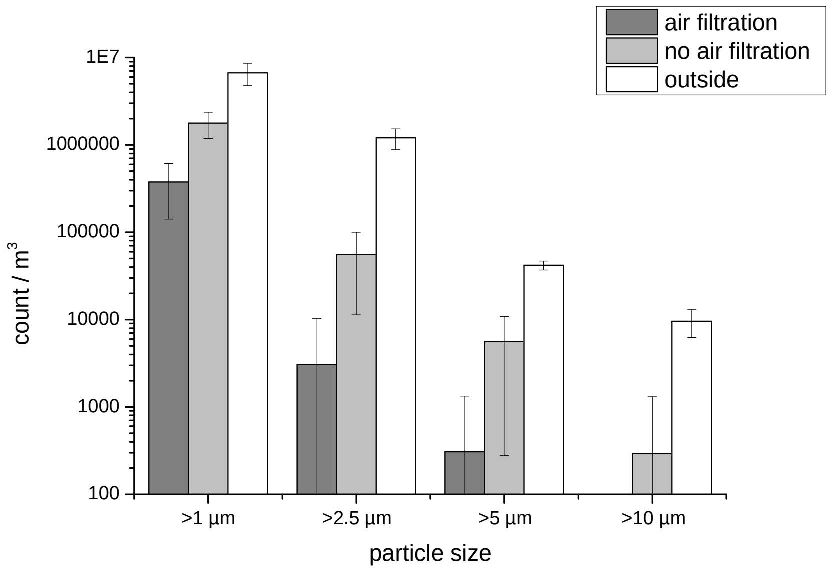


Figure 4.11: Average concentrations of particles in logarithmic scale, March 2010.

During the third visit the focus was on monitoring particle concentrations in the two repositories. Particle sizes monitored were >0.5 µm, >1 µm, >2.5 µm, >5 µm and >10 µm, where the largest and smallest particle concentrations were measured for a day and the middle three ones were measured for two days.

Particle monitoring results are shown in Figures 4.12 and 4.13.

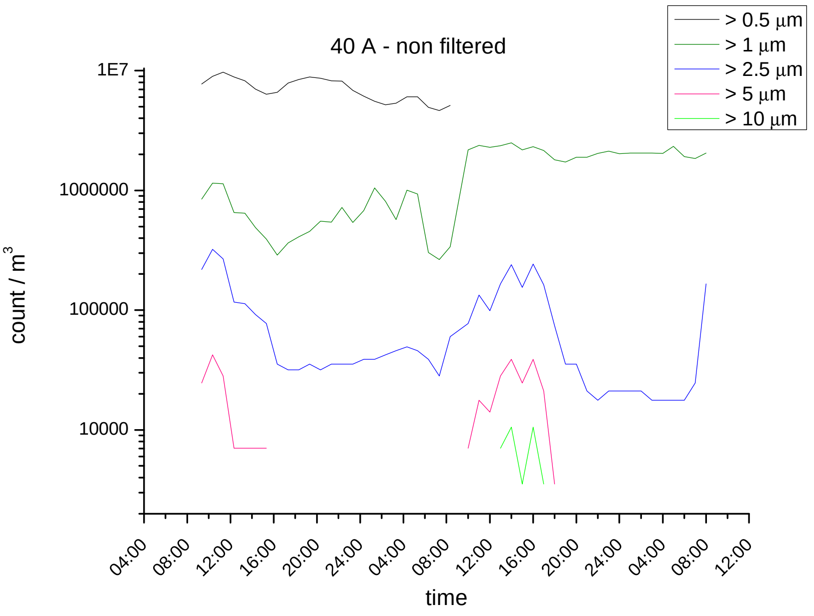


Figure 4.12: Particle concentrations in the repository without air filtration (in logarithmic scale), June 2010.

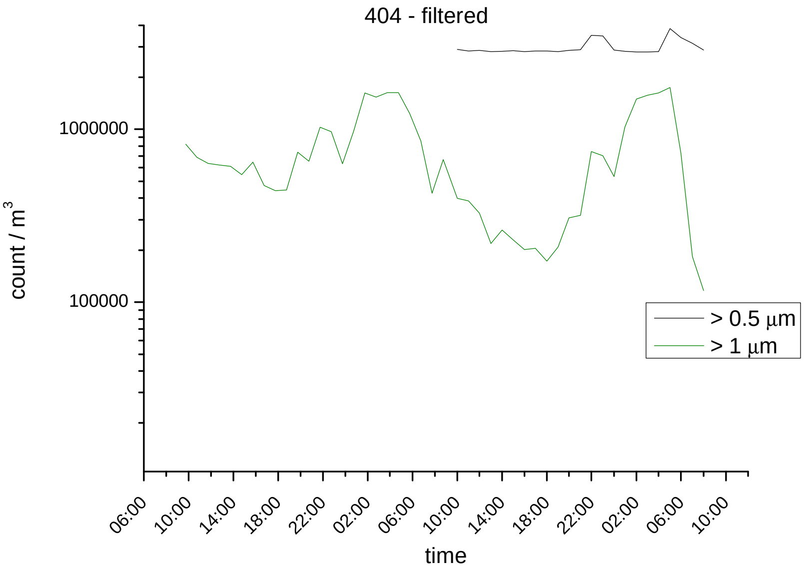


Figure 4.13: Particle concentrations in the repository with air filtration (in logarithmic scale), June 2010.

Significant concentrations of the largest particles were not observed in either location. Significant concentrations of particles, larger than 2.5 µm, were only found in the repository without air filtration, whereas the smallest particles (>0.5 µm) were the most abundant ones in both repositories.

The results of the two day monitoring in the repository without air filtration indicate that the concentration of particles, larger than 2.5 µm, is the lowest and quite steady from about 5 pm until about 8 am, then starts rising and reaches its peak between 2 and 4 pm. These results showed that particle concentrations are higher during working hours, which is unsurprising. No daily profile could be observed for > 1 µm particles in the same repository, but similarly to the larger particles the particle count was significantly increased after 8 am, probably due to human activity. An interesting daily profile for 1 µm particles could be seen in the repository with air filtration. The concentration reaches its peak between midnight and 4 am and then decreases steadily, reaching the lowest value at around 4 pm.

Average concentrations of particles are shown in Figure 4.14.

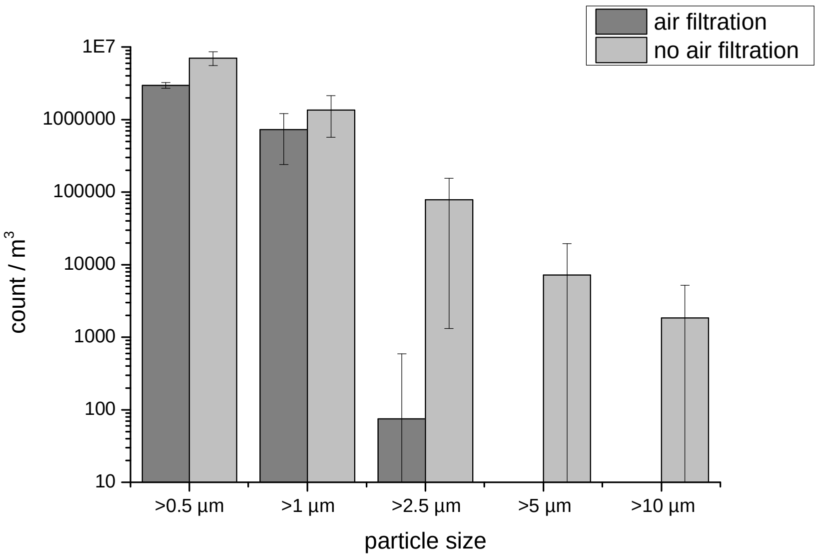


Figure 4.14: Average concentrations of particles in logarithmic scale, June 2010.

The concentrations of particles of all sizes are higher in the repository without air filtration, however the difference between the smallest particles in both locations is not very large. Differences between the repositories are statistically significant in the case of the smaller particles (>0.5 µm, >1 µm and >2.5 µm). The larger two however cannot be statistically compared, as most values were zero in both cases, with only a few above zero in the non-filtered repository (statistically both series are the same). Those however contribute significantly to the average, which can be misleading (Figure 4.14).

During the fourth research visit the two repositories were monitored for two days, measuring particles of the following sizes: >1 µm, >2.5 µm, >5 µm and > 10 µm. Results are shown in Figures 4.15 and 4.16.

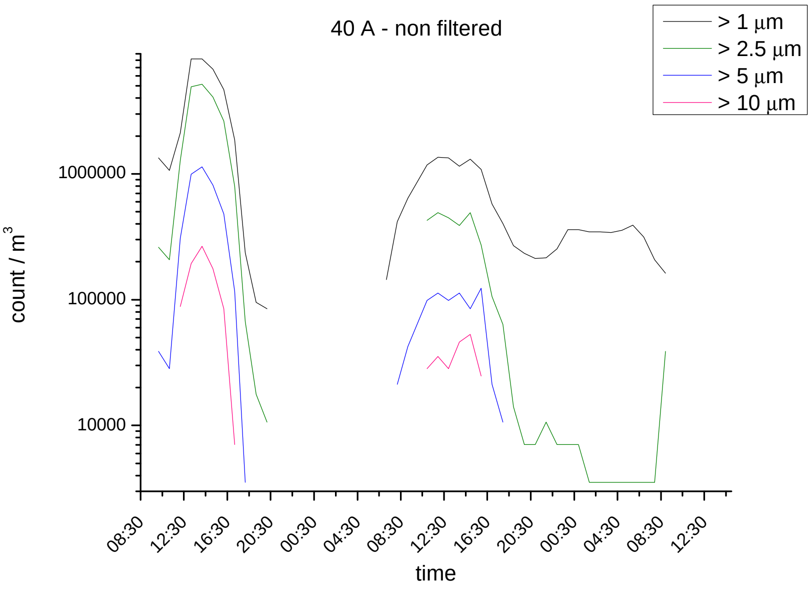


Figure 4.15: Particle concentrations in the repository without air filtration (in logarithmic scale), November 2010.

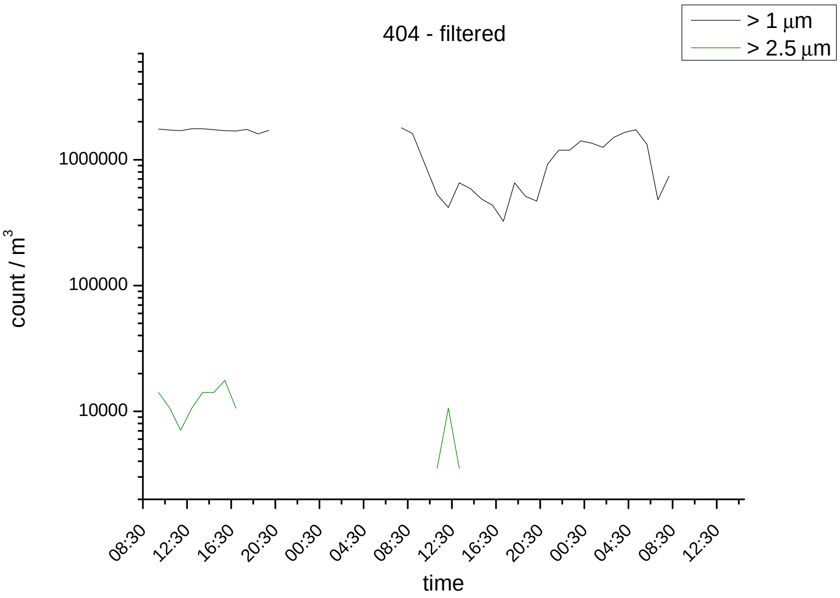


Figure 4.16: Particle concentrations in the repository with air filtration (in logarithmic scale), November 2010.

Similar to the measurements, taken in June, particle concentrations were the highest during the working hours. During this measuring campaign the concentrations in the repository without air filtration were unusually high, as the contents of the repository were being moved to a different location, which is assumed to have resuspended a lot of dust. No daily profile can be observed in the repository with air filtration, partly due to the power being switched off during the first night of monitoring, hence the missing data on both graphs. However it does seem that the concentration of the smallest particles is higher during the night than during working hours. Average concentrations of particles are shown in Figure 4.17.

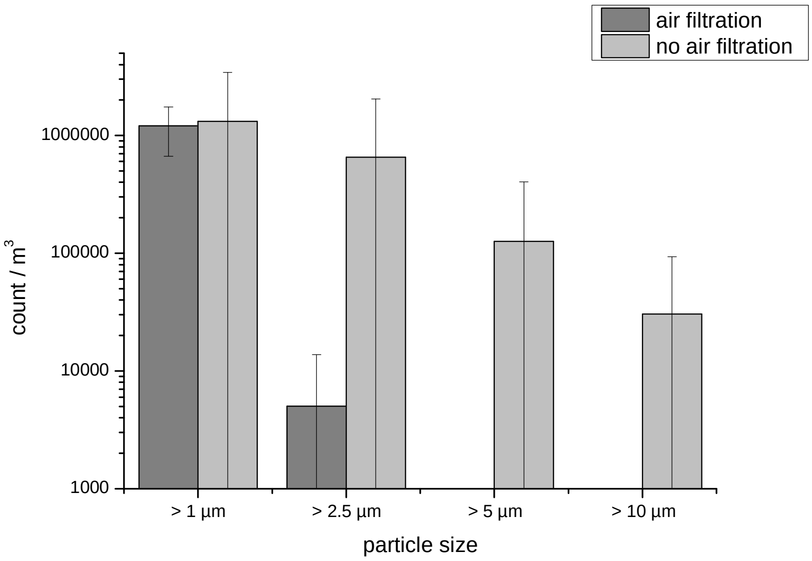


Figure 4.17: Average concentrations of particles in logarithmic scale, November 2010.

As mentioned earlier particle concentrations in the repository without air filtration were relatively high during this measuring campaign. Results from the other repository are similar to previous measuring campaigns, with the smallest particles as the most abundant species and the larger particles below detection limit.

There is a slight difference between the first period of monitoring, carried out in December, and the other three, carried out in March, June and November. In the first monitoring a higher concentration of the smallest particles was measured in the repository with air filtration (404) compared to the repository without air filtration (40 A), whereas in the second, third and fourth monitoring the repository 404 had the lowest concentrations of particles of all sizes. It should however be noted, that continuous monitoring was not carried out during the first measuring campaign, which might be the reason behind the difference.

Average particle concentrations, calculated from all four measuring campaigns, are shown in Figure 4.18.

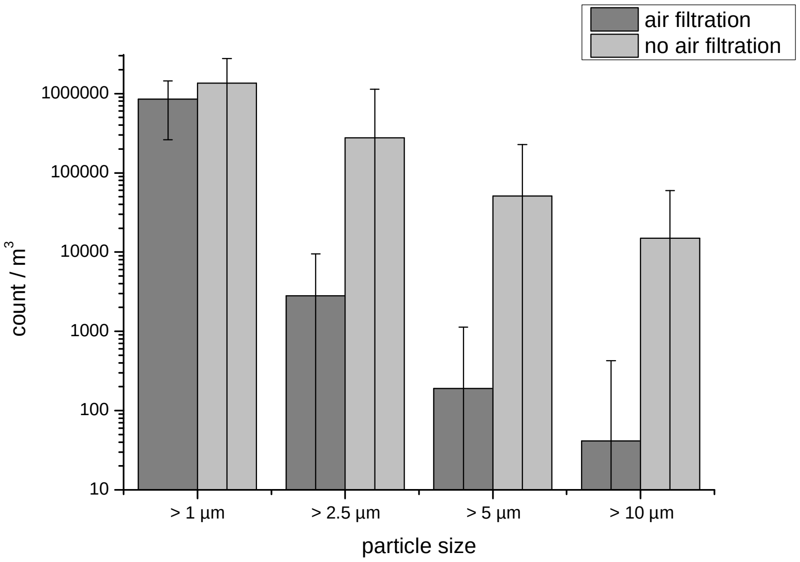


Figure 4.18: Overall average concentrations of particles in logarithmic scale.

Differences between the concentrations of particles of all sizes in the two repositories are statistically significant with 95% confidence. Higher particle counts for particles of all sizes were consistently observed in the repository without air filtration. The differences between the repositories increased with increasing particle size, although measurement uncertainties were significant as well, as shown in Figure 4.20.

As mentioned earlier the standards only provide mass concentration limits and the Gradko instruments can only measure particle counts, so a direct comparison between the measured values and suggested limits could not be made. Approximate conversions between the two are possible if the particle sources are known, however this was not of interest in this research, as the focus was on the most abundant outdoor- and indoor-generated pollutants.

4.3.3. Acid gases and ozone

The concentrations of acid gases (NO_2 and SO_2) and O_3 in both repositories (404 with and 40A without air filtration) and outside the archival building, determined in all four monitoring campaigns, are shown in the Table 4.5.

Table 4.5: NO_2, SO_2 and O_3 concentrations, determined in four monitoring campaigns.

position	pollutant	Dec	Mar	Jun	Nov
404 box	NO_2 /ppb	< L.O.D.	< L.O.D.	<L.O.D.	0.09
404 box	NO_2 /ppb	< L.O.D.	tube lost	<L.O.D.	0.28
404 repository	NO_2 /ppb	< L.O.D.	< L.O.D.	<L.O.D.	0.11
404 repository	NO_2 /ppb	< L.O.D.	0.97	0.08	0.08
40 A box	NO_2 /ppb	1.47	0.35	<L.O.D.	0.51
40 A box	NO_2 /ppb	0.42	1.83	0.85	2.46
40 A repository	NO_2 /ppb	9.58	9.14	7.56	8.98
40 A repository	NO_2 /ppb	10.4	8.83	7.38	8.94
outside	NO_2 /ppb	17.81	14.84	12.32	15.77
outside	NO_2 /ppb	17.14	12.89	11.93	14.74
404 box	SO_2 /ppb	< L.O.D.	< L.O.D.	<L.O.D.	< L.O.D.
404 box	SO_2 /ppb	< L.O.D.	tube lost	<L.O.D.	< L.O.D.
404 repository	SO_2 /ppb	< L.O.D.	< L.O.D.	<L.O.D.	< L.O.D.
404 repository	SO_2 /ppb	< L.O.D.	0.97	<L.O.D.	< L.O.D.
40 A box	SO_2 /ppb	< L.O.D.	< L.O.D.	<L.O.D.	< L.O.D.
40 A box	SO_2 /ppb	< L.O.D.	< L.O.D.	<L.O.D.	0.28
40 A repository	SO_2 /ppb	< L.O.D.	< L.O.D.	<L.O.D.	< L.O.D.
40 A repository	SO_2 /ppb	< L.O.D.	< L.O.D.	0.18	3.53
outside	SO_2 /ppb	< L.O.D.	0.65	0.85	0.27
outside	SO_2 /ppb	< L.O.D.	0.36	1.15	0.43
404 box	O_3 /ppb	< L.O.D.	1.30	1.43	3.31
404 box	O_3 /ppb	< L.O.D.	1.69	1.00	2.48
404 repository	O_3 /ppb	< L.O.D.	1.69	0.57	3.31
404 repository	O_3 /ppb	< L.O.D.	0.91	<L.O.D.	1.24
40 A box	O_3 /ppb	< L.O.D.	2.08	<L.O.D.	1.25
40 A box	O_3 /ppb	< L.O.D.	2.08	<L.O.D.	4.57
40 A repository	O_3 /ppb	< L.O.D.	1.69	3.14	4.15
40 A repository	O_3 /ppb	< L.O.D.	1.69	2.71	0.42
outside	O_3 /ppb	11.53	25.66	32.62	14.89
outside	O_3 /ppb	9.2	25.28	36.47	14.48

In the first monitoring campaign the concentrations of all three pollutants were below the limits of detection (L.O.D.) in the repository with air filtration (both in boxes and the general environment). Measurable (L.O.D. = 0.34 µg/m^3 = 0.18 ppb), but still very low concentrations of NO_2 were measured in boxes in the repository without air filtration. The concentration of NO_2 in the repository was roughly half of the outdoor concentration. Significant concentrations of O_3 were only found outside the archival building (L.O.D. = 3.44 µg/m^3 = 1.7 ppb), whereas the concentrations of SO_2 were below detection limits in all the measuring locations (L.O.D. = 1.14 µg/m^3 = 0.44 ppb).

Unlike in the first monitoring, the concentrations of pollutants in most locations were above limits of detection in the second one, which indicates that pollutant concentrations may be somewhat higher in the warmer months. The repository with air filtration, presumably the ‘cleanest’, showed no measurable concentrations of pollutants in the first monitoring, whereas in the second O_3 could even be measured in the box. In the general environment measurable concentrations of all three pollutants were present, approximately 1 ppb each. Interestingly even SO_2 was present in the general environment of this repository, in the same concentration range as outside (in all other locations SO_2 was below the limit of detection). Statistically there was no difference between the SO_2 concentration in 404 and on the roof. As mentioned before, O_3 concentrations were significantly higher in March compared to December; the outside concentration increased from 10 to 25 ppb and the others from below L.O.D. to 1 – 2 ppb. Concentrations of NO_2 were similar to the first monitoring in December; statistically there was no significant difference between measurements in the same locations.

Results, obtained in June/July were very similar to those obtained in March. The most obvious difference was the elevated external O_3 concentration (approximately 10 ppb higher than in March), which was not surprising, as the O_3 concentration always rises in the summer. SO_2 concentration outside was approximately the same as in March, but could also be determined in the repository without air filtration besides externally.

In November most of the measurement results were very similar to the ones obtained in the previous measuring campaigns. NO_2 and O_3 could be measured in all measuring locations; unsurprisingly the O_3 concentration was significantly lower than in the summer. SO_2 concentration could only be determined outside and in the repository without air filtration.

Average pollutant concentrations, calculated from all four measuring campaigns, are shown in Figure 4.19.

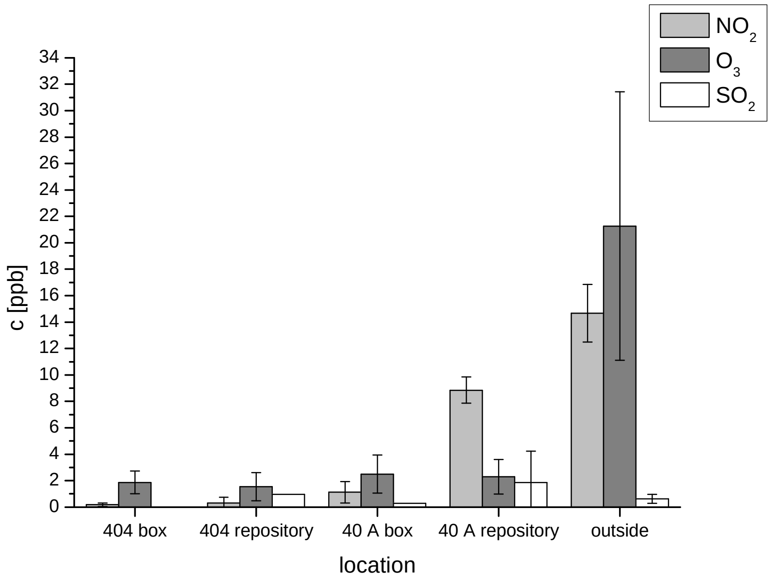


Figure 4.19: Overall average concentrations of pollutants in all measuring locations, N = 4.

As can be seen from the graph, the differences between measuring campaigns, represented by error bars, are small (most standard deviations are approximately 1 ppb), with the exception of outdoor O_3.

The measurements, taken during all four visits (December 2009, March, June/July and November 2010) are in agreement with the recommendations, given in the Dutch standard [133], only NO_2 in the repository without air filtration (40 A) is close to the recommended limit value of 10 ppb. O_3 concentration was found to be higher than the limit value, specified in the contract between the Nationaal Archief and the filtration supplier, in all measuring locations. NO_2 and SO_2 concentrations in the repository with air filtration were in agreement with the contract, whereas the repository without air filtration had higher concentrations in the general environment, but lower in the archival boxes.

The difference between the two repositories is significant, especially in terms of NO_2, where the average concentrations in repositories 404 and 40 A were 0.3 and 8.9 ppb, respectively.

4.3.4. Acetic acid

AcOH concentrations were only measured once. As AcOH is difficult to quantify (especially without an on-site laboratory or access to ion chromatography, usually used for AcOH analysis [138]) a commercially available method offered by Gradko was used. The method involves GC-MS analysis, which is not ideal for AcOH, making the method semi-quantitative.

In July 2012 the ground floor of the archival building was reconstructed. As the repository without air filtration (40 A) is located there, the measurements could no longer be carried out in this location. The sampling was therefore carried out in another repository without air filtration (Central Bureau for Genealogy), but with a different temperature set point, 20 °C instead of 18 °C.

The measurement results are shown in Figure 4.20.

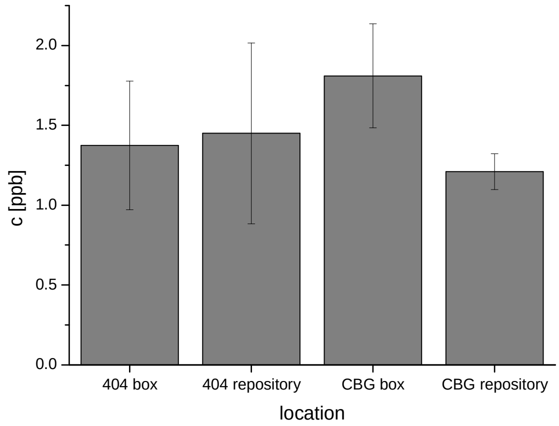


Figure 4.20: Average concentrations of AcOH in all measuring locations.

The concentrations, obtained from semi-quantitative analysis, were much lower than expected. Studies in other archives or libraries have shown considerably higher concentrations [87,105], up to two orders of magnitude higher compared to the results shown here. Since the method was semi-quantitative and commercial, little is known about its actual sensitivity, which might have been problematic. Another possible explanation for very low results is that some of the analyte might have escaped from the Chromosorb diffusion tubes, if they were not closed properly after exposure. The time between exposure and analysis was possibly too long as well, as the tubes had to be sent back from The Netherlands and then to Gradko. All this might have contributed to unusually low AcOH concentrations.

No difference was observed between the box and the general environment in the repository with air filtration (404), whereas the concentration is somewhat higher in the box in the repository without air filtration. All determined concentrations, however, are very low, possibly due to an unknown experimental error.

4.3.5. Temperature and relative humidity monitoring

Results of temperature and relative humidity monitoring in a typical box in both repositories are shown in Figures 4.21 and 4.22.

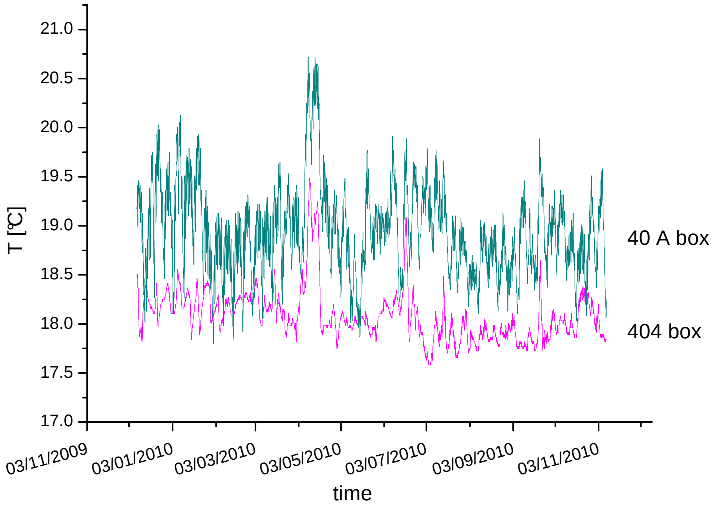


Figure 4.21: Temperature in an archival box in both repositories (404 - with air filtration, 40 A - without air filtration), December 2009 – November 2010.

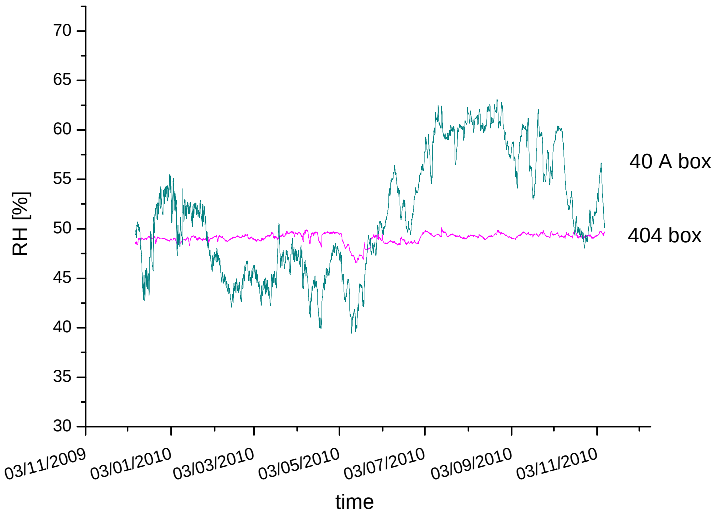


Figure 4.22: Relative humidity in an archival box in both repositories (404 - with air filtration, 40 A - without air filtration), December 2009 – November 2010.

Less variation can be observed in the repository with air filtration. The reasons for this are likely to be more material stored in this repository, which would provide a buffering effect, and no air recirculation in the non-filtered repository, which makes *T* and RH control more difficult. *T* is slightly higher and RH lower or higher, depending on the season, in the repository without air filtration. RH varies significantly more in the repository without air filtration, up to ±10% RH from the median value, whereas the difference in the temperature is less significant, ±1.5 °C.

Conditions in individual repositories and outside the Archives building (on the roof) are shown in Figures 4.23 - 4.35.

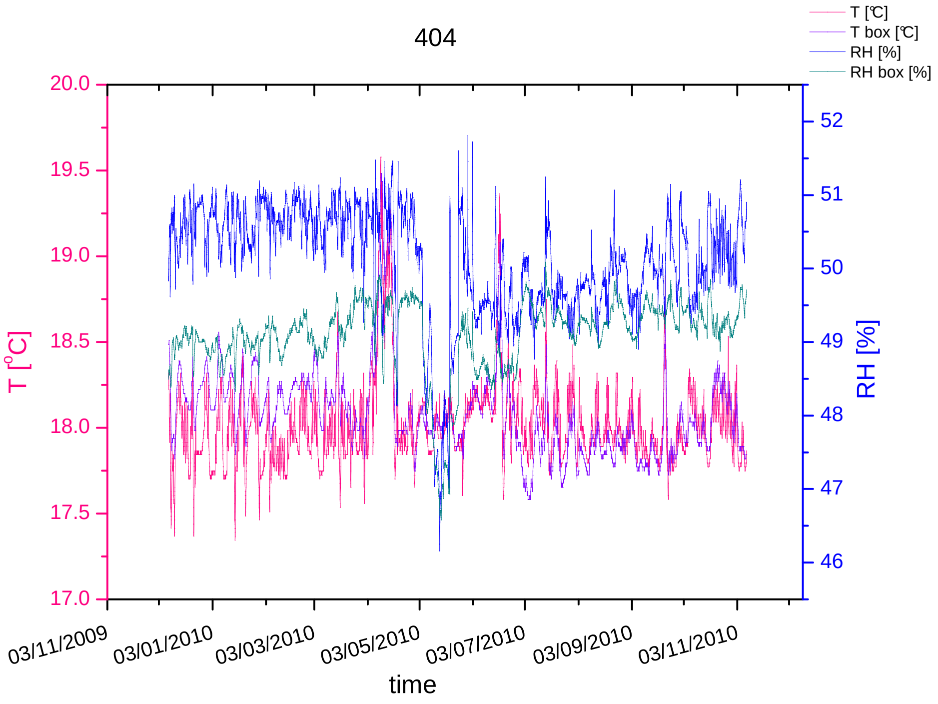


Figure 4.23: *T* and RH in a box and in the general environment in the repository with air filtration.

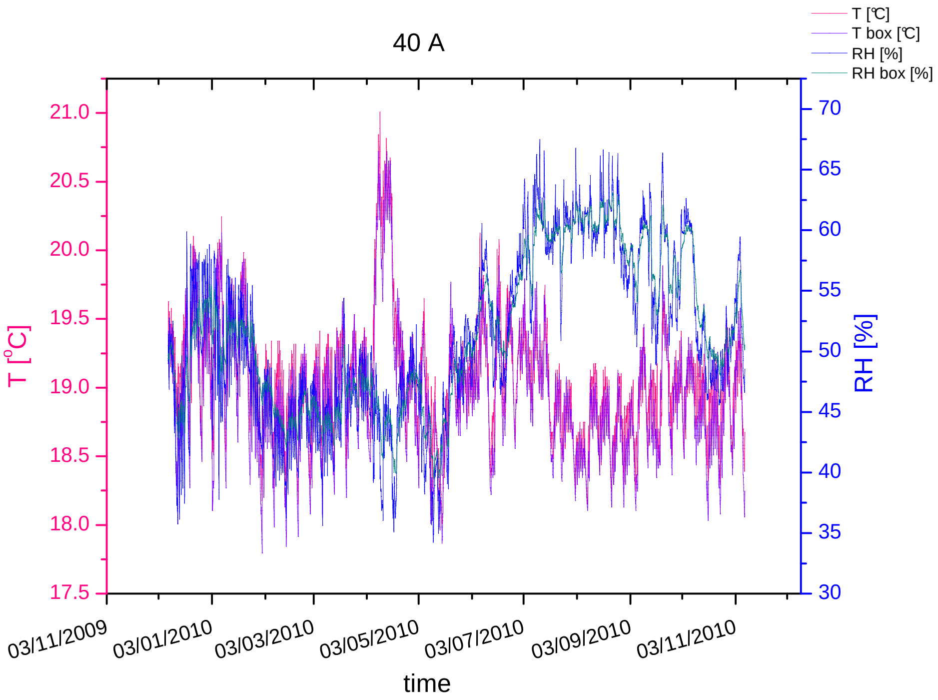


Figure 4.24: *T* and RH in a box and in the general environment in the repository without air filtration.

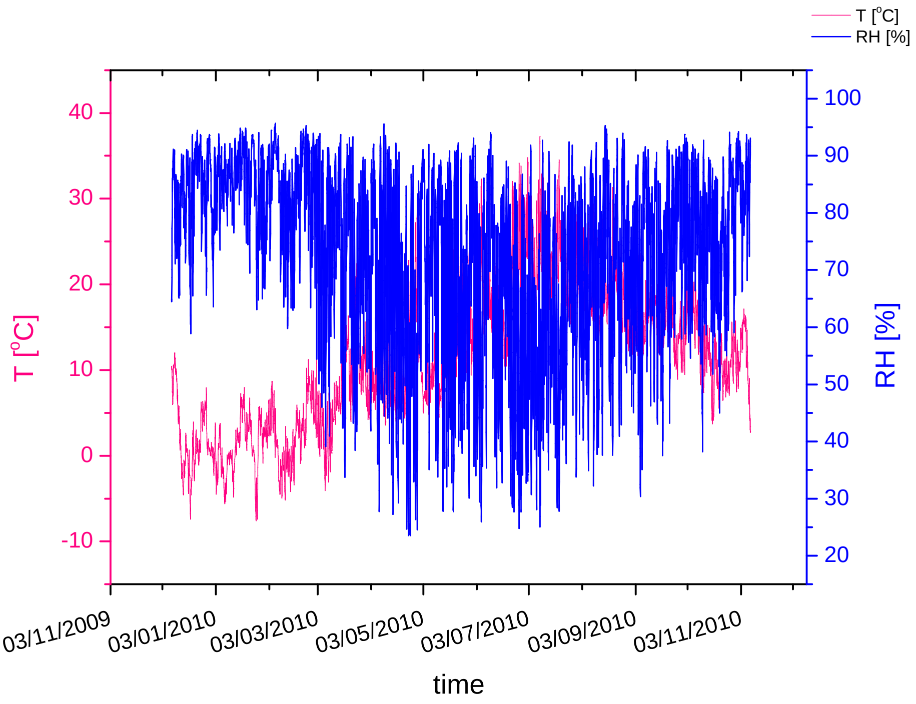


Figure 4.25: *T* and RH on the roof of the Nationaal Archief building.

Figures 4.23 and 4.24 show that environmental changes are always slower and less pronounced in a box compared to the general environment. Interestingly RH is a bit lower in the box, compared to the general environment, in the repository with air filtration. On the other hand there is no obvious difference in the average RH of the box and the general environment of the repository without air filtration. The maximum difference however, is only approximately 2%. Unlike RH, temperature is slightly higher in the box in the first half of the monitoring and lower in the second half, but always within a 1 °C interval.

RH varies significantly more in the repository without air filtration, up to ± 10% in the beginning, but generally up to ±5%, whereas the difference in the temperature is less obvious. A daily profile with a maximum in the early afternoon (between 12 and 3 pm) can be observed for temperature fluctuations in both repositories, although the changes are small (within a 1 °C interval). A daily profile cannot be observed for RH fluctuations, as the fluctuations usually last several days and do not have a repeating pattern.

T and RH averages, obtained from monitoring over the course of one year, are shown in Table 4.6.

Table 4.6: Average *T* and RH in a box and the general environment of both monitored repositories.

repository	$T_{av.}$ /°C	$RH_{av.}$ /%	$T_{av.}$ box /°C	$RH_{av.}$ box /%
40 A (no air filtration)	19 ± 0.4	51 ± 7	19 ± 0.5	52 ± 6
404 (air filtration)	18 ± 0.2	50 ± 1	18 ± 0.3	49 ± 1

Temperature and RH values are always within the limits specified in the Dutch environmental standard (18 °C (± 2 °C) and 50% (± 5%)) [133] in the repository with air filtration, while the variations are somewhat larger in the other repository, especially in the general environment, where RH values are 50% (±10%). The effect of boxes is very apparent here, as the box mostly sustains the RH just within the limits. Average temperature and relative humidity are well within recommended limits. The filtered repository has average *T* and RH values almost exactly at the recommended values, whereas the non-filtered one deviates slightly, although still within the recommended limits. However as discussed in the previous Chapter (Section 3.4.), small *T* and RH fluctuations (±5 °C, ±10% RH) are probably not very harmful to the collection, so slightly larger changes in the repository without air filtration compared to the filtered repository should not be a reason for concern. The annual average outside temperature, measured on the roof of the Archives building, was 11.6 °C.

4.4. Conclusion

Concentrations of traffic-generated pollutants are higher in the repository without air filtration compared to the repository with air filtration. Annual average concentrations of NO_2 in the general environment are 8.9 and 0.3 ppb for the non-filtered and filtered repository respectively, whereas the differences between the SO_2 and O_3 concentrations are not significant. The concentrations of the latter two are significantly lower as well, reaching only up to 2 ppb. All the pollutant concentrations are within the limits, recommended by the Dutch standard, even those measured in the repository without air filtration.

Particle counts were significantly lower in the repository without air filtration as well, although unfortunately a comparison with the standard cannot be made due to a different measuring principle. Particles >5µm were only detected in this repository.

Temperature and relative humidity are mostly within the recommended limits as well, although RH in the repository without air filtration deviates somewhat from the recommendations. Spikes of high and low relative humidity (±15%) can be observed throughout the year, with lower RH in the colder and higher RH in the warmer part of the year. The average T and RH, however, are well within the recommended limits.

Environmental monitoring at the Nationaal Archief showed that air filtration significantly reduces the concentration of NO_2 in a repository, but does not have a significant effect on the concentrations of SO_2 and O_3, which were much lower in comparison. In order to assess the benefit of air filtration the effect of NO_2 therefore needs to be studied. Although determining the concentration of AcOH in repositories was unsuccessful, it is known from the literature that VOCs, including short carboxylic acids and carbonyls, are more abundant in archival repositories compared to outdoor-generated pollutants. Since they are generated within the collection, air filtration would have a much smaller effect on their concentrations compared to outdoor-generated pollutants. A quantitative assessment of beneficial effects of air filtration should therefore include both the most common VOCs and NO_2.

5. Methodology

In this Chapter only experimental work on paper will be presented, as environmental monitoring was already discussed in the previous Chapter.

5.1. Steady-state experiments

The main degradation factors, identified in Chapter 3, were studied experimentally. The emphasis was on the effect of the most abundant pollutants in a typical archival repository, which were identified in the previous Chapter and from the literature. Unlike most pollution research carried out so far, where model papers were used for experiments, the experiments presented here were carried out using sacrificial materials, chosen from a historical reference collection as the most representative examples of what historic archives and libraries might have in storage today.

5.1.1. Samples

Six different paper types were used in the experiments: two acidic (A1 and A2, A2 being the less acidic sample), alkaline (B), purified cotton linters cellulose (Whatman filter paper No. 1, Maidstone) (W), paper made of cotton rags (R, two different rag samples were used in preliminary experiments and the third in degradation rate experiments) and lignin containing paper (L). All but the Whatman paper, which is a model paper, are real historic papers taken from books produced in the 20th century (Table 5.1). Samples from the SurveNIR historic paper reference collection were used [139]. Initial pH and *DP* values for each paper type were measured as described further in this Chapter (section 5.1.3.) and are listed in Table 5.1, together with year of production (in the case of rag paper exact year was not known), fibre composition and rosin content, which affects the paper pH and can therefore contribute to the degradation process (section 3.5.).

Table 5.1: Samples with their pH values, initial degrees of polymerisation (DP_0), year of production, fibre composition and sizing information.

code	SurveNIR sample	pH	DP_0	year / approx. time	fibre composition*			rosin* /mg/g
					groundwood	wood pulp cellulose	cotton cellulose	
A1	sur 648	5.3	560	1910		1		2.57
A2	sur 780	5.6	740	1936		0.1	0.8	2.33
B	sur 2229	7.4	2260	1997		1		0
R 806	JP 806	5.3	1350	19th C			1	
R 807	JP 807	5.2	1340	19th C			1	
R	JP 425	5.1	1430	19th C			1	
L	sur 847	5.2	-	1939	0.9	0.1		1.16
W	Whatman	5.4	2640	2008			1	

*** fibre compositions and rosin content obtained from the SurveNIR database**

The papers vary significantly in their initial degree of polymerisation and somewhat in their pH, as most samples have pH values between 5 and 6. As discussed in the previous chapters, paper acidity plays an important role in the degradation process, as papers with a lower pH degrade faster than the ones with higher pH values. The initial *DP* value is an indication of how degraded the paper was before the experiment. DP_0 of both acidic papers (A1 and A2) was low to begin with (560 and 740 respectively), which is not surprising considering the dates of their production. There are two reasons for that, the first is that in the first half of the 20th century relatively acidic low-quality papers were produced and second that they are both approximately 100 years old, so it can be assumed that significant degradation had already taken place. The alkaline paper had a high DP_0 (2260), indicating good mechanical properties, partly because the paper was only approximately 10 years old when the experiments started. The initial *DP* of pure cellulose (Whatman paper) is similar. Rag samples have a DP_0 of approximately 1300, which puts them between the relatively undegraded alkaline and degraded acidic papers. Paper sample L has a high groundwood fibre content, which means it was made from pulp, obtained by grinding wood. Lignin is not removed from the pulp during this process, groundwood paper therefore typically has a high lignin content. *DP* measurements cannot be carried out on lignin containing paper, because lignin is not soluble in cupriethylenediamine, the solvent used in viscometric *DP* measurements. There is therefore no information on DP_0, the paper is, however, quite acidic.

All papers were cut into 2 cm × 2 cm squares. Squares were cut from different pages, avoiding the margins of the book, which could be more acidic and degraded due to increased pollutant absorption and possible exposure to light in the past. *DP* values were similar throughout the book and the starting *DP* was determined as an average of five measurements on different pages. The paper squares were attached to a stainless steel spiral (Figure 5.1).

In the first two rounds of preliminary experiments this was done by sewing the paper squares on a thread and then wrapping the thread around a steel coil, and in the third the samples were attached directly onto the spiral, without the thread (Figure 5.1). The same sample setup was used in degradation rate experiments as well. The metal coil was assumed to have no effect on the degradation process due to relative inertness of stainless steel.

Figure 5.1: Samples, attached directly to a stainless steel spiral.

Two parallels for each paper type were used in preliminary experiments. In degradation rate experiments the same set of samples was used as in the preliminary study, with the exception of the rag sample, which had to be changed. The reason was that rag paper samples, large enough to use in all the experiments, were not available.

For each degradation rate determination (experimental design explained in the following section), six pieces of A1, A2, B, L and W and four pieces of R (due to sample shortage) were attached to a stainless steel spiral and inserted into a 1-L flask. Individual paper samples were removed from the flask and analysed in equal time intervals. A decision to use six paper pieces per sample was made in order to provide enough data points to allow calculation of degradation rates, which were assumed to be linear, but at the same time to allow sample analysis in the time available for experiments. Only four pieces of rag paper were used due to the limited amount of rag paper available.

5.1.2. Experimental setup

The samples, attached to the steel spiral, were placed in 1-L flasks (GL 45, Schott Duran®, Wertheim/Main), which were closed with plastic 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 flushing (Figure 5.2). Tubing porosity was assumed not to be problematic, as the material was chemically resistant and the air flow was at least 100 mL/min.

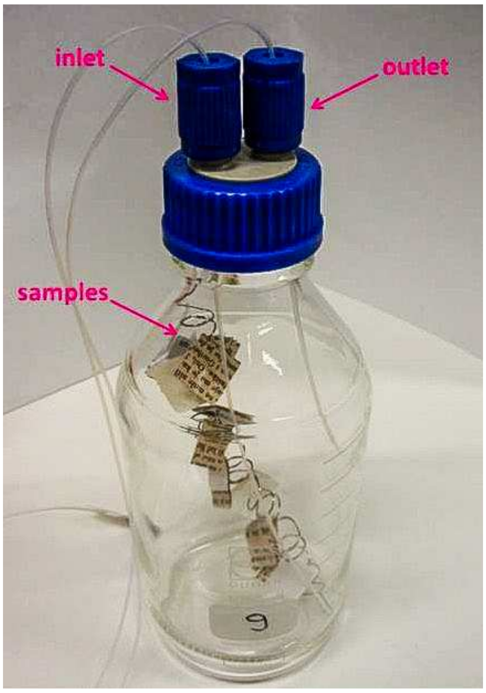


Figure 5.2: Flask with the tubing, used for flushing the samples.

5.1.2.1. Preliminary experiments

The aim of preliminary experiments was to investigate how much effect the most abundant pollutants in a typical archival repository have on paper degradation and if the effects are comparable. It was found previously that nitrogen dioxide (NO_2), acetic acid (AcOH) and formaldehyde (HCHO) were present in repositories in the highest concentrations [105], so they were the pollutants, selected for the experiments.

The experiments were set up to investigate the effect of the pollutants at a constant temperature and relative humidity. To obtain desired humidity conditions, a humidity generator was used (InstruQuest V-Gen™ Dew Point/RH generator model 1, InstruQuest, Coconut Creek, FL). A pollutant generator with pollutant permeation devices (AcOH and formaldehyde permeation tubes and NO_2 permeation wafer, Vici, Poulsbo, WA) was used to obtain the desired concentrations of the respective pollutants (Vici Metronics Model 150 Dynacalibrator®, Vici, Poulsbo, WA). The outlet concentration of the pollutant was set by controlling the temperature of the generator chamber, where the permeation device is inserted, which determines the permeation rate, and the air flow through the chamber. Most research so far has been carried out using saturated solutions to achieve the desired RH and pollutant concentration, which might lead to additional degradation, caused by the salt [131]. Using a setup involving RH and pollutant generators, which create humidified / polluted air, therefore eliminated that risk.

The generators were connected to form a purpose-built setup, using PTFE tubing and flow controllers (Aalborg mass flow controller GFC17, Aalborg, Orangeburg, NY) to obtain air with appropriate pollutant concentrations and relative humidity (Figure 5.3). The air flow through the RH generator was 300 mL/min and through the pollutant generator 100 mL/min. The humidified air and the polluted air were joined using a tee joint and mixed in a mixing coil. The mixed (i.e. humidified and polluted) air would then enter the reactor. All the connections were made inside the oven to avoid condensation.

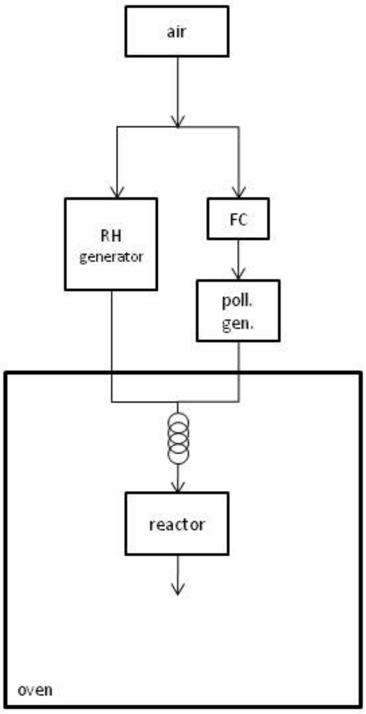


Figure 5.3: Scheme of the setup, used for flushing the samples (FC – flow controller).

Flasks with samples were constantly kept in the oven at 80 °C and flushed with air, containing 1000 ppb of a respective pollutant and 60% RH, every 2-3 days. After flushing inlet and outlet tubing was closed using stainless steel caps (Swagelok, Solon, OH). A set of control samples was also degraded at the same time, exposed only to 60% RH and 80 °C, but without pollutants. The flushing setup was the same for both the control and the other sample sets, as the pollutant generator was still a part of the setup, but did not contain a pollutant permeation device during the flushing.

Reactors, containing the samples, were flushed every 2-3 days as an assumption was made that the absorption of pollutants into paper was slow enough for the conditions to remain constant (steady-state) between two flushing campaigns. As there was 1 L of humidified polluted air surrounding 14 pieces of paper with a combined surface area of 112 cm^2 (taking into account both sides of a sample) it seemed reasonable that not all of the pollutant would be absorbed and react in the relatively short time frame.

The preliminary experiments were carried out three times in order to ensure that the results were reproducible, since further experiments would be based on the findings.

Another reason for repeating the experiment was to alter and improve the experimental set-up.

In the first and second preliminary experiments the flushing took 1 h, and in the third 5 min, which is 18 and 1.5 air exchanges, respectively. After the second experiment the flushing time was shortened significantly, as some condensation was observed in the flasks. The reason for this were water droplets, coming from the humidity generator instead of humidified air (condensation occurred somewhere in the tubing). This resulted in droplets in the reactors, which did not evaporate at the same rate as they were introduced, which means the humidity inside the reactor is likely to have been increasing throughout the experiment. Therefore it might have actually been higher than 60%. Unfortunately no measuring equipment, suitable for logging the conditions during the actual experiment, was available, as most simple data loggers, small enough to be inserted into reactors, cannot operate at 80 °C and 60% RH. To avoid too much water being introduced into the flask the flushing time was therefore shortened to 5 min. In the first two experiments the samples were exposed for 13 and in the third for 9 days and flushed five or four times during the experiment, respectively.

5.1.2.2. Degradation rate experiments

Based on the results from preliminary experiments two pollutants were chosen for further experiments, AcOH and NO_2. The effect of the two pollutants at different concentrations was planned to be studied together with the effects of temperature and relative humidity at different levels, to investigate possible synergistic effects. In order to achieve this, the experiment was designed statistically. A face centred central composite design (CCF), using four factors on three levels, was used. This design yields 31 experiments, 9 at the highest and lowest temperature and relative humidity (80 °C and 50 °C, 60% and 20% RH) and 13 at the median T and RH (65 °C, 40% RH) [140].

A similar setup was used as in the preliminary experiments, however some changes were made. The same humidity and pollutant generators were used, although the set-up was slightly more complicated (Figure 5.4).

As both pollutants had to be used simultaneously, another pollutant generator was added to the setup. This increased the total polluted air flow, so the flow had to be split after the two pollutants were mixed in order to obtain high enough humidity levels. A trap for water droplets was also added at the end, to avoid possible condensation issues. The flows were also adjusted, the RH flow was set to 200 mL/min and the pollutant flow to 25 mL/min, meaning the total air flow through a reactor was 225 mL/min. The reason for the low flows was the humidity, as it was not possible to reach high enough levels with larger air flows through the V-Gen instrument. The pollutant flow therefore had to be minimised in order to reach 60%. All sample reactors were flushed using the same set-up and air flow, with pollutant permeation tubes removed for flushing the control set.

The setup is shown in Figures 5.4 and 5.5.

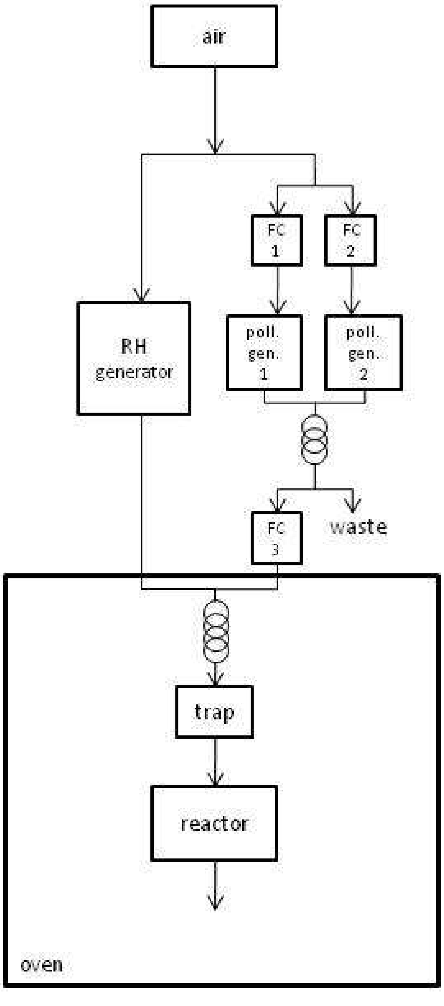


Figure 5.4: Scheme of the setup (FC – flow controller).

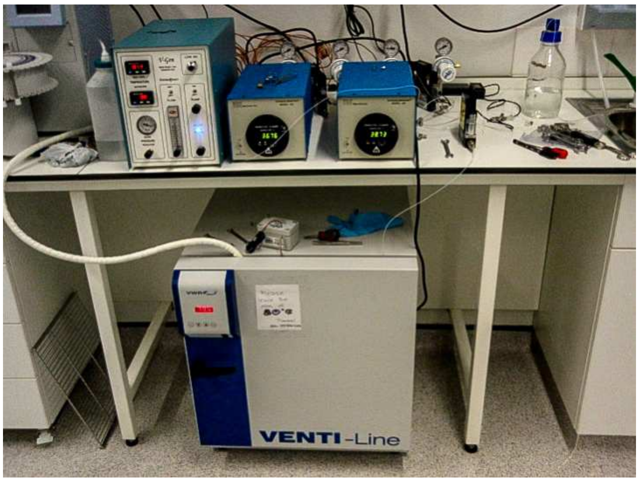


Figure 5.5: The setup in the laboratory (RH generator, 2 pollutant generators, and oven).

The experiments were to be carried out in batches depending on the temperature (1 batch = 1 oven). The experiments at 80 °C were run first and were carried out in a similar way as the preliminary experiments. The samples were flushed every 2-3 days, and the duration of flushing was 30 min. This was decided based on the flow (combined flow was 225 mL/min), so each flask was flushed at least six times during the flushing period.

The sampling rate depended on the conditions to which the papers were exposed. An assumption was made that the samples, exposed to 60% RH, would degrade significantly faster than the ones exposed to lower humidity levels. The samples, exposed to the highest humidity were therefore sampled every five days, with the last samples being removed after one month. In the case of lower humidity levels the sampling rate depended on the paper type. The least stable acidic samples (A1) were removed from the flask every five days, the last therefore being removed after one month, and the rag samples (R) were removed every ten days, with the last ones removed after 1.5 months. The other paper types were assumed to be significantly more stable, so the whole experiment lasted 2.5 months, with the samples being removed every 12-13 days.

While the 80 °C experiment was running, the 50 °C experiment was also started in another oven. This experiment was expected to last for approximately 1 year, with samples removed monthly (acidic paper 1 and Whatman samples) or bimonthly (all other samples). The samples, exposed to 50 °C, were flushed in the same way as previously described, but less frequently. An assumption was made that at 50 °C the reactions inside the flasks were considerably slower than at 80 °C (following the Arrhenius principle), so the pollutants and the humidity would get absorbed and would react more slowly and therefore the flushing could be less frequent. Based on this assumption the flasks were flushed weekly.

5.1.3. Sample analysis

The samples were analysed using viscometry to determine the degree of polymerisation (BS ISO 5351:2004) [13]. Intrinsic viscosity was determined by measuring the time a paper solution (in cupriethylenediamine, CED) needed to flow through a glass capillary viscometer and comparing it against the time required for the solvent only, taking into account the weight of the paper sample.

DP was then calculated from intrinsic viscosity, using the Mark-Houwink-Sakurada equation [141]:

$$DP^{0.85} = 1.1[\eta]. \tag{38}$$

20 ± 1 mg of paper sample was used for each measurement. The average uncertainty of DP determination was assessed to ± 2%. The viscometry measurement setup is shown in Figure 5.6.

Figure 5.6: Capillary viscometer (left and bottom right), defibred paper sample in water with copper wire, used to mechanically defibre the samples (top right) and a cupriethylenediamine (CED) solution of paper (bottom middle).

The second analytical method used was colorimetry using the CIEDE2000 system (ΔE_{00}) [23,142,143]. Although it is quite common to only measure changes in yellowness of paper (b^* component of the CIE $L^*a^*b^*$ system), overall colour change was chosen, as b^* was not the only component changing during the experiments (L^* and a^* changed significantly as well). Visible region (Vis, 400 – 700 nm) reflectance spectra were measured using an X-Rite 530 SpectroDensitometer (X-Rite Inc., Grand Rapids, MI, Figure 5.7) and overall colour change was calculated according to the ΔE_{00} equation [23]:

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T\left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right),} \tag{39}$$

where

$$\Delta L' = L'_0 - L_s' \qquad (L' = L^*), \tag{40}$$

$$\Delta C' = C'_0 - C_s' \tag{41}$$

$$\mathrm{C'} = \sqrt{\mathrm{a'}^2 + \mathrm{b'}^2} \tag{42}$$

$$\mathrm{a'} = (1 + \mathrm{G})\mathrm{a}^* \tag{43}$$

$$\mathrm{b'} = \mathrm{b}^*$$

$$\mathrm{G} = 0.5\left(1 - \sqrt{\frac{\overline{\mathrm{C}^*_{0,s}}^{7}}{\overline{\mathrm{C}^*_{0,s}}^{7} + 25^7}}\right) \tag{44}$$

$$\Delta\mathrm{H'} = 2\sqrt{\mathrm{C'}_0\mathrm{C'}_s}\,\sin\frac{\Delta\mathrm{h'}}{2} \tag{45}$$

and

$$\Delta\mathrm{h'} = \mathrm{h'}_0 - \mathrm{h'}_s \tag{46}$$

$$\mathrm{h'} = \tan^{-1}\frac{\mathrm{b'}}{\mathrm{a'}} \tag{47}$$

$$R_T = -\sin(2\Delta\theta)\, R_C \tag{48}$$

$$R_C = 2\sqrt{\frac{\overline{\mathrm{C'}}^7}{\overline{\mathrm{C'}}^7 + 25^7}}\ ;\ \Delta\theta = 30\exp\left\{-\left[\frac{(\overline{\mathrm{h'}} - 275^0)}{25}\right]^2\right\} \tag{49}$$

and

$$S_L = 1 + \frac{0.015(\overline{L'} - 50)^2}{\sqrt{20 + (\overline{L'} - 50)^2}} \tag{50}$$

$$S_C = 1 + 0.045\overline{C}' \tag{51}$$

$$S_H = 1 + 0.015\overline{C}'T\ , \tag{52}$$

where

$$T = 1 - 0.17\cos(\overline{h'} - 30^0) + 0.24\cos(2\overline{h'}) + 0.32\cos(3\overline{h'} + 6^0) - 0.20\cos(4\overline{h'} - 63^0). \tag{53}$$

Subscripts 0 and s refer to reference (before the experiment) and sample (after the experiment) and k_L, k_C and k_H all equal 1 [23].

The measured area was 3 mm in diameter and an average ΔE_{00} was calculated from three measurements at different locations on the sample. Typical uncertainty of ΔE_{00} determination was ± 1.5%.

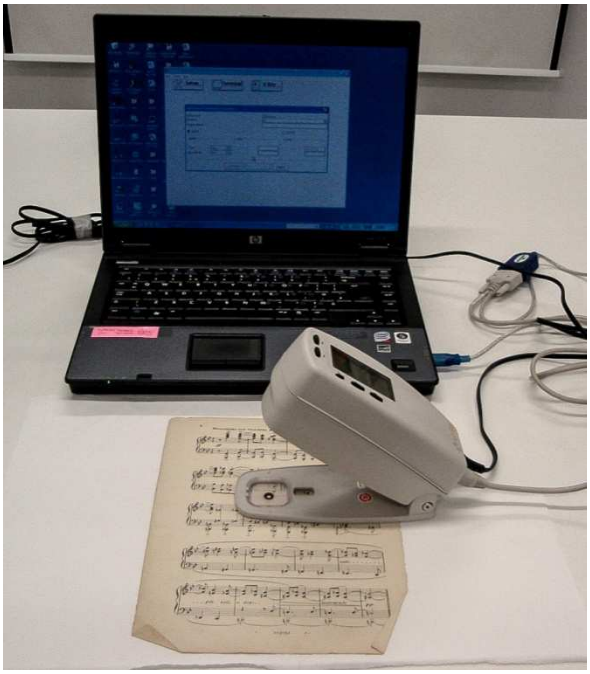


Figure 5.7: Colour measurement using the X-Rite 530 SpectroDensitometer.

CIEDE2000 was introduced as an improvement to the CIELAB formula, as it includes lightness, chroma and hue weighting functions and also an interactive term between hue and chroma differences, which improves the performance for blue colours, and a scaling factor for the CIELAB a^* component, which improves the performance for gray colours [23]. It is said to be not entirely without its flaws [142,143,144], however it is the most accurate method available.

pH of paper was determined using the cold extraction method. This is a micro-destructive technique where 25 µL of deionised water is added to a small paper sample, extracted from a paper sample using a needle (approximately 200 µg), and left for 24 h. The pH of the solution is then measured using a micro electrode, making sure the paper sample is not touching the electrode during the measurement. The pH meter used was SevenGo Pro™ Portable pH/Ion Meter SG8 (Mettler Toledo International Inc.) and the electrode was InLab® Micro pH combination electrode (Mettler Toledo International Inc., Figure 5.8).

Figure 5.8: pH measurement using the micro electrode.

5.1.4. Degradation rate calculation

Cellulose chain scission rates for individual paper types (all but paper sample L) were calculated using the Ekenstam equation described in previous chapters:

$$kt = \frac{1}{DP} - \frac{1}{DP_0}, \qquad (12)$$

k being the degradation rate, t time, DP_0 initial degree of polymerisation and DP degree of polymerisation determined at time t.

Colour change rates were calculated in a similar way, using the following equation:

$$kt = \Delta E_{00},$$

where k is the colour change rate, t is time and ΔE_{00} is the colour change, calculated as described above.

Degradation rates were plotted as $1/DP - 1/DP_0$ vs. t, following the Ekenstam equation, or ΔE_{00} vs. t, but were not forced through the intercept. This allows an initial faster rate, i.e. a two step mechanism, described by several authors [34-38]. Linear regressions were carried out using OriginPro 8.6 software.

5.1.5. GC-MS analysis

As discussed in the next Chapter, the degradation rates did not show the expected pollutant-dependence. It therefore seemed possible that the environments in different flasks were not as different as planned. Headspace analysis using GC-MS was therefore performed in four flasks, where samples were previously exposed to 50 °C and 20% RH or 50 °C, 20% RH and 1000 ppb AcOH, 1000 ppb NO_2, or 1000 ppb of each for 50 days.

A solid phase micro-extraction fibre (Supelco™ SPME Fiber DVB/Carboxen™/PDMS StableFlex™ 50/30 μm with Supelco™ Fiber Holder, Sigma Aldrich, St. Louis, MO) was used for headspace sampling in the four flasks at 20% RH to avoid excessive moisture interference. The sampling took 60 min, after which the SPME fibre was inserted into the GC injector at 270 °C and the absorbed VOCs were analysed. The instrument was a GC Clarus 500 (PerkinElmer, Waltham, MA), coupled with a Clarus 560 D mass spectrometer, a quadrupole mass analyzer that employs electron ionisation (EI) mode to identify the sample. A Supelco Vocol™ column 60 m × 0.25 mm × 1.5 μm (Sigma Aldrich, St. Louis, MO) was used and the temperature program was: 5 min at 50 °C, then heating to 200 °C at the rate of 10 °C/min, after which the temperature was kept constant for another 5 min.

5.2. Dynamic experiments

The main concern in the previous experiments (section 5.1.) was that the pollutants were being absorbed into paper relatively quickly, which meant that the paper samples were not constantly exposed to the same pollutant concentration, as the flasks were only flushed every 2-3 days at 80 °C and once a week at 50 °C. To overcome this, an experiment at the same concentration, but with continuous (dynamic) flushing, was designed. Along with continuously introducing polluted humidified air into reactors, the experimental setup would constantly remove the VOCs, produced during paper degradation. This means that this setup was not directly representative of the real ageing process, however this was not seen as problematic as the most harmful and abundant VOC is AcOH, which was one of the investigated pollutants. The effect of VOCs was therefore simplified to the effect of a constant concentration of the most abundant indoor-generated pollutant.

5.2.1. Samples

The same set of samples was used as in the experiments described in the previous section, with the exception of rag paper. As rag samples, available for the experiments, were relatively small sheets, a different one had to be used for each set of experiments. They were, however, all produced in the 19th century and came from the same batch of rag papers from the Swedish Archives. Since approximately a year had passed since DP_0 of all samples was first determined, the measurements were repeated. The DP_0 values used in calculations, based on dynamic experiments, are shown in Table 5.2, together with DP_0 values determined a year earlier. The initial $L^*a^*b^*$ values, representing the starting colour of samples, are shown as well.

Table 5.2: DP_0 values for all papers, used in the following experiments, together with initial pH and $L^*a^*b^*$ values.

code	SurveNIR sample	pH	$DP_{0\ steady\text{-}state}$	DP_0	L^*	a^*	b^*
A1	sur 648	5.3	560	560	85.53	3.59	17.54
A2	sur 780	5.6	740	680	91.40	0.67	11.46
B	sur 2229	7.4	2260	2330	94.07	2.09	-8.01
R	JP 423	5.1	-	1570	88.65	0.43	11.69
R	JP 427	5.4	-	1850	90.17	0.28	10.64
L	sur 847	5.2	-	-	85.32	2.82	15.49
W	Whatman	5.4	2640	2530	96.38	-0.14	0.95

JP 427 was used in preliminary experiments and experiments at 80 °C and 70 °C and JP 423 was in the 60 °C and low RH experiments.

For preliminary experiments three 2 cm x 2 cm pieces of each paper type were attached onto a stainless steel spiral and inserted into a flask; four flasks for four different experiments were prepared.

In degradation rate experiments six paper pieces per sample were used for all paper types except for rag paper, where only four pieces were used due to sample shortage.

5.2.2. Experimental setup

There are obvious instrumental limitations to the dynamic approach, where the reactors need to be constantly connected to the generators. Since only three humidity generators and two pollutant generators were available, only three flasks could be flushed simultaneously (two with pollutants and one without), i.e. only three experiments could be run at the same time. This meant that the original statistical experimental design had to be abandoned. According to the central composite design 31 experiments would have to be carried out, 9 or 13 simultaneously at the same temperature, which would only be possible if many more generators were available.

5.2.2.1. Preliminary experiments

Another set of preliminary experiments was carried out similar to the steady-state preliminary experiments, except that the samples were now flushed with humidified polluted air continuously. The aim of the preliminary study was to compare the effects of the most common (e.g. in the Nationaal Archief) repository pollutants again in order to decide which pollutants to use in the following experiments.

The pollutant selection and concentration were left unchanged with respect to the preliminary experiments described in section 5.1.2.1. The setup consisted of a pollutant and a humidity generator, similar to all the previous experiments, except that the flow through the flasks was now continuous for a week. The selected conditions were 80 °C, 43% RH and 1000 ppb of a pollutant. Relative humidity was selected to be in a realistic range, but in order to use commercially available T and RH sensors, small enough to fit inside the flasks, it had to be below 45% (the operational range of the data logger was up to 45% RH at 80 °C). Temperature and relative humidity were monitored using Signatrol SL54TH data loggers (Signatrol Ltd., Tewkesbury), which were inserted into the flasks, containing the samples.

Because of the changes in the setup and therefore reduced number of experiments, the experiment investigating the effect of AcOH, NO_2 and formaldehyde therefore had to be carried out in two consecutive sets.

The first two sets of samples were exposed to AcOH and NO_2, the third to formaldehyde and the fourth was the control, which was flushed in the same way but with no permeation tube in the pollutant generator (therefore only exposed to 80 °C and 43% RH). All the samples were exposed for 168 h (one week).

A humidity generator (Instruquest V-Gen™ Dew Point/RH generator model 1) and a pollutant generator (Vici Metronics Model 150 Dynacalibrator®) were connected by PTFE tubing. A flow controller (Aalborg mass flow controller GFC17) was used to ensure the appropriate flow into the pollutant generator to obtain the desired concentration. After the mixing coil a trap for possible water droplets was added to avoid introducing liquid water into the flasks. The setup is shown in Figure 5.9.

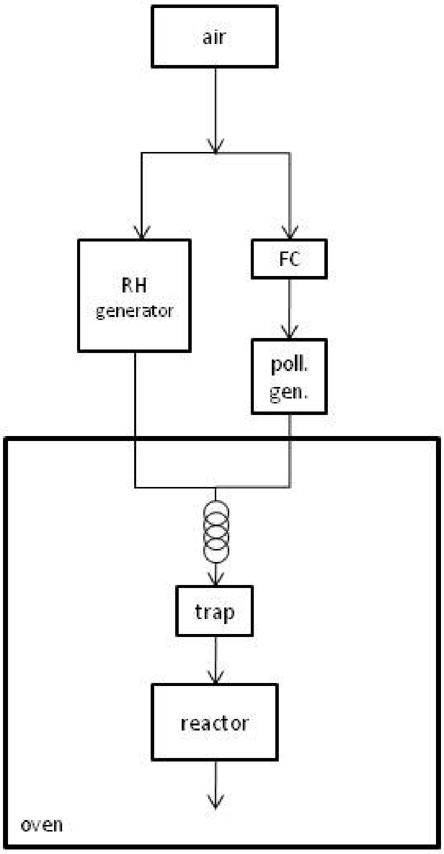


Figure 5.9: Scheme of the setup, used for flushing the samples (FC – flow controller).

To obtain 43% RH and 1000 ppb of each pollutant (AcOH, NO_2 and HCHO), the RH generator flow was set to 200 mL/min and the pollutant generator to 100 mL/min.

5.2.2.2. *Degradation rate experiments*

Since the number of experiments was now limited to simultaneously running two that involve pollutants and a control (same *T* and RH, but no pollutants), the decision was made to run experiments at 1000 ppb of a respective pollutant, 43% RH and three temperatures: 60 °C, 70 °C and 80 °C. This would allow for extrapolation of degradation rates to lower temperatures. Pollutant concentration was selected to be no more than two orders of magnitude above realistic conditions (10 ppb or 100 ppb for NO_2 and AcOH, respectively).

Following the three-temperature experiment, an experiment would be carried out at a lower relative humidity to explore the RH effect as well.

Because of previously described instrumental limitations only three experiments (two pollutants and control) could be carried out simultaneously. Humidity and pollutant generators were connected as shown in Figure 5.4 in the previous section, for exposure to both pollutants. When exposing samples to only one pollutant, a single pollutant generator was used instead of two. The control samples, which were only exposed to T and RH, were flushed using the humidity generator only.

Four sets of samples were exposed to 80 °C and 43% RH. Pollutant exposures for different sample sets were 1000 ppb AcOH, 1000 ppb NO_2, 1000 ppb AcOH + 1000 ppb NO_2 and control, which was not exposed to pollutants.

At the lower two temperatures (70 °C and 60 °C) only three sample sets were exposed, 1000 ppb AcOH, 1000 ppb NO_2 and control.

To test the effect of RH on degradation rates, an experiment was carried out at a low RH, 21%. Due to instrumental limitations and the lack of time a full Arrhenius study was not carried out, only the control set was exposed to 80 °C and 21% RH.

5.2.3. Sample analysis

The *DP* of all but the lignin-containing paper (L) was determined according to the BS ISO 5351:2004 standard [13]. The VIS reflectance spectra of all samples were taken using an X-Rite 530 SpectroDensitometer and the colour change calculated according to the CIEDE2000 formula. Degradation rates were calculated as described in section 5.1.4.

After the degradation rate experiments the pH of paper samples was determined as well, using the cold-extraction method, described in section 5.1.3.

5.2.4. Uncertainty analysis

In complex experiments, described in previous sections, uncertainties can originate from many different sources. Some of them are straightforward to assess, such as errors in RH or temperature settings, whereas others are difficult to even detect, let alone estimate. An example of such an error would be potential small leaks in connections between generators, which could lead to a loss in pollutant flow and therefore a lower pollutant concentration. Unlike in the steady-state preliminary experiments described in section 5.1.2.1 and discussed in Chapter 6, no larger leaks were observed in the experimental setup, so these possible errors were neglected in the overall estimation.

The first step in assessing prediction uncertainties was to determine the uncertainties in degradation rates, used for further calculations. As degradation rates were determined for every paper type under different conditions separately, the uncertainties were as well. Degradation rate is defined as the slope of the line, obtained when plotting $1/DP - 1/DP_0$ versus t. The uncertainty of the slope is defined as the combined uncertainty of y (Δy) and x (Δx), which in this case is:

$$\frac{\Delta k}{k} = \sqrt{\left(\frac{\Delta\left(\frac{1}{DP} - \frac{1}{DP_0}\right)}{\frac{1}{DP} - \frac{1}{DP_0}}\right)^2 + \left(\frac{\Delta t}{t}\right)^2}, \qquad (54)$$

where k is the degradation rate (i.e. the slope) and t is time. The uncertainties in measuring time are much smaller compared to the uncertainties in DP, which depend on a range of parameters. The second term, describing the time uncertainty, was therefore dismissed.

The first term depends on the accuracy of the analytical method used for determining DP (or any other measured property), and also on parameters affecting the degradation process. These are temperature, RH and pollutant concentration, so the uncertainties in determining these had to be assessed and taken into account. The equation therefore becomes [145]:

$$\frac{\Delta k}{k} = \frac{\Delta\left(\frac{1}{DP} - \frac{1}{DP_0}\right)}{\frac{1}{DP} - \frac{1}{DP_0}} = \sqrt{\left(\frac{\Delta DP}{DP}\right)^2 + \left(\frac{\Delta RH}{RH}\right)^2 + \left(\frac{\Delta k_T}{k_T}\right)^2 + \left(\frac{\Delta k_c}{k_c}\right)^2}\,, \qquad (55)$$

where k_T is the temperature-dependent degradation rate and k_c is the concentration-dependent degradation rate (because these two effects are not linear the uncertainties in rates had to be taken into account). Two assumptions are made to simplify uncertainty determination, additivity of temperature and pollutant effects and their independence. Although this might not necessarily hold (pollutant effects might be temperature dependent as well), it was assumed to be a good enough approximation for the purpose of assessing uncertainties. As T and c dependence are not as straightforward as RH dependence (which was assumed to be linear for the purpose of determining uncertainties), the uncertainties in rates had to be calculated, rather than just taking into account the uncertainties in T and c measurements directly. For T this means:

$$\frac{\Delta k_T}{k_T} = \frac{e^{\frac{-E_a}{RT_{max}}} - e^{\frac{-E_a}{RT}}}{e^{\frac{-E_a}{RT}}}, \tag{56}$$

where T is the set temperature, used in calculations, and T_{max} is the maximum deviation from that value. Actual errors in concentration are not known, as the concentration in sample flasks was not measured, but uncertainties were calculated from permeation device and generator specifications. The manufacturer provides the permeation rate, together with the uncertainty, for each permeation device. These were used as concentration uncertainties, as concentration is linearly dependent on the permeation rate. The concentration-dependent rate uncertainty was then determined as:

$$\frac{\Delta k_c}{k_c} = \frac{k_{\max c} - k_c}{k_c}, \tag{57}$$

where k_c is the determined degradation rate at the set concentration, used in calculations, and $k_{\mathrm{max\ c}}$ is the degradation rate, calculated at the concentration, obtained at the highest possible permeation rate (at the highest end of the uncertainty interval). The maximum degradation rate at the highest concentration was calculated using extrapolation, assuming a linear effect of the concentration on the degradation rate. Uncertainty calculation for chain scission rate of acidic paper 1, exposed to 1000 ppb NO_2 at 80 °C is shown below (chain scission results will otherwise be discussed in Chapter 7).

$$\frac{\varDelta k_{A1}}{k_{A1}} = \sqrt{\left(\frac{\varDelta DP}{DP}\right)^2 + \left(\frac{\varDelta RH}{RH}\right)^2 + \left(\frac{\varDelta k_T}{k_T}\right)^2 + \left(\frac{\varDelta k_c}{k_c}\right)^2}$$

$$= \sqrt{0.02^2 + \frac{3.43^2}{43} + \left(\frac{e^{\frac{-57800\frac{J}{mol}}{R*353.5K}} - e^{\frac{-57800\frac{J}{mol}}{R*353.15K}}}{e^{\frac{-57800\frac{J}{mol}}{R*353.15K}}}\right)^2 + (\frac{3.40*10^{-5} - 3.03*10^{-5}}{3.40*10^{-5}})^2}$$

$$= \sqrt{0.02^2 + 0.0798^2 + 0.0197^2 + 0.120^2} = 0.147 \qquad (58)$$

$$\varDelta k_{A1} = 0.147 * k_{A1} = 4.46 * 10^{-6} day^{-1} \qquad (59)$$

As can be seen from the example above, the largest contribution to the rate uncertainty comes from uncertainty in concentration, i.e. from the uncertainty in the permeation rate of the permeation device. The contribution of temperature is actually the smallest, despite the rate's exponential dependence on *T*, as the temperature of the oven, where experiments took place, was controlled well.

The rate uncertainty, determined from linear regression, is of the same order of magnitude, in this example larger by approximately a factor of 2 (discussed in Chapter 7). This shows that the contribution of data scatter is comparable to the uncertainty calculated above. In order not to underestimate the overall uncertainties of degradation rate predictions, both determined uncertainties (i.e. the calculated one and the one, determined from linear regression) were combined (Equation 60), although the data scatter partly arose as a consequence of the uncertainties in the environmental test conditions, described above. This means that the assessed uncertainties are probably to an extent overestimated.

$$\frac{\varDelta k}{k} = \frac{\varDelta k_{calculated} + \varDelta k_{regression}}{k} . \qquad (60)$$

Similar to the degradation rates, linear regression uncertainties and concentration dependencies were different for different paper types, the overall uncertainty was calculated for each type and set of conditions individually. The actual uncertainties therefore differ according to paper type, temperature, RH and pollutant conditions (uncertainties in permeation rates were different for AcOH and NO_2 and the control samples were not affected by uncertainties in pollutant concentrations).

5.2.5. Extrapolation of degradation rates

In order for the degradation rates, obtained from the experiments described in section 5.2.2.2, to be useful for assessing the behaviour of paper in real archival conditions, the rates had to be extrapolated to room conditions, both in terms of T and pollutant concentrations.

5.2.5.1. Arrhenius study

Chain scission and colour change rates described earlier were used to calculate linear regression according to the linearised form of the Arrhenius equation:

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A. \tag{61}$$

The uncertainties obtained, as described in the previous section, were used as error bars for data points in the linear regressions (each degradation rate is one data point and three data points, i.e. degradation rates obtained at 80, 70 and 60 °C, were used for each regression) (Equation 62).

$$\delta z = \delta(\ln y) \approx d(\ln y) = \frac{\delta y}{y}, \tag{62}$$

therefore

$$\delta z \approx \frac{\Delta k}{k}, \tag{63}$$

Which means the data points can be plotted as $\ln k \pm \Delta k/k$.

Linear regression was carried out using OriginPro 8.6 software. Lines were drawn using linear regression with errors as weights, with direct weighting instead of instrumental weighting. Instrumental weighting would weight the points with smaller errors more, which was undesirable, because only three points were used. Line slopes and intercepts with standard errors were obtained and used to calculate the activation energy, E_a, and the pre-exponential factor, A, from the Arrhenius equation.

Arrhenius plots, described above, were used to predict degradation rates at lower temperatures. As described in Chapter 4, the recommended temperature for the Nationaal Archief is 18 ± 2 °C. Temperature monitoring showed that the actual temperature was within those limits, with 18 °C in the repository with air filtration and 19 °C in the repository without air filtration. Average temperature at The National Archives (UK), measured in 2009, was similar, 19 ± 0.4 °C [146]. Degradation rate extrapolations were therefore carried out to 18 °C. Predictions were made for each paper type and pollution condition separately.

Arrhenius plot slope uncertainty intervals were used to calculate uncertainties in degradation rates at lower temperatures. Obtained degradation rate uncertainties are asymmetrical, which is a consequence of recalculating the symmetrical intervals of a logarithmic quantity (ln$k$) into non-logarithmic values, following the Arrhenius equation. As asymmetrical uncertainty intervals are difficult to present, degradation rate minima and maxima were calculated (see Appendix B for an example of calculation).

5.2.5.2. Realistic pollutant concentrations

The experiments presented here were carried out at elevated pollutant concentrations, generally one or two orders of magnitude higher than what would normally be found in an archival repository. To predict degradation of paper in realistic archival conditions, extrapolations to lower pollutant concentrations were carried out from the degradation rates, obtained for 1000 ppb.

A linear dependence of the degradation rate on the pollutant concentration 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 (i.e. ‘zero’). Assumptions made here are different to the ones used for interpolation, proposed by Tétreault [73] when he introduced the dose concept in which concentration, multiplied by time, is a constant. The main difference between the two approaches is that Tétreault’s 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 1000 ppb.

This interpolation is based on two assumptions, the first being linear dependence of the degradation rate on the pollutant concentration and the second that T and RH-induced degradation and pollutant-induced degradation are additive processes (the overall degradation rate is the sum of the rate, affected by *T* and RH, and the rate, affected by pollutant exposure). This might not be entirely correct, as pollutant effects might depend on *T* and RH as well, e.g. pollutant absorption is temperature-dependent and pollutant dissociation, leading to increased acidity and possibly damage, is RH-related. These relationships, however, are difficult to decouple and therefore study, and much more research would be required to understand them better. Additivity of effects is therefore the best approximation currently available without additional research at different pollutant concentrations and *T* and RH levels.

Degradation rate minima and maxima, described in the previous section, were used to calculate uncertainty intervals of interpolated rates. Interpolations were made across two orders of magnitude and rates were calculated for pollutant concentrations of 10 and 100 ppb (see Appendix B for an example of calculation).

5.3. Assessing the lifetime of paper

Degradation rates at realistic environmental conditions were obtained for five representative historic papers and one model paper, as described in the previous section. They could then be used for predicting the lifetimes of paper.

Paper permanence has previously been evaluated and presented in different ways, all in attempt to describe how different conditions (environmental or the paper type itself) will affect its degradation. As described in Chapter 2, different approaches have been introduced so far, from loss of a mechanical property by a certain percent [40,52], to very well received isoperms, introduced by Sebera [54].

As these approaches give little idea of how long a document can still be used, before it becomes ‘too degraded’, a different approach was taken here. Lifetimes of paper were considered to be a better measure of comparing different environmental conditions and paper compositions. Lifetimes are defined in terms of the purpose, a document is used for, and the property of paper, affecting that particular purpose. For example if a document is to be handled safely, it needs to be mechanically stable. On the other hand its mechanical properties can be much poorer if a document is only to be displayed and handled infrequently and by trained professionals. For display purposes, however, the colour of the document could be very important. Lifetime is therefore defined as the time needed until paper is no longer usable for particular purpose, which could either be handling or display.

Handling lifetime is defined as the time needed for the paper *DP* to decrease to the safe handling threshold, *DP* = 300 [14,47]. With a known starting *DP* and a chain scission rate, extrapolated from the experiments as described in the previous section (5.2.5.), the lifetime can be calculated from the Ekenstam equation:

$$k_{DP}t_{handling} = \frac{1}{300} - \frac{1}{DP_0}\,. \tag{64}$$

Handling lifetime is therefore defined similarly to the lifetime of paper insulation in transformers [6], although with a higher threshold value for safe handling.

Display lifetime is defined as the time needed for paper to reach a value of ΔE_{00}, which is perceived as unacceptable. The definition, introduced by Ashley-Smith et al. [147] for a museum environment, was used. A colour difference of 1.5 CIEDE2000 units ($\Delta E_{00} = 1.5$) was selected as 'perceptible change' (PC) and 10 PCs were suggested as a 'life' of an object. Display lifetime was therefore calculated, using extrapolated colour change rates and the following equation:

$$k_{\Delta \mathrm{E}}t_{display} = 15. \tag{65}$$

When discussing display lifetimes it should be noted that photo-induced degradation was not included in the experiments, discussed here. Although light is known to be an important factor in paper degradation [4,65,66,110], 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 project. Display lifetimes are therefore calculated excluding photo-induced degradation, which means the papers would only actually reach them if they were mainly kept in the dark and only illuminated infrequently. Photo-induced degradation could also lead to both bleaching and yellowing, and only yellowing (or darkening) was investigated here. The aim was not to predict exact lifetimes, but to quantitatively compare effects of pollutants on colour change in realistic archival conditions.

5.3.1. Uncertainties in lifetime assessment

Uncertainties, obtained from linear regression, described in section 5.2.5.1, were used to calculate uncertainties in lifetime predictions. When the uncertainty intervals for expected lifetimes are calculated in years, the uncertainty intervals are asymmetrical, which results from asymmetrical degradation rate uncertainty intervals and is a consequence of recalculating the symmetrical intervals of a logarithmic quantity into non-logarithmic values. An example of lifetime calculation is shown in Appendix B.

5.3.2. Conclusion

Six paper types (five real historic papers and a model paper) were chosen for experiments. Based on their properties they were selected to represent a real archival collection.

Experiments were designed to investigate paper degradation in the presence of the most abundant pollutants in a typical archival repository. Originally, a statistical experimental design was created to carry out steady-state experiments in closed reactors with regular flushing of samples.

The experimental setup was then changed to a dynamic system, where the samples were flushed continuously. Due to instrumental limitations of a dynamic system the original statistical design was abandoned and experiments were carried out as an Arrhenius study.

The methods used to assess degradation rate uncertainties and extrapolate (or interpolate) them to room conditions (T and pollutant concentration) are explained. The method used to predict paper lifetime throughout this thesis is shown as well.

6. Steady-state experiments

Experiments were carried out as described in the previous Chapter, starting with preliminary experiments to determine to most harmful pollutants in an archival environment. These were followed by experiments, designed to determine degradation rates at different *T*, RH and pollutant concentrations.

6.1. Preliminary study of the effects of pollutants on paper degradation

Results of preliminary experiments are presented in terms of the difference between the *DP* before and after degradation rather than degradation rate, as the papers were only analysed after the experiment and compared to papers, not subjected to accelerated degradation. This also makes *DP* results more comparable to the colour change results, as those are presented as ΔE_{00} values, calculated from *L*a*b** measurements before and after accelerated degradation, rather than colour change rates, as well. The results of the first preliminary experiment are shown in Figures 6.1 and 6.2. All paper samples were degraded in the same reactor, including the L sample, not shown in Figure 6.1.

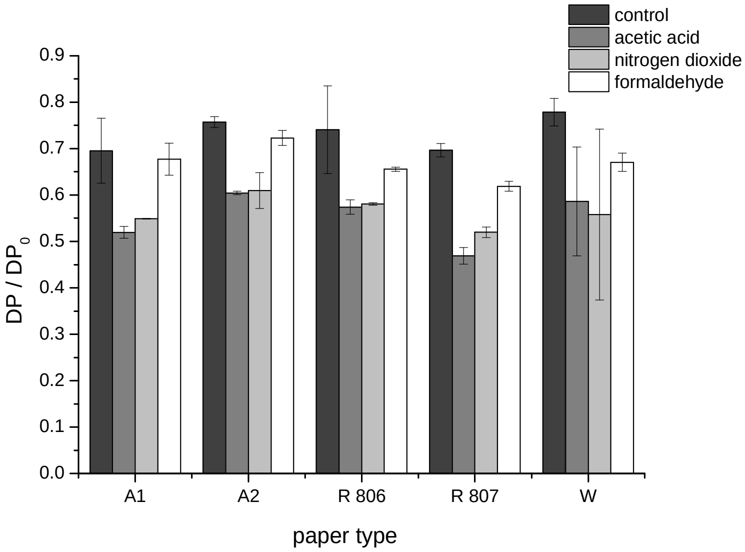


Figure 6.1: First preliminary results, difference between the *DP* before and after degradation, error bars represent the difference between two duplicates. T = 80 °C, RH = 60%, c_{poll} = 1000 ppb, 13 days.

The graph shows the loss of *DP* during the experiment, represented by *DP / DP*$_0$. The error bars are based on two replicates, i.e. two pieces of paper exposed in the same reactor and analysed separately. Significant degradation occurred during the 13-day experiment, as the *DP* values decreased by at least 20% even for the control samples. The papers exposed to AcOH or NO_2 degraded significantly more than those exposed to formaldehyde and the control group. The effects of AcOH and NO_2 are also comparable, whereas the effect of formaldehyde is significantly smaller. The *DP* of the acidic and one of the rag samples decreased to about half of its original value when exposed to NO_2 or AcOH, which suggests a very significant effect of the pollutants on these two paper types. Formaldehyde, on the other hand, had hardly any effect on acidic papers and some effect on the two rag samples and Whatman paper, but less than NO_2 or AcOH. The effects on alkaline paper are not presented as the originally used sample was not suitable for viscometric analysis. The paper was not dissolvable in cupriethylenediamine, solvent used for carrying out the measurements, probably due to the presence of lignin. This sample was discarded is therefore not described in Table 5.1. As a result of this, a new alkaline sample was selected for future experiments (described in Table 5.1 in the previous Chapter).

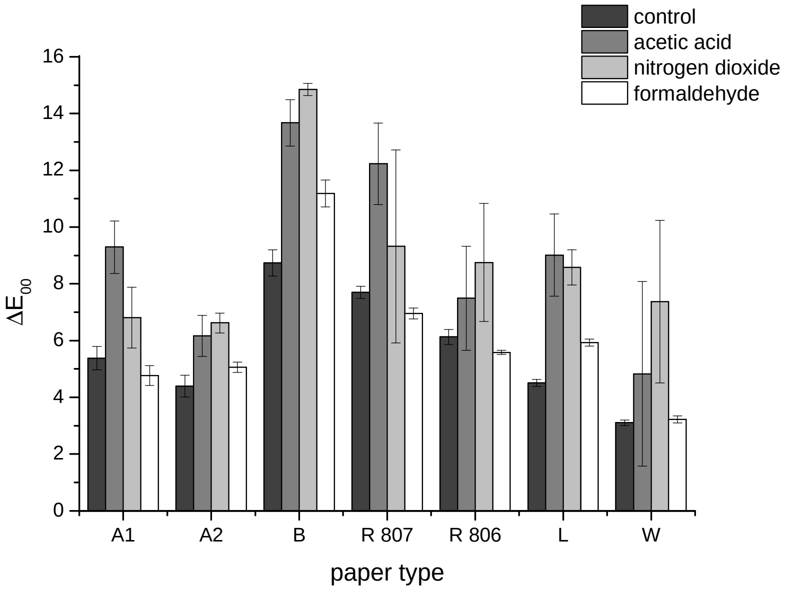


Figure 6.2: First preliminary results, colour change. Error bars represent standard deviation based on three measurements. T = 80 °C, RH = 60%, c_{poll} = 1000 ppb, 13 days.

The graph shows colour change during the first preliminary experiment, obtained by comparing the samples before and after the experiment. Pollutant effects on colour change were similar to the effects on *DP* loss. AcOH and NO_2 seem to promote colour change considerably more than formaldehyde, which has a very small effect and is comparable to the control. A significant effect of formaldehyde could only be observed for the alkaline and lignin-containing sample. Colour change was the largest for the alkaline sample, up to $\Delta E_{00} = 15$ for NO_2 exposure. The acidic sample 1, one of the rag samples and the lignin-containing sample were more affected by AcOH than NO_2.

To ensure these results were repeatable, another experiment was carried out under the same conditions. The results are shown in Figures 6.3 and 6.4.

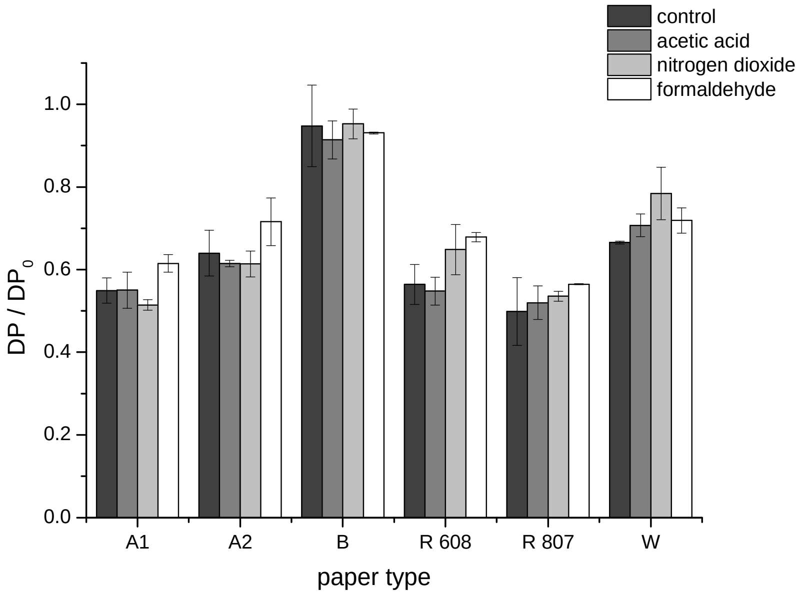


Figure 6.3: Second preliminary results, difference between the *DP* before and after degradation, error bars represent the difference between two duplicates. T = 80 °C, RH = 60%, c_{poll} = 1000 ppb, 13 days.

Again the graph shows *DP* loss, represented by DP / DP_0. The results, obtained from the second experiment, were very different compared to the ones, obtained from the first. No pollutant effect could be observed for most samples, rag and Whatman samples even seemed to have degraded the most under control conditions. The flasks seemed to be closed well, which means an air leak was not the reason for this unexpected behaviour.

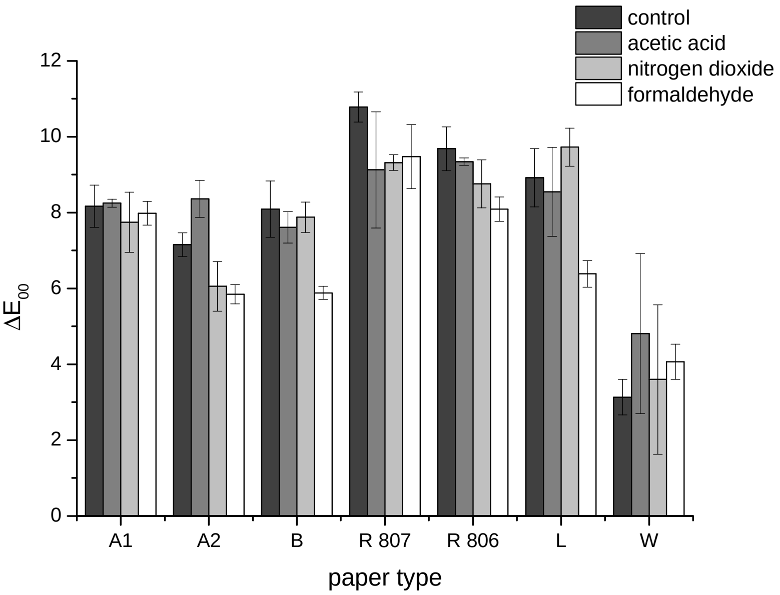


Figure 6.4: Second preliminary results, colour change. Error bars represent standard deviation based on three measurements. T = 80 °C, RH = 60%, c_{poll} = 1000 ppb, 13 days.

Similar to *DP* loss, colour change in the second experiment seemed not to be affected by pollutant exposure. ΔE_{00} also reached higher values compared to the first experiment for all samples, except the alkaline, which changed colour significantly less. No trend could be observed and similar to the *DP* loss results, the control conditions seemed to be the most harmful for several samples (alkaline, both rag samples and lignin-containing sample). As explained in section 5.1.1.2. the control samples were flushed in the same way as the other three sample sets, which means there was no additional VOC build-up, resulting from paper degradation (the air exchange was the same in all sample sets).

There seemed to be no pollutant effects at all, both in terms of *DP* loss and colour change. No trends could be observed and generally the extent of degradation and colour change under different conditions seemed quite randomly distributed. As this was very unexpected and unusual, it raised suspicions of a flaw somewhere in the setup. A leak in the tubing, leading to the pollutant generator, was indeed discovered, which meant the air flow to (and consequently from) the generator was much less than expected. As this meant the results could basically be discarded, a third set of preliminary experiments was carried out.

The setup and the conditions were mostly unchanged (except for replacing the leaking tubing), although the flushing time was shortened to 5 min to minimise condensation and exposure time was shortened from 14 to 9 days, due to lack of time. The results are shown in Figures 6.5 and 6.6.

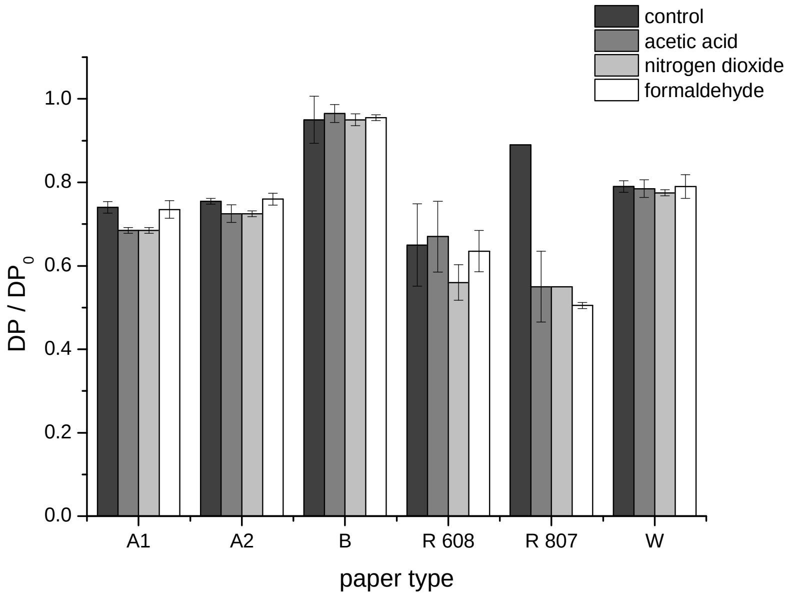


Figure 6.5: Third preliminary results, difference between the *DP* before and after degradation, error bars represent the difference between two duplicates. T = 80 °C, RH = 60%, c_{poll} = 1000 ppb, 9 days.

The *DP* loss results appeared to be similar to the first set of preliminary experiments. The effect of NO_2 and AcOH on acidic papers was significant in comparison to formaldehyde and control conditions. Hardly any degradation was observed for alkaline paper regardless of pollutant exposure. This was expected, as alkaline paper has some alkaline reserve, which makes it more resistant to hydrolytic degradation, and a high initial *DP*. Unexpectedly the two rag samples behaved differently, with significant formaldehyde effect only observable in one of them. The error bars for rag samples, however, were significantly larger compared to the other samples. The missing error bars for one of the rag samples (R 807) are due to one of the control samples being discarded as it was observed to have a water stain, which could bias the results (paper degradation in direct contact with water may be different to degradation at 60% RH). The reason there is no error bar for the R 807 exposed to NO_2 is that both parallels gave exactly the same result. It can, however, be concluded that at least NO_2 at 1000 ppb had a significant effect on the degradation process. All papers degraded to a lesser degree compared to the first set of experiments as this experiment was shorter, but the degradation trends were similar (especially compared to the second set).

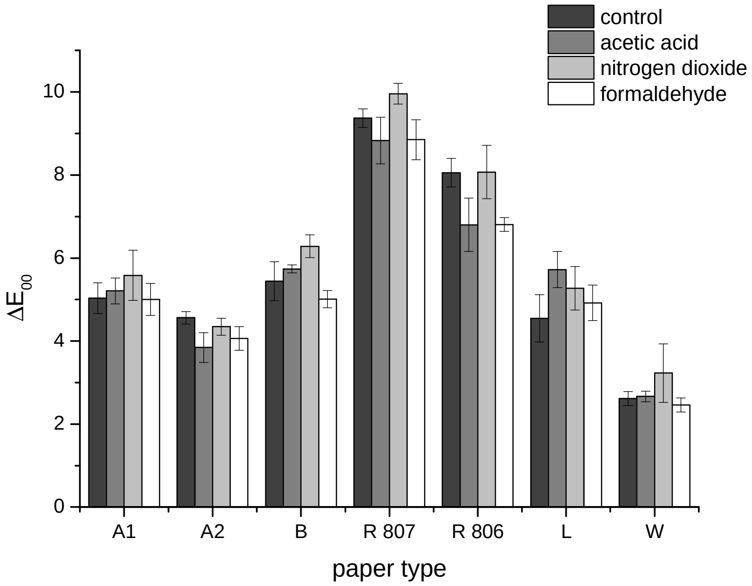


Figure 6.6: Third preliminary results, colour change. Error bars represent standard deviation based on three measurements. T = 80 °C, RH = 60%, c_{poll} = 1000 ppb, 9 days.

For most paper types the colour change was most pronounced if the samples were exposed to NO_2. AcOH also had a considerable effect on some paper types, especially lignin-containing paper. Overall the colour changes were smaller compared to the first set of experiments, as were the differences between different pollutant conditions. The reason for that is not only shorter experiment time but possibly also shorter flushing time (only 5 min compared to 60 min), which meant that less pollutant was actually introduced into the flask. An assumption was made that the conditions inside the flask were steady, once the flushing was complete and flask closed. The second assumption was that the flushing time was not that important as long as all the air inside a flask was replaced during flushing (1.5 air exchanges was thought to be enough to achieve that) and the third that there was no cross-contamination of the samples, since the air inside a reactor was replaced every 2-3 days. The assumptions later turned out to be false, which will be discussed in the next chapter.

However, even at shorter flushing times (and an overall shorter experiment) the degradation trends were similar in the first and third set of preliminary experiments. The effects of AcOH and NO_2 were not as obvious and significant as in the first experiment, but there was still indication that these two pollutants are more harmful to paper than formaldehyde. Based on these results, AcOH and NO_2 were selected for further experiments.

6.2. Degradation rate experiments – effects of pollutants in steady-state conditions

To observe the effect of pollution on paper degradation, experiments performed at the same RH were compared first. Four experiments (i.e. flasks) were carried out at 60% RH and four at 20%. Out of the four, one is pollutant-free (the samples were only exposed to elevated T and RH), and the other three contain 1000 ppb AcOH, 1000 ppb NO_2 and 1000 ppb of each pollutant, respectively.

Results for acidic paper 1 at 60% RH are shown in Figure 6.7. The graph shows the degradation rate (chain scission rate), plotted as ($1/DP - 1/DP_0$) as the dependent and time (in days) as the independent variable, following the Ekenstam equation (Equation 10). All of the following degradation rate graphs will be plotted in the same manner.

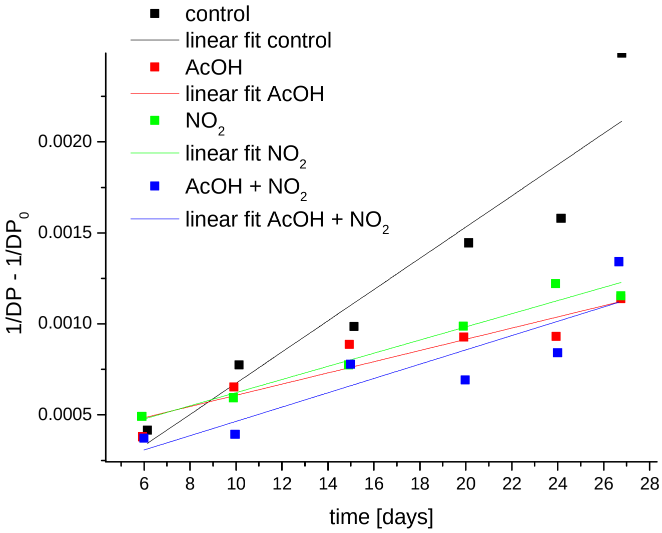


Figure 6.7: Chain scission rates of paper sample A1 at four different conditions at 80 °C, 60% RH. The lines represent chain scission rates and were created using best-fit linear regression.

Interestingly, the degradation rate was the highest for the control sample, i.e. the sample not exposed to any pollutants. There was no significant difference between the other three conditions (each pollutant separately and both combined). The degradation actually being the fastest in the pollutant free flask indicated that the pollutants did not have a negative effect on paper degradation under these conditions, which was unexpected. A possible explanation for this might be that not enough of the pollutant was introduced into the flask during the flushing to actually ensure different conditions in different flasks between two flushing campaigns or this might be due to an unknown systematic error in the experimental setup. Results for all paper types appeared very similar as the degradation was always the most pronounced for the sample set, which was only exposed to T and RH (the control). No trend concerning degradation rates under the other three conditions was observed. The rates were very similar within the same paper type, but seemed randomly distributed in terms of magnitude for different pollutant conditions, again indicating no pollutant effect. Linear fits for all real paper samples were relatively good ($R^2 > 0.8$, mostly above 0.9) and satisfactory for Whatman paper ($R^2 > 0.7$). The linear regression data for all samples is shown in the Appendix C.

At 20% RH the chain scission rates, obtained under different pollutant conditions, were quite similar, with some differences observable only for acidic sample 1 (Figure 6.8).

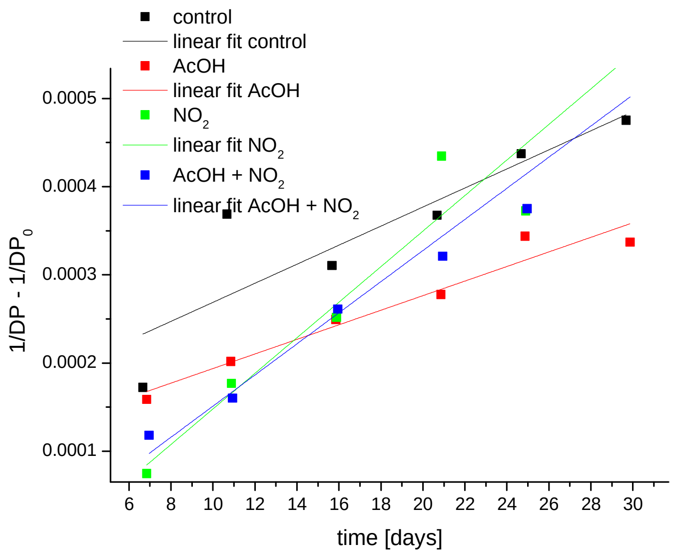


Figure 6.8: Chain scission rates of paper sample A1 at four different conditions at 80 °C, 20% RH. The lines represent chain scission rates and were created using best-fit linear regression.

The slope (*k*, rate) appears larger for the samples, exposed to NO_2 and both pollutants combined, compared to the control and AcOH. The scatter of data, however, was quite significant especially for the control set, so it is difficult to conclude the differences are due to anything other than experimental uncertainty. The chain scission rates for the acidic sample 2 are shown in Figure 6.9.

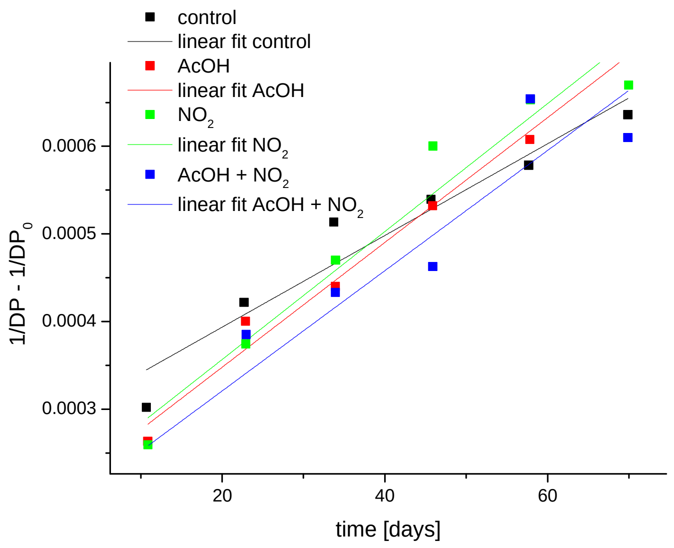


Figure 6.9: Chain scission rates of paper sample A2 at four different conditions at 80 °C, 20% RH. The lines represent chain scission rates and were created using best-fit linear regression.

All four degradation rates are comparable. Taking into account the scatter of data there was no significant difference between the samples, exposed to pollutants and the control, or between different pollutants. The behaviour of alkaline and Whatman paper was very similar (with the exception of somewhat larger data scatter for Whatman paper), with no significant differences between the degradation rates under different conditions (see Appendix C for all regression data). Chain scission rates of rag paper were somewhat different and are shown in Figure 6.10.

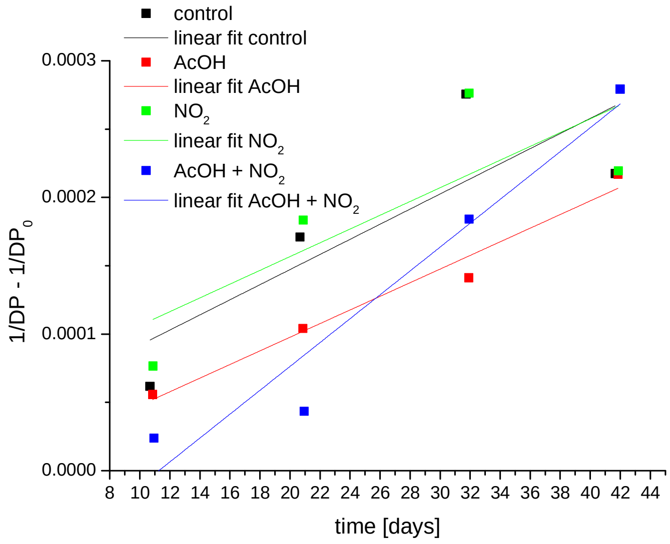


Figure 6.10: Chain scission rates of paper sample R at four different conditions at 80 °C, 20% RH. The lines represent chain scission rates and were created using best-fit linear regression.

Degradation rates of rag samples, exposed to the combination of both pollutants, seems significantly higher compared to the other three conditions. The first two data points (i.e. samples) under this condition, however, were the lowest of the four different conditions and generally all the data points seem very scattered. Conclusions on significant pollutant effects can therefore hardly be drawn from this graph.

The graphs generally show that the samples, exposed to pollutants, did not degrade any faster compared to the control samples, only exposed to *T* and RH. In fact, the highest degradation rates were obtained at 60% RH (which is unsurprising) and no pollutants (which was surprising). This was the case for all different paper types.

Colour change of the acidic sample is shown in Figure 6.11. The graph shows colour change rates, plotted as ΔE_{00} against time (in days). All following graphs showing the rate of colour change will be plotted the same way.

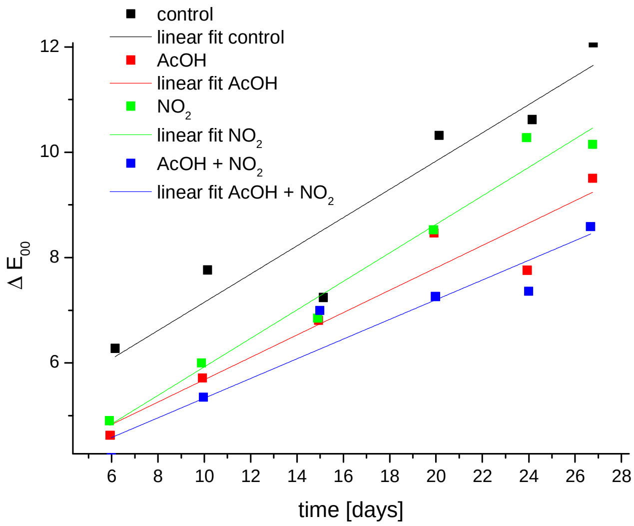


Figure 6.11: Colour change rates of paper sample A1 at four different conditions at 80 °C, 60% RH. The lines represent colour change rates and were created using best-fit linear regression.

The largest colour change was observed for the control sample set, although the differences between the four rates were small (differences between the control and NO_2 and AcOH and both pollutants combined are insignificant). These results indicate no effect of pollutants at the experimental conditions, and it seems likely that the predominant effect was that of relative humidity. Very similar results were obtained for all paper types. The order of colour change rates differs according to paper type (similar to degradation rates described earlier), although the differences are very small (see Appendix C). Slightly different behaviour was observed for lignin-containing paper (Figure 6.12).

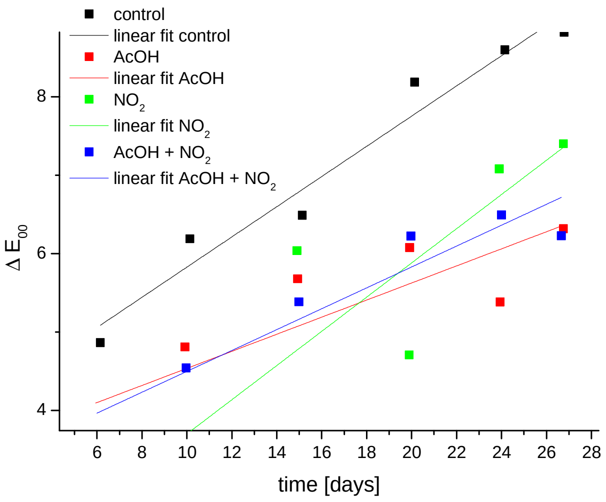


Figure 6.12: Colour change rates of paper sample L at four different conditions at 80 °C, 60% RH. The lines represent olour change rates and were created using best-fit linear regression.

The slope is the largest for the samples, exposed to NO_2. The actual colour change (ΔE_{00} value), however, was the largest for the control samples, similar to the other paper types. Considering this and the data scatter it could be concluded, that the difference between the control and NO_2 sets is not significant. The same conclusion can be made for the AcOH and both pollutants sample sets.

Colour change rates for acidic paper 1 at 20% RH are shown in Figure 6.13.

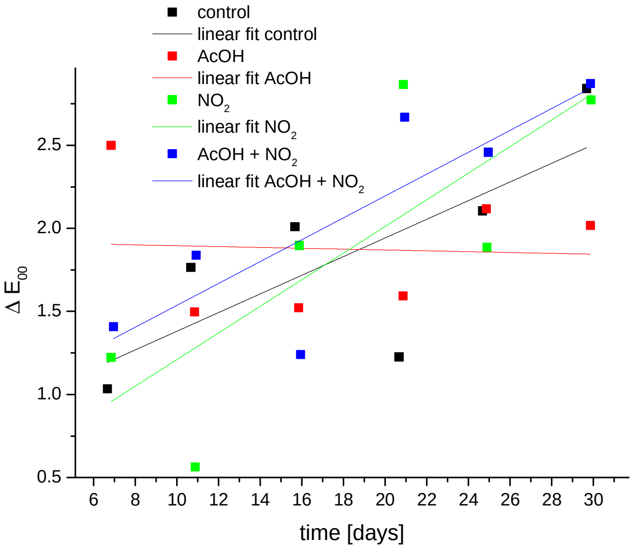


Figure 6.13: Colour change rates of paper sample A1 at four different conditions at 80 °C, 20% RH. The lines represent colour change rates and were created using best-fit linear regression.

The results show clearly that pollutants, introduced into the flasks periodically during short periods of flushing, did not have an effect on colour change. The effect of elevated RH, shown in Figure 5.19, was confirmed by this low-RH experiment, where the observed colour change was very small ($\Delta E_{00} < 3$) under the same pollutant conditions. Considering that measurement uncertainties can be in the same order of magnitude (as shown in the results of preliminary experiments) and that the data points seem randomly distributed it can be concluded that no significant effect was observed for acidic paper 1. R^2 values are accordingly low as well. Larger colour changes with less data scattering were obtained for acidic paper 2 (Figure 6.14).

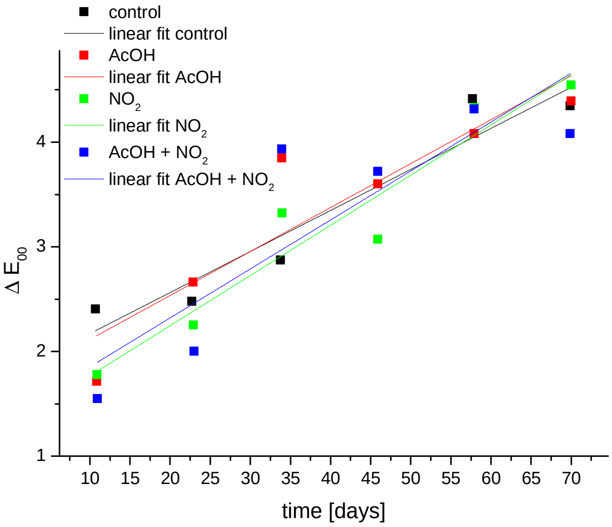


Figure 6.14: Colour change rates of paper sample A2 at four different conditions at 80 °C, 20% RH. The lines represent colour change rates and were created using best-fit linear regression.

Scatter of the data was less pronounced for this paper type, however there was still no significant effect of any of the pollutant conditions. There was no significant difference between the four colour change rates and similar results were obtained for alkaline and Whatman paper as well. The same lack of a trend was observed for rag and lignin-containing paper, although there seemed to be some difference between the rates. Data scatter, however, was larger for the rag and lignin-containing samples, so the differences are hardly significant (see Appendix C for all regression data).

Similar to the *DP* change, the colour change seemed independent of pollutant presence, as the rate of change at 20% RH was basically the same for all four conditions and no repeated pattern of pollutant-induced degradation was observed.

The colour change rates under the four different pollutant conditions did not differ significantly for any of the paper types. At 60% RH all four rates were very similar as well and no trend (in terms of pollutant effect) could be observed.

At this point the experiment at 50 °C was already running. As an assumption was made that some degradation would be observed in a month (at least for the most sensitive acidic paper 1), the first samples (A1 and W) were removed to check whether a pollutant effect could be observed at 50 °C. Since one data point is not enough to calculate the degradation rate accurately, only *DP* values before and after 36 days of degradation under different pollutant conditions were compared. DP/DP_0 for acidic paper 1 and Whatman paper at 60% RH is shown in Figure 6.15.

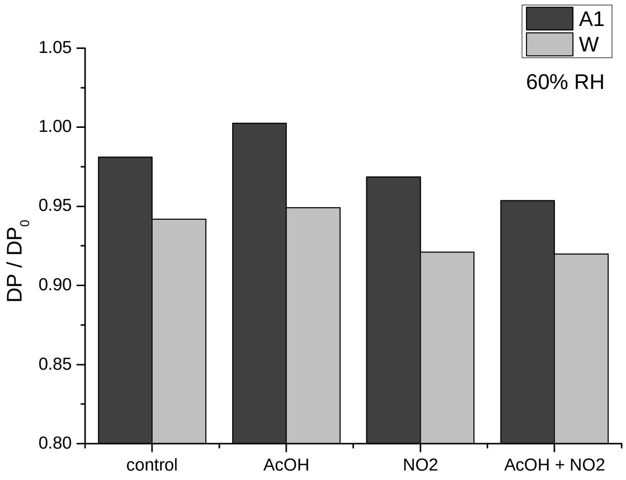


Figure 6.15: DP/DP_0 after 36 days for paper samples A1 and W at 50 °C and 60% RH.

Since the temperature was low, not much degradation was observed in the relatively short experiment time. Still it seems like the samples, exposed to NO_2 and the combination of both pollutants, degraded slightly more than those exposed to AcOH and no pollutants. To check, whether what was observed was significant or not, the results obtained at 20% RH were compared as well (Figure 6.16).

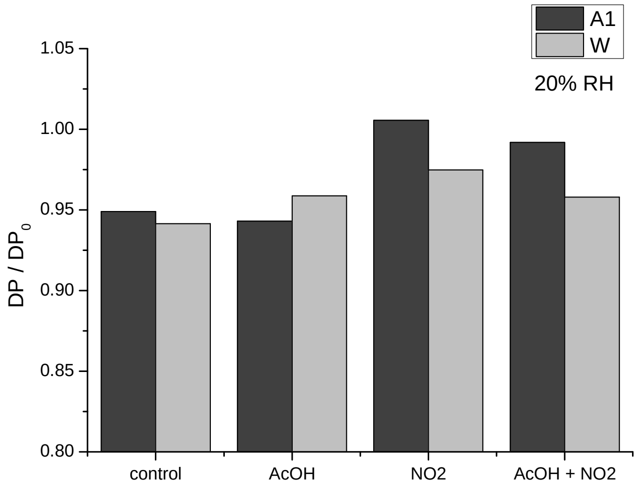


Figure 6.16: ***DP/DP*$_0$ after 36 days for paper samples A and W at 50 °C and 20% RH.**

Interestingly, the exact opposite was observed at the lower RH. The samples degraded the least when exposed to NO_2, which is the opposite of what would be expected. Similar to the results, obtained at 80 °C, the most degradation was observed for the control sample of Whatman paper and the acidic sample behaved similarly under the control conditions and when exposed to AcOH.

Overall it can be concluded there was no significant (and repeatable) pollutant effect at 50 °C, similar to the results obtained at 80 °C.

6.3. Problems and outcomes

Based on preliminary results and literature review (Chapter 3, section 3.2.) it seemed unlikely that 1000 ppb of either pollutant would have no observable effect whatsoever. Based on previous experiments [148] it was known that VOC absorption rate increases significantly when the temperature is increased. This could mean that the pollutants were quickly absorbed into paper after flushing the flasks and therefore the concentration in the flask was no longer 1000 ppb, but significantly less. If a speculation was made, that all the pollutants were absorbed into the paper samples soon after flushing, it could be concluded, that the 'environment' in all four flasks at the same RH was roughly the same, which would explain the same degradation rates (within experimental uncertainties).

As it seemed like there really was no difference between the conditions in the four flasks at the same RH level (containing no pollutants, 1000 ppb AcOH, 1000 ppb NO_2 and with 1000 ppb of each), the atmosphere inside four flasks was analysed using GC-MS.

There was no analytical technique available to measure such a small amount of NO_2 as the most common techniques are diffusion tubes or active-sampling chemiluminometric analyzers, which both require a much larger quantity of air. Only AcOH could therefore be determined and used as an indication of processes inside the reactors. It is known that GC-MS is not the technique of choice for quantitative AcOH analysis, however it should be suitable for semi-quantitative assessment. From previous work on VOCs emitted from paper [149] it was known that a peak for AcOH can be observed, so AcOH concentrations could be compared at least semi-quantitatively between flasks.

As shown in Figure 6.17, some peaks were observed, but none of them belonged to AcOH. This was the case in all four flasks, which all gave almost identical chromatograms. This means the conditions were indeed roughly the same in all of them and that AcOH is most likely to have been absorbed into the paper.

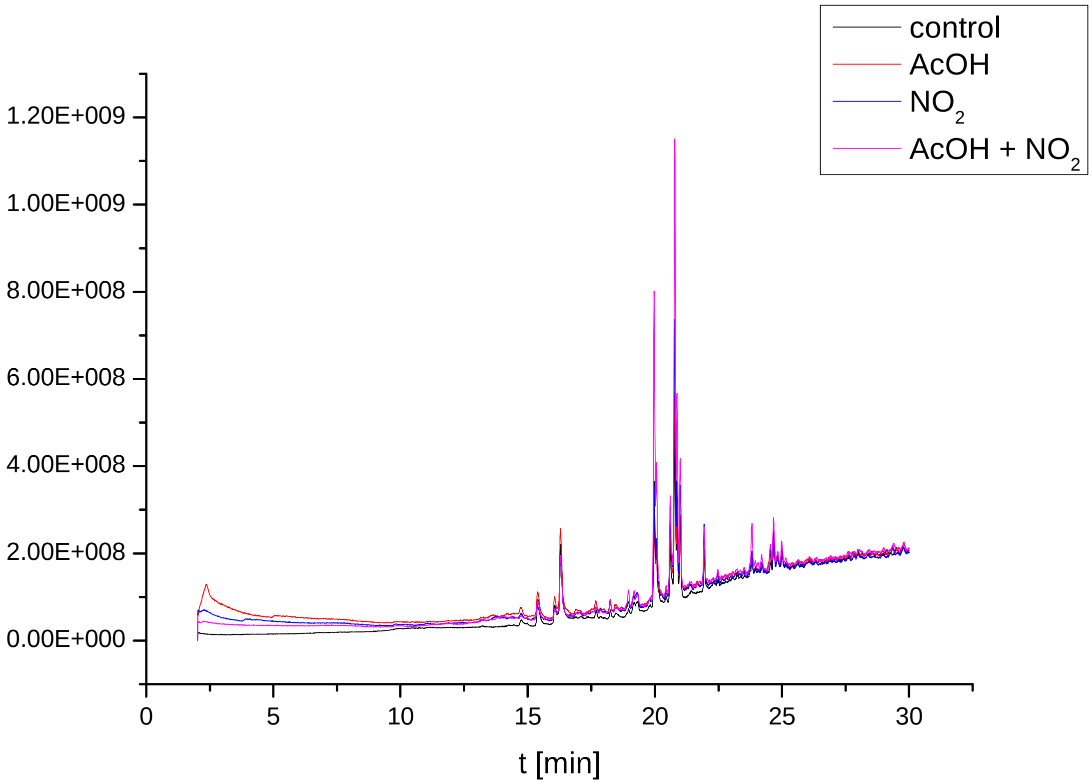


Figure 6.17: Chromatograms of all four 'environments', after exposure to 50 °C, 20% RH and pollutants for 50 days, the sampling was carried out through a septum. The chromatograms overlay almost perfectly, if AcOH was present, a peak would be present at cca. 10 min.

This confirmed the assumption that the flasks with samples were not flushed often enough to ensure steady-state conditions, so it is likely that the conditions in all flasks were in fact very similar. This is why the degradation rates under presumably different pollutant conditions were not significantly different and no pollutant effect could be observed.

6.4. Conclusion

Preliminary experiments showed that NO_2 and AcOH have more effect on paper degradation than formaldehyde and were therefore selected for further experiments, planned according to a statistical experimental design. In experiments, carried out fully at 80 °C and only partly at 50 °C, no significant difference between different pollutant conditions was observed, which was most likely due to pollutant absorption into paper. This implied the assumptions, made when designing the experiment, were incorrect, and the experimental design therefore had to be discarded. This meant the experimental setup and procedure were rethought and redesigned. The results did show, however, that both chain scission and colour change are linear processes and chain scission can be evaluated using the Ekenstam equation.

7. Dynamic experiments

Following the first set of steady-state experiments, which showed no increase in degradation rates in the presence of pollutants (AcOH and NO_2) presumably due to quick absorption, another set of experiments was designed to further investigate the possible effect pollutants might have on paper degradation, as described in Chapter 5 (section 5.2).

7.1. Preliminary dynamic study

Preliminary experiments were carried out first to investigate the effects of the most abundant pollutants in an archival environment, similar to the previous Chapter (section 6.1). *DP* loss for all paper types after a week exposure to 80 °C, 43% RH and 1000 ppb of a pollutant is shown in Figure 7.1.

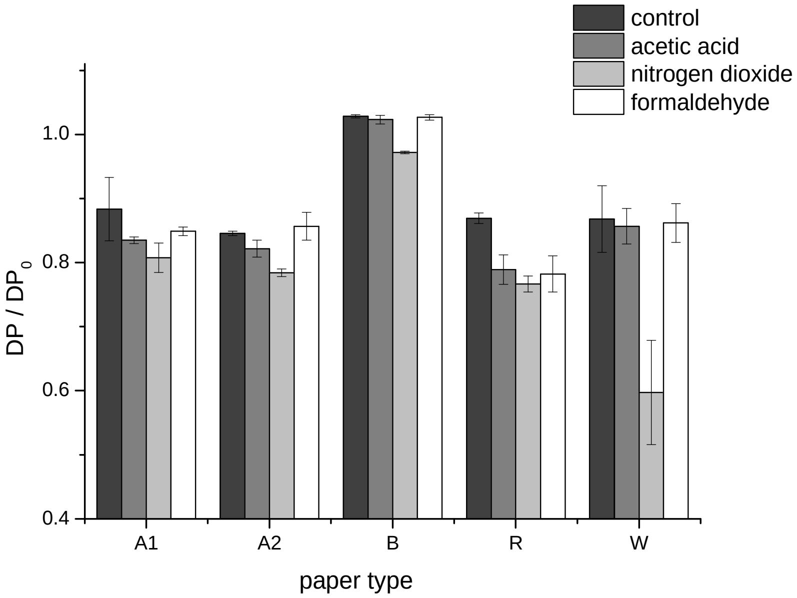


Figure 7.1: ***DP*** **before and after degradation (expressed as** ***DP/DP₀)*** **for all paper types after one week exposure to 80 °C, 43% RH and different pollutants. Error bars represent the standard error, based on three sample parallels.**

All paper types have degraded the least when not exposed to pollutants. The differences between *DP* loss for the control samples and those, exposed to pollutants, were generally not within uncertainty intervals, which indicated a significant effect. For all paper types the degradation was most pronounced for samples, exposed to

NO_2, with the *DP* loss significantly larger compared to the control. Whatman paper, exposed to NO_2, degraded significantly more compared to other paper types. Alkaline paper (B) only degraded slightly when exposed to NO_2, however no degradation was observed in any other condition. Generally, exposure to AcOH caused more degradation compared to exposure to formaldehyde, however both effects were of the same order of magnitude. Both acidic papers and rag paper behaved very similarly, being most affected by NO_2 and less affected by AcOH and HCHO.

As degradation was more pronounced in the presence of pollutants, *DP* loss results were also compared relative to the control samples (Figure 7.2).

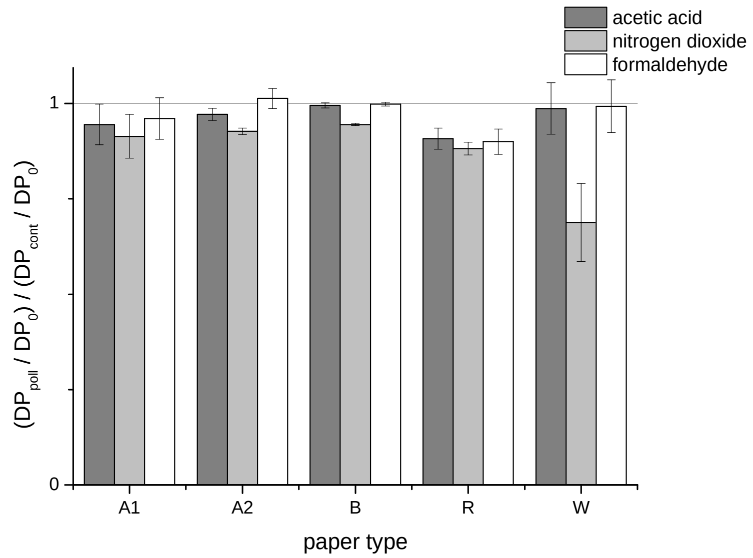


Figure 7.2: *DP* before and after degradation, relative to *DP* before and after degradation of the control sample ($DP_{pollutant}/DP_0$) / ($DP_{control}/DP_0$) for all paper types. Error bars represent the standard error, based on three sample parallels.

The horizontal gridline at $(DP_{pollutant}/DP_0) / (DP_{control}/DP_0) = 1$ represents no pollutant effect, i.e. the sample in the presence of a pollutant would degrade to the same extent as the control sample. This was the case with acidic 2, alkaline and Whatman paper exposed to formaldehyde and alkaline paper exposed to AcOH (within uncertainty intervals).

NO_2 was the most harmful pollutant regardless of the paper composition. This is not entirely surprising, as NO_2 is a good oxidant (section 3.2.) and can also react with water, adsorbed in the paper fibres, 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 would dissociate in paper easily, producing H_3O^+, which catalyse hydrolysis. AcOH had some effect on all samples, except the alkaline sample (B). Sample B presumably had enough alkaline reserve, which reacts with acids and therefore neutralises them, to not be affected by 1000 ppb AcOH. Problems with the alkaline paper may, however, occur after long term exposure, if the alkaline reserve was consumed by AcOH. Formaldehyde could be oxidised by the oxygen, present in the flasks, to form formic acid, which could consequently hydrolyse and therefore cause damage, however the exposure only seemed to affect acidic (A) and rag (R) paper.

Pollutant exposure also had some effect on the colour of samples (Figure 7.3), assessed according to CIEDE2000 (ΔE_{00}).

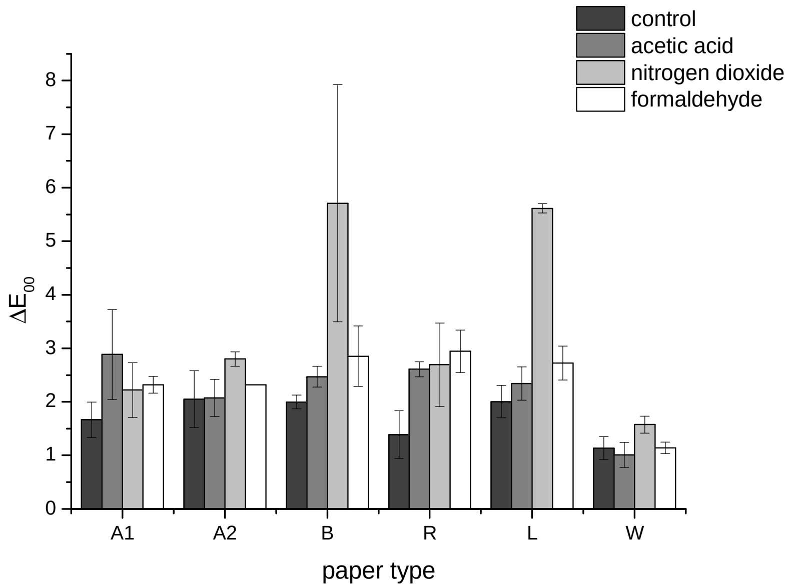


Figure 7.3 ΔE_{00} for all paper types after one week exposure to 80 °C, 43% RH and different: pollutants.

Similar to chemical properties, optical properties of the papers, exposed to NO_2, generally deteriorated the most. The change was most pronounced for lignin-containing paper, which is unsurprising, as colour change is known to be particularly pronounced in lignin-containing papers [40]. The significant colour change of lignin-containing samples, exposed to NO_2, was probably due to the presence of lignin increasing the paper's sensitivity to oxidation [59]. Alkaline paper changed colour significantly due to NO_2 exposure as well. The effects of AcOH and formaldehyde were similar and unlike the chemical properties, the colour seemed to be more affected by the presence of formaldehyde, except for acidic paper. The differences between the two pollutants are, however, fairly small and mostly within the experimental uncertainties. The colour changes were the smallest for control samples (for all real papers), indicating that pollutant exposure in this concentration range (1000 ppb) does have an effect on the colour of paper.

As could be observed from both *DP* and colour measurements, NO_2 generally causes the most damage to paper of several different compositions. It is worth noting though that AcOH concentrations in repositories and especially archival boxes are significantly higher than those of nitrous oxides, and formaldehyde concentrations are the lowest of the three [105]. Although extrapolation to room conditions is necessary, there is therefore some indication that in a real repository the effects of AcOH and NO_2 would be comparable and the effect of formaldehyde would be minimal.

7.2. Effect of pollutants at different temperatures

As NO_2 and AcOH had the most effect on *DP* decrease and colour change, they were selected for further experiments, similar to the (unsuccessful) experiments, described in the previous Chapter. The initial concentration of each was 1000 ppb. The experiments were performed at 80 °C, 70 °C and 60 °C and 43% RH. As mentioned before, the RH level was selected to be in a realistic range for Nationaal Archief (and archives in Northern Europe and Northern America), since the pollutant effect could depend on humidity as well (e.g. hydrolysis not enabled because of the absence of water or pollutant effect overpowered by the effect of a high RH).

7.2.1. Chain scission

Degradation rates were plotted as $1/DP - 1/DP_0$, following the Ekenstam equation, but were not forced through the intercept. This allows an initial faster rate, i.e. a two step mechanism, described by several authors [34-38]. Linear regressions were carried out using OriginPro 8.6 software. Regression data (line slopes and intercepts with respective standard errors) for cellulose chain scission are shown in Table 7.1.

Table 7.1: Chain scission rates at 80, 70 and 60 °C with standard errors and R^2 values. At 80 °C the experiment took 21 days, at 70 °C 69 days and at 60 °C 135 days for the control, 131 days for AcOH and 127 days for NO_2 exposure. Sampling was done 6 times in equal time intervals for samples A1, A2, B and W and 4 times for sample R.

sample	pollutant conditions	T /°C, RH /%	intercept		slope		R^2
			value	st. error	value	st. error	
A1	control	80, 43	1.38E-04	8.55E-05	1.57E-05	6.30E-06	0.51
	AcOH	80, 43	7.33E-06	5.24E-05	2.89E-05	3.82E-06	0.92
	NO_2	80, 43	2.50E-04	1.13E-04	3.03E-05	8.21E-06	0.72
	AcOH + NO_2	80, 43	8.38E-05	4.61E-05	1.99E-05	3.39E-06	0.87
A2	control	80, 43	5.74E-05	2.14E-05	1.46E-05	1.57E-06	0.94
	AcOH	80, 43	6.51E-05	2.11E-05	1.69E-05	1.54E-06	0.96
	NO_2	80, 43	5.04E-05	1.54E-05	3.55E-05	1.12E-06	1.00
	AcOH + NO_2	80, 43	1.23E-05	6.58E-05	1.62E-05	4.84E-06	0.67
B	control	80, 43	2.99E-06	5.47E-06	7.05E-07	4.03E-07	0.29
	AcOH	80, 43	-4.99E-06	6.57E-06	1.73E-06	4.79E-07	0.71
	NO_2	80, 43	-1.70E-05	1.27E-05	7.47E-06	9.26E-07	0.93
	AcOH + NO_2	80, 43	-5.45E-06	3.09E-06	1.43E-06	2.28E-07	0.89
R	control	80, 43	-4.90E-06	4.19E-05	1.25E-05	3.00E-06	0.84
	AcOH	80, 43	3.24E-05	1.34E-05	6.06E-06	9.59E-07	0.93
	NO_2	80, 43	1.69E-04	8.83E-05	8.86E-06	6.29E-06	0.25
	AcOH + NO_2	80, 43	7.04E-06	9.16E-06	1.14E-05	6.55E-07	0.99
W	control	80, 43	-6.45E-05	7.10E-05	1.68E-05	5.23E-06	0.65
	AcOH	80, 43	6.83E-05	9.47E-05	1.04E-05	6.90E-06	0.20
	NO_2	80, 43	-7.08E-05	3.95E-05	4.17E-05	2.88E-06	0.98
	AcOH + NO_2	80, 43	5.83E-05	5.14E-05	4.95E-06	3.79E-06	0.12
A1	control	70, 43	4.38E-06	8.93E-05	1.03E-05	1.92E-06	0.85
	AcOH	70, 43	-5.93E-05	1.10E-04	9.63E-06	2.39E-06	0.75
	NO_2	70, 43	1.22E-04	1.23E-04	2.34E-05	2.67E-06	0.94
A2	control	70, 43	-3.88E-05	3.02E-05	7.63E-06	6.48E-07	0.97
	AcOH	70, 43	6.02E-05	7.07E-05	5.29E-06	1.54E-06	0.68
	NO_2	70, 43	8.75E-07	9.30E-05	1.73E-05	2.02E-06	0.94
B	control	70, 43	-1.34E-05	3.73E-06	8.16E-07	8.00E-08	0.95
	AcOH	70, 43	-2.75E-06	6.12E-06	5.45E-07	1.33E-07	0.76
	NO_2	70, 43	5.32E-06	1.88E-05	2.17E-06	4.08E-07	0.84
R	control	70, 43	6.88E-05	9.43E-06	1.83E-06	1.97E-07	0.97
	AcOH	70, 43	5.51E-05	2.54E-05	1.67E-06	5.31E-07	0.75
	NO_2	70, 43	-1.81E-05	1.11E-04	9.99E-06	2.31E-06	0.85
W	control	70, 43	-1.19E-04	6.53E-05	9.05E-06	1.40E-06	0.89
	AcOH	70, 43	5.01E-05	7.68E-05	4.55E-06	1.67E-06	0.56
	NO_2	70, 43	1.55E-05	2.01E-04	2.36E-05	4.36E-06	0.85
A1	control	60, 43	7.96E-05	6.69E-05	1.81E-06	7.71E-07	0.47
	AcOH	60, 43	1.72E-04	4.11E-05	1.75E-06	4.84E-07	0.71
	NO_2	60, 43	2.65E-04	1.75E-04	9.35E-06	2.12E-06	0.79

A2	control	60, 43	6.27E-05	3.87E-05	1.28E-06	4.46E-07	0.59
	AcOH	60, 43	4.84E-05	3.01E-05	1.71E-06	3.55E-07	0.82
	NO_2	60, 43	1.01E-04	3.00E-05	6.02E-06	3.64E-07	0.98
B	control	60, 43	-9.91E-06	5.92E-06	1.97E-07	6.82E-08	0.60
	AcOH	60, 43	-2.73E-06	5.23E-06	1.19E-07	6.16E-08	0.35
	NO_2	60, 43	-2.99E-06	1.28E-05	8.84E-07	1.56E-07	0.86
R	control	60, 43	1.85E-05	2.06E-05	4.81E-07	2.19E-07	0.56
	AcOH	60, 43	1.91E-05	7.44E-06	6.69E-07	8.31E-08	0.96
	NO_2	60, 43	2.24E-04	9.87E-05	3.12E-06	1.14E-06	0.69
W	control	60, 43	-3.55E-05	4.53E-05	1.60E-06	5.22E-07	0.63
	AcOH	60, 43	3.35E-05	5.61E-05	8.23E-07	6.61E-07	0.10
	NO_2	60, 43	8.38E-05	7.07E-05	7.92E-06	8.59E-07	0.94

Acidic paper 1 was expected to be the most sensitive and prone to degradation of all six paper types, with an initial degree of polymerisation (*DP*) 560 and initial pH 5.3. The paper consists of cellulose fibres and is rosin sized, which is likely to be one of the causes of its acidity (Chapter 3, section 3.5.). Initial pH of acidic paper 2 was somewhat higher, pH = 5.6. Its initial *DP* was higher as well, i.e. 680. However, this is still considered a low *DP* value (significantly lower compared to rag or contemporary papers [1,53]). The fibre composition was different to that of acidic paper 1, as acidic paper 2 was made mainly of cotton, with about 10% of bleached cellulose pulp. The rosin content was similar to acidic paper 1, which is reflected in the paper's pH as well.

Both acidic papers degraded the most in the presence of NO_2 at all three temperatures. There were, however, some differences in the effect of AcOH. At 80 °C the chain scission rate of the A1 sample was comparable for AcOH and NO_2 exposure, although this trend was not repeated at the lower two temperatures. Initial degradation, however, was much more pronounced for the NO_2 set, which can be observed from the significantly larger intercept, which means overall more degradation occurred in the samples, exposed to NO_2. At 70 °C the chain scission rate of the A2 sample was significantly lower for the AcOH set compared to the control set. Differences between AcOH and the control for the rest of acidic papers were within uncertainty intervals.

Interestingly the combined effect of AcOH and NO_2, only investigated at 80 °C, was very small compared to individual effects of the two pollutants, with the degradation rate only somewhat higher in comparison to the rate of the control. However, as investigating different combinations of pollutants was out of the scope of this project due to instrumental limitations, the combination of both pollutants was abandoned in the following experiments. No evidence of reactions between AcOH and NO_2 at room conditions and realistic concentrations was found in the literature.

The quality of regressions expressed with R^2 values was mostly satisfactory. The highest data scatter was observed for the control sample A1 with an R^2 value of approximately 0.5 at 80 and 60 °C, but the other data sets gave better R^2 values. The data scatter was somewhat larger than expected, possibly due to inhomogeneity of real historic papers.

Taking into account the somewhat lower R^2 values for control and AcOH it could be said that both acidic papers degraded at roughly the same rate in the presence of AcOH and absence of all pollutants. The degradation process was much faster in the presence of NO_2 and the difference increased with decreasing temperature. NO_2 is known to contribute to paper degradation [4,40,99,101,117]. The increase in the rate of degradation is due to two reasons, the first being the increased acidity of paper (adsorbed NO_2 hydrolyses in water in paper, yielding nitrous and nitric acid) and the second is its oxidizing potential, although it is generally believed that oxidation is more significant for alkaline papers [26]. Generally papers with lower pH values degrade faster, so the additional decrease in pH, due to NO_2, is bound to accelerate the degradation rate. AcOH apparently does not contribute significantly to the degradation rate of acidic paper. This is possibly because the paper was already acidic before exposure to AcOH, which consequently would not dissociate significantly. The predominant mechanism in the degradation of both acidic papers is acid-catalysed hydrolysis. NO_2 contributes to acid-catalysed hydrolysis by additionally lowering the pH of paper, whereas AcOH does not seem to have that much effect.

Alkaline paper, used in the experiments, had an initial pH of 7.4 and a DP_0 of 2330, which was significantly higher compared to the previously described acidic papers. Similar to acidic paper 1 the fibre composition of alkaline paper is pure cellulose. An important difference is that it was not rosin sized and contained an alkaline reserve. Alkaline reserve is typically added to contemporary papers to reduce raw material costs [2], but it also inhibits the degradation process. It was therefore expected that the behaviour of this paper type would be somewhat different.

The chain scission rates of alkaline paper were between one and two orders of magnitude smaller compared to those of both acidic papers. Hardly any degradation occurred in the control, AcOH and both pollutants sample sets at 80 °C, so the regression lines were relatively horizontal (which is actually not regression) compared to the regression lines described above, which also explains the poorer linear fits. The control set stood out with a $R^2 = 0.3$, which was the lowest for all the rates obtained. This might make the control degradation rate unusable in further calculations.

Very little degradation occurred in the control and AcOH sets at 70 °C as well. This could also be seen from the slopes being very similar to the ones obtained at 80 °C despite a 10 °C difference, which would normally have a large effect. The qualities of regression were, however, better ($R^2 > 0.8$) compared to the ones obtained at 80 °C. Similar to the higher two temperatures the chain scission of AcOH exposure and control sets was almost negligible at 60 °C. Alkaline paper degraded the most in the presence of NO_2, the differences in the rate being almost an order of magnitude at all three temperatures.

Although alkaline papers are known for their increased stability compared to more acidic ones, the degradation process is not suspended under alkaline conditions. The degradation mechanism, however, moves from acid-catalysed hydrolysis towards autoxidation [4]. As NO_2 is a good oxidising agent it contributes to the oxidation process, therefore accelerating the degradation process. It has been shown that the presence of alkaline reserve, present in the alkaline paper used for the experiments, increases the absorption of NO_2 [97], which offers additional explanation of the increased degradation rate under NO_2 exposure. AcOH generally did not contribute to the degradation process, as additional H_3O^+ ions introduced into paper with AcOH exposure were probably neutralised by the alkaline reserve.

Two different rag samples were used in the experiments. The reason is that rag paper was only available in relatively small sheets (approximately 10 by 15 cm), whereas the rest of the samples were taken from sacrificial books, so sample consumption was not problematic. If the same rag paper was to be used in more than one experiment, only four pieces of paper could be used per flask, which meant the degradation rates were calculated using only four points instead of six. Even with sample consumption as low as possible, not all experiments could be performed on the same sheet of rag paper. Two similar rag samples were therefore selected, one for preliminary experiments and experiments at 80 °C and 70 °C and the other for the experiment at 60 °C and the following experiment at a lower RH, as described further in this Chapter (section 7.3.).

Initial pH of the first rag paper was between the values for acidic papers, 5.4. Initial *DP* on the other hand was much higher, 1850. This is typical for rag paper, which is made of cotton (or sometimes linen or hemp), producing better quality fibres compared to wood-pulp [2]. Initial pH and *DP* values of the second rag paper were somewhat lower, but an assumption was made that the two papers are similar enough to exhibit comparable degradation rates. What sets this paper type apart from the others is that it was made of rags, and probably gelatine sized (as it is common for rag papers), which was assumed to influence its properties more that a small difference in initial pH and *DP*.

Chain scission rates of rag paper were obtained using only four points, which in some cases also lead to poorer regressions. At 80 °C the chain scission rates were in the same value range as those of acidic papers. Interestingly, the rate for NO_2 exposure was actually lower compared to the control, the regression coefficient for the former, however, was very poor ($R^2 = 0.5$) and the difference between the two rates was within uncertainty intervals. Extensive initial degradation, taking place before the first sampling, was observed in the case of NO_2 exposure, but not under any other condition. Similar initial fast degradation was observed for NO_2 exposure at 60 °C, but not at 70 °C, however the uncertainty in determining the intercept at 70 °C was significant.

The chain scission rate of samples, exposed to AcOH at 80 °C, was significantly lower than the other three. At 70 °C the difference between AcOH and control rates was within uncertainty intervals and at the lowest temperature the AcOH rate was higher compared to the control, which was in disagreement with the results, obtained at 80 °C.

Generally, the chain scission rates of rag paper were lower than the ones, obtained for acidic papers, despite a similar initial pH. A significant difference between them, however, was their initial *DP* value, which was approximately 1000 units higher for rag paper, although theoretically this should not have affected the degradation rate. Rag paper is known to be of better quality and less prone to degradation compared to other paper types, and the difference partly lies in the supramolecular structure differences between cotton and wood cellulose [4]. The origin of cellulose and the processing of the raw material differ for the two types, and this affects the stability. Better stability of cotton paper compared to acidic paper, but worse compared to alkaline paper, which is ‘buffered’ by alkaline reserve, is in agreement with the findings by Adelstein et al. [99]. Based on the pH of papers used in the experiments, the prevailing mechanism was probably acid-catalysed hydrolysis. The significant effect of NO_2, however, suggests oxidation might play a role in the degradation process as well.

Whatman filter paper is made of pure cellulose with no additives. This means that the observed effects of pollutants can be attributed to reactions between pollutants and cellulose only, without any other influences. It has also been used extensively in paper degradation studies as a model paper, which is why it was also included in this study. Initial pH of the Whatman paper sample was 5.4, which is similar to rag paper and between the pH values for acidic papers. The initial *DP* was 2530 which is much higher compared to acidic papers (also due to the fact that Whatman paper samples were new and not previously naturally degraded like the two acidic samples), and more similar to modern alkaline paper. Whatman paper does not contain any sizing, fillers or other additives.

Despite the fact that Whatman paper was expected to be the most homogeneous of all the samples used (being a new model paper, not taken from a real book), which meant the best and most repeatable results were expected, the quality of regressions was the poorest and R^2 values the lowest. It was, however, still apparent that the degradation rate of the samples, exposed to NO_2, was the highest, with the difference of nearly a factor of 5 at 60 °C. Generally the chain scission rates for AcOH exposure seem lower compared to the control, however when regression line intercepts are compared it can be observed that a similar extent of degradation occurred in both sample sets at all three temperatures.

Based on the initial pH of Whatman paper it can be assumed that the predominant mechanism in the degradation of Whatman paper is acid-catalysed hydrolysis. Since Whatman paper does not contain any alkaline reserve it would be prone to changes in acidity due to pollutant exposure. NO_2 was expected to decrease the pH of paper, which would be reflected in the increase in degradation rate. Similar to previously discussed paper types AcOH did not have the same effect despite being a carboxylic acid, most likely because of the difference in pK_a values of AcOH and dissociated NO_2, HNO_3 + HNO_2. As Whatman paper, both acidic samples and rag paper were all acidic (initial pH between 5.3 and 5.6), AcOH (pK_a = 4.75) would not dissociate significantly, contributing little to lowering the paper's pH and acceleration of the degradation process. Lower pK_a values of nitric and nitrous acids, likely results of NO_2 absorption, would result in better dissociation and therefore more H_3O^+ ions contributing to acid-catalysed hydrolysis.

DP values of lignin-containing paper cannot be measured using viscometry, as lignin does not dissolve in cupriethylenediamine, the solvent used for viscometry measurements. This is why only optical properties and pH values were determined for this set of samples.

Chain scission rates at three temperatures, relative to the chain scission rate of the control sample set, are shown in Figures 7.4-7.8.

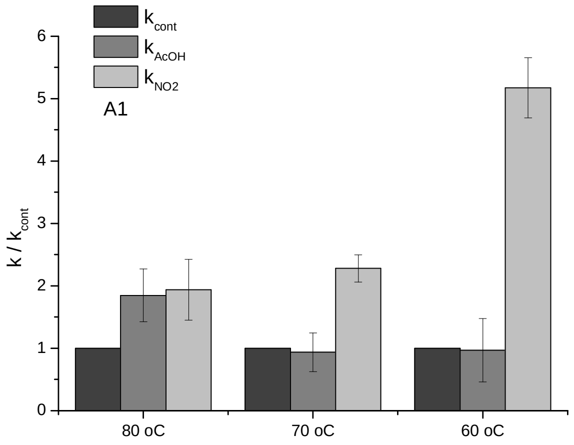


Figure 7.4: Chain scission rates of acidic paper 1 relative to the control (k/k_{cont}).

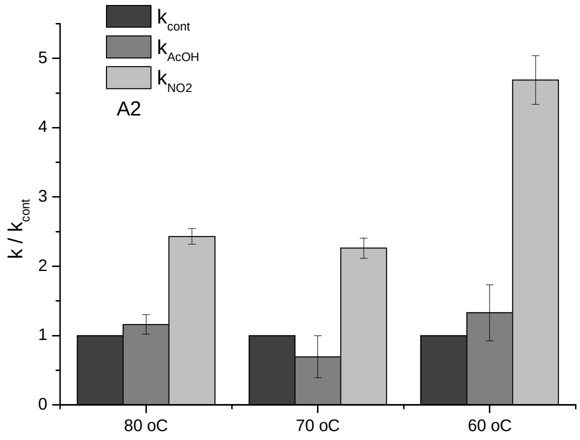


Figure 7.5: Chain scission rates of acidic paper 2 relative to the control (k/k_{cont}).

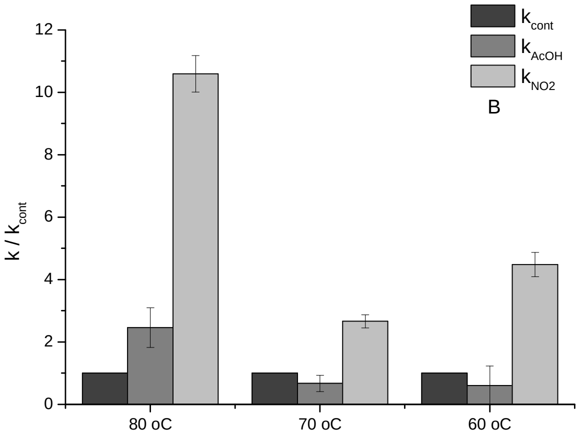


Figure 7.6: Chain scission rates of alkaline paper relative to the control (k/k_{cont}).

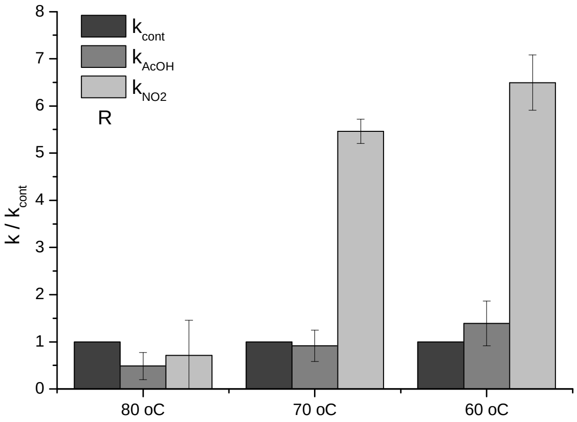


Figure 7.7: Chain scission rates of rag paper relative to the control (k/k_{cont}).

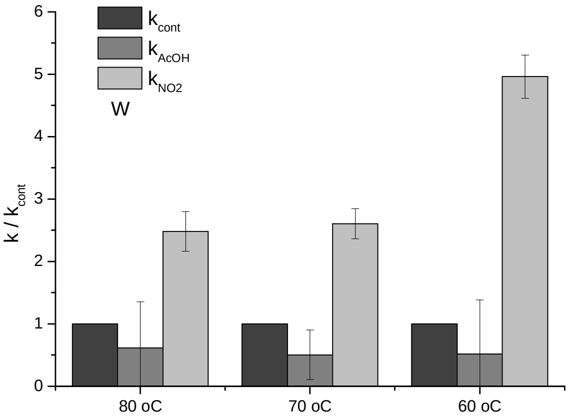


Figure 7.8: Chain scission rates of Whatman paper relative to the control (k/k_{cont}).

In terms of NO_2-induced degradation the behaviour of both acidic papers and Whatman paper is very similar. The relative effect of NO_2 increased as the temperature decreased, with the rate increasing by approximately a factor of 5 when the papers were exposed to 1000 ppb of NO_2 at 60 °C. The most likely reason for the observed temperature dependant increase is that the degradation, promoted by elevated temperature, was much slower at 60 °C compared to 80 °C, and was therefore not masking the NO_2-induced (or accelerated) degradation. If the value of one of the parameters, influencing the degradation process (in this case temperature), is decreased and the others remain unchanged (relative humidity and pollutant concentration), the relative importance of the latter is bound to increase, although NO_2 absorption could be affected by temperature as well.

Chain scission rate of acidic paper 1 was increased by the presence of AcOH only at 80 °C, and at 80 °C and 60 °C for acidic paper 2. The reason for different results at different temperatures is unknown, although the fairly large uncertainties in determining the degradation rates are likely to have contributed to this observation. No effect of AcOH was observed for Whatman paper.

Alkaline paper behaved quite differently to acidic and Whatman paper, as the same trend of NO_2 having more effect relative to the control at lower temperatures was not observed. At 60 °C the rate of chain scission of the samples exposed to NO_2 was 4-5 times higher compared to that of the control samples, which is similar to the paper types discussed above. The results at 80 °C, however, were very different. The degradation rate of the NO_2 sample set was an order of magnitude higher than the control and even the AcOH sample set had a significantly higher degradation rate compared to the control set. As mentioned before though, the degradation rates of control and AcOH samples were very small as hardly any degradation occurred at all. This makes such comparisons, similar to the other paper types, somewhat misleading, as the control chain scission rate was low and the data scatter significant. In order to observe more degradation of alkaline paper the duration of the experiment would need to be increased.

The behaviour of rag paper at 80 °C was different to any other paper type described so far. It should be stressed, however, that despite the degradation rate (i.e. the slope of the line) being lower for NO_2 than for the control set, the samples did actually degrade more during the experiment and the data scatter was significant. Significant degradation took place before the first sampling, which is apparent from the intercept of the line rather than from the slope. The NO_2 effect at the lower two temperatures was more similar to the other paper types and it increased with decreasing temperature. The trend was a bit different to the one observed for acidic and Whatman papers, where the promotion of degradation due to NO_2 seemed almost exponential. Relatively to the control experiment, NO_2 effect on rag paper did increase with decreasing temperature, but not to the same degree. Some effect of AcOH could only be observed at 60 °C. The reason might be that the effect at higher temperatures is masked by more extensive thermal degradation (if the processes are simplified to being additive), however the effect was still very small even at 60 °C.

7.2.2. Colour change

Linear regression was carried out in the same way as for chain scission, assuming linear colour change, which was established in the previous Chapter (section 6.2.) and confirmed by the results presented here. The lines were not forced through the intercept, allowing a fast initial colour change. Regression data for colour change is shown in Table 7.2.

Table 7.2: Colour change rates at 80, 70 and 60 °C with standard errors and R^2 values. At 80 °C the experiment took 21 days, at 70 °C 69 days and at 60 °C 135 days for the control, 131 days for AcOH and 127 days for NO_2 exposure. Sampling was done 6 times in equal time intervals for samples A1, A2, B, L and W and 4 times for sample R.

			intercept		**slope**		
sample	**pollutant conditions**	**T** /°C, **RH** /%	value	st. error	value	st. error	$\mathbf{R^2}$
A1	control	80, 43	5.57E-01	2.34E-01	1.04E-01	1.73E-02	0.88
	AcOH	80, 43	7.39E-01	2.99E-01	7.52E-02	2.18E-02	0.69
	NO_2	80, 43	6.78E-01	2.05E-01	1.59E-01	1.50E-02	0.96
	AcOH + NO_2	80, 43	4.08E-01	1.61E-01	9.81E-02	1.19E-02	0.93
A2	control	80, 43	4.03E-01	1.50E-01	1.21E-01	1.10E-02	0.96
	AcOH	80, 43	8.29E-01	1.53E-01	8.46E-02	1.12E-02	0.92
	NO_2	80, 43	1.19E+00	1.84E-01	1.28E-01	1.34E-02	0.95
	AcOH + NO_2	80, 43	6.36E-01	2.92E-01	1.02E-01	2.15E-02	0.81
B	control	80, 43	1.38E+00	2.73E-01	6.39E-02	2.01E-02	0.65
	AcOH	80, 43	1.36E+00	2.12E-01	6.80E-02	1.55E-02	0.79
	NO_2	80, 43	2.80E+00	1.69E+00	3.41E-01	1.23E-01	0.57
	AcOH + NO_2	80, 43	1.50E+00	1.16E-01	4.86E-02	8.57E-03	0.86
R	control	80, 43	4.20E-01	4.62E-01	1.24E-01	3.30E-02	0.81
	AcOH	80, 43	6.79E-01	3.03E-02	6.80E-02	2.16E-03	1.00
	NO_2	80, 43	1.52E+00	1.18E+00	1.48E-01	8.40E-02	0.41
	AcOH + NO_2	80, 43	2.52E-01	2.78E-01	1.06E-01	1.99E-02	0.90
L	control	80, 43	1.41E+00	2.72E-01	1.08E-01	2.00E-02	0.85
	AcOH	80, 43	2.02E+00	2.45E-01	6.51E-02	1.79E-02	0.71
	NO_2	80, 43	3.18E+00	2.01E-01	2.55E-01	1.47E-02	0.98
	AcOH + NO_2	80, 43	1.46E+00	1.93E-01	9.89E-02	1.42E-02	0.90
W	control	80, 43	5.90E-01	1.88E-01	9.15E-02	1.38E-02	0.90
	AcOH	80, 43	8.43E-01	1.55E-01	6.06E-02	1.13E-02	0.85
	NO_2	80, 43	7.43E-01	8.06E-01	2.33E-01	5.87E-02	0.75
	AcOH + NO_2	80, 43	8.11E-01	8.13E-02	5.84E-02	5.99E-03	0.95

A1	control	70, 43	3.78E-01	1.77E-01	3.67E-02	3.80E-03	0.95
	AcOH	70, 43	3.26E-01	4.13E-01	3.00E-02	8.98E-03	0.67
	NO_2	70, 43	6.94E-01	4.88E-01	8.99E-02	1.06E-02	0.93
A2	control	70, 43	5.33E-01	4.64E-01	3.69E-02	9.96E-03	0.72
	AcOH	70, 43	3.17E-01	1.72E-01	2.45E-02	3.73E-03	0.89
	NO_2	70, 43	1.08E+00	3.74E-01	6.88E-02	8.13E-03	0.93
B	control	70, 43	5.21E-01	2.04E-01	4.61E-02	4.37E-03	0.96
	AcOH	70, 43	1.28E+00	1.34E-01	1.26E-02	2.90E-03	0.78
	NO_2	70, 43	1.18E+00	1.15E+00	3.21E-01	2.51E-02	0.97
R	control	70, 43	1.05E-01	2.36E-01	3.67E-02	4.93E-03	0.95
	AcOH	70, 43	8.27E-01	3.70E-01	1.53E-02	7.74E-03	0.49
	NO_2	70, 43	7.69E-02	1.46E+00	1.27E-01	3.06E-02	0.84
L	control	70, 43	1.18E+00	1.63E-01	4.60E-02	3.49E-03	0.97
	AcOH	70, 43	9.92E-01	2.15E-01	4.84E-02	4.67E-03	0.96
	NO_2	70, 43	3.85E+00	3.69E-01	1.27E-01	8.01E-03	0.98
W	control	70, 43	6.14E-01	3.42E-01	3.51E-02	7.34E-03	0.81
	AcOH	70, 43	3.81E-01	1.95E-01	3.60E-02	4.24E-03	0.93
	NO_2	70, 43	1.08E+00	1.32E+00	1.24E-01	2.88E-02	0.78
A1	control	60, 43	1.34E-01	1.26E-01	7.04E-03	1.45E-03	0.82
	AcOH	60, 43	8.39E-01	3.35E-01	5.19E-03	3.95E-03	0.13
	NO_2	60, 43	1.21E+00	2.94E-01	2.18E-02	3.58E-03	0.88
A2	control	60, 43	4.21E-01	1.31E-01	7.57E-03	1.51E-03	0.83
	AcOH	60, 43	2.53E-01	2.89E-01	7.95E-03	3.41E-03	0.47
	NO_2	60, 43	1.47E+00	2.14E-01	2.45E-02	2.61E-03	0.95
B	control	60, 43	4.98E-01	1.07E-01	1.04E-02	1.23E-03	0.93
	AcOH	60, 43	4.49E-01	1.31E-01	1.17E-02	1.54E-03	0.92
	NO_2	60, 43	1.42E+01	4.34E+00	5.11E-02	5.27E-02	-0.01
R	control	60, 43	5.84E-01	1.00E-01	4.27E-03	1.07E-03	0.83
	AcOH	60, 43	2.34E-01	4.56E-01	8.13E-03	5.10E-03	0.34
	NO_2	60, 43	3.65E+00	8.91E-01	2.15E-02	1.03E-02	0.53
L	control	60, 43	1.33E+00	2.95E-01	8.12E-03	3.40E-03	0.49
	AcOH	60, 43	1.30E+00	2.15E-01	1.23E-02	2.53E-03	0.82
	NO_2	60, 43	5.54E+00	5.59E-01	3.77E-02	6.79E-03	0.86
W	control	60, 43	5.21E-01	2.22E-01	1.00E-02	2.56E-03	0.74
	AcOH	60, 43	7.24E-01	3.41E-01	8.80E-03	4.02E-03	0.43
	NO_2	60, 43	2.16E+00	1.28E+00	3.81E-02	1.56E-02	0.50

Similar to *DP* decrease, NO_2 had the most effect on colour change of both acidic papers. The relative contribution of NO_2 to the colour change rate was, however, smaller compared to the relative contribution to the chain scission rate. This indicates that the mechanical properties of acidic paper, influenced and represented by *DP*, are more sensitive to the oxidative and potentially acidic (if hydrolysed in water) properties of NO_2 than its optical properties (i.e. chain scission is more affected by NO_2 than colour change). AcOH and the combination of both pollutants did not contribute to the colour change of either acidic paper. The rate of colour change for AcOH exposure was in some cases even smaller than the control rate, however the differences were within uncertainty intervals. Regression coefficients were mainly satisfactory, except where the colour change was very small (<1.5 ΔE_{00} units), resulting in low colour change rates.

The effect of NO_2 on colour change of paper has been documented [4,97,99]. Non-buffered papers are more sensitive to colour change due to NO_2, which explains the increased colour change rate of acidic papers, used in these experiments. Acidity itself, however, has only a small effect on colour change [99]. Since the chain scission rate of acidic paper, exposed to NO_2, increased significantly, it can be speculated that increased colour change is the result of more degradation taking place in the NO_2 sample set. No additional colour change due to AcOH exposure was noticed, which is in agreement with the chain scission results.

Unlike chain scission, the colour change of alkaline paper was significant. If exposed to NO_2, alkaline paper exhibited pronounced yellowing and therefore overall colour change. Despite the data scatter being larger than expected ($R^2 = 0.57$), the trend of extensive colour change was apparent. For the samples, exposed to AcOH, or both pollutants, and the control set, the colour change was comparable to colour change of acidic papers and the three colour change rates were very similar at 80 °C.

At 70 °C the samples, exposed to AcOH, changed colour less than the ones not exposed to pollutants. However as this was not observed at the other two temperatures, the reason was probably experimental uncertainty. On the other hand alkaline paper, exposed to NO_2 at 70 °C, changed colour even significantly more than at 80 °C, reaching ΔE_{00} values over 20.

Interestingly initial colour change for the samples, exposed to NO_2 at 60 °C, was much larger than under any other conditions. This suggests a quick reaction in the paper, producing coloured chromophores, but not really affecting the cellulose, since no significant initial *DP* change was observed. Another explanation is the presence of an optical brightener, which could degrade in the presence of NO_2. However as the same behaviour was not observed at higher temperatures, this seems unlikely. Rapid increase in yellowness of alkaline paper, exposed to NO_2 at 25 °C and 50% RH, has been reported by Adelstein et al. [99]. After the initial extensive yellowness increase they noticed asymptotic behaviour of Δb^*, however the maximum yellowness seemed to depend on the concentration of NO_2 (concentrations between 1 and 30 ppm were used).

If alkaline reserve increases the absorption of NO_2 [97] it is not surprising that colour change was much more pronounced for alkaline paper compared to acidic and neutral paper. Generally alkaline fillers increase resistance to pollution [97], which explains the limited chemical degradation observed. NO_2 does, however, affect optical properties to a greater extent [97], which is consistent with the results, obtained from the experiments described above.

Colour changes observed in rag paper were similar to those of the acidic papers and considerably smaller when compared to the alkaline paper. The reasons are both the absence of optical brighteners, sometimes found in contemporary alkaline papers, and a similar initial colour of the samples (see $L^*a^*b^*$ values in Table 5.2, section 5.2.1.). At 80 °C the colour change rate for NO_2 exposure was not much higher compared to the other conditions, however a somewhat larger initial colour change did take place, which then lead to an overall larger colour change. There was significant scatter in the NO_2 exposure data, with $R^2 = 0.61$. AcOH and the combination of both pollutants had no effect on the colour change of rag paper, with smaller rates in comparison to the control samples. However if the intercepts are taken into account as well it can be observed that the colour change was actually similar (and very small) in all three cases. The effect of NO_2 increased at the lower two temperatures. At 60 °C the initial colour change was significantly larger for the sample set exposed to 1000 ppb NO_2. There was not much difference between samples, exposed to AcOH and the control set. The colour change rates were in fact very low, as hardly any colour change occurred at all, similar to the acidic papers.

The increase in the colour change rate due to NO_2 exposure was similar to the increase in the chain scission rate, which means no additional mechanism contributed to colour change. The difference is most likely to be due to additional cellulose degradation in the presence of NO_2.

Lignin-containing paper is known to change colour significantly during ageing and this was observed here as well. The colour change of samples, exposed to NO_2, was extensive, with ΔE_{00} values only exceeded by alkaline paper. Both initial colour change, represented by the intercept, and the rate of change were significantly higher compared to the other pollutant conditions at all three temperatures.

The effect of AcOH was not repeatable and different results were obtained at different temperatures. At 80 °C the rate was lower for the AcOH sample set compared to the control, however the initial colour change was higher, which meant the actual ΔE_{00} for the two sets were similar. There was no significant difference between the intercepts at the lower temperatures and the rates at 70 °C. At 60 °C, however, a small effect of AcOH can be observed. Similar to AcOH both pollutants combined did not have an effect on colour change of lignin-containing paper. Since this was observed in all paper types for both chain scission and colour change, which were both generally significantly affected by NO_2, it is possible that there was a systematic error somewhere in the experiment, possibly in the set-up.

Fairly high initial colour change, generally observed for lignin paper, is in agreement with the results presented by Adelstein et al. [99]. It has been shown previously that brightness of lignin-containing paper decreases faster compared to lignin-free papers during accelerated degradation in the dark [16] and it is known that lignin containing papers are generally less stable in terms of optical properties [150]. Coloured chromophores are formed during the process, for example quinones, which are thought to be responsible for the darkening of lignin [151]. Similar to alkaline fillers, described earlier in the text, lignin is thought to increase NO_2 absorption [97]. As NO_2 is already known to greatly affect the optical properties of paper, the presence of lignin would only enhance that effect, which was also confirmed by the experiments presented here.

Exaggerated concentrations of AcOH might have some effect on the colour change of lignin-containing paper, but this was only noticed at the lowest temperature. NO_2, however, contributes more to the process of colour change. In part this is due to the oxidative nature of NO_2, as pulps containing significant amounts of lignin are known to yellow due to thermal oxidation, which is likely to be increased in the presence of NO_2 [97].

The colour change of Whatman paper is interesting to study because its initial colour is white, similar to alkaline paper, but unlike modern alkaline paper it does not contain an alkaline reserve or optical brighteners, which makes it more similar to the other paper types studied. On the other hand it does not contain any other additives, such as sizing, and has not been aged prior to the experiments. These differences, however, make the applicability of the results, obtained for Whatman paper, to real papers debatable.

The colour change rate of Whatman samples, exposed to NO_2, was higher compared to the other three conditions at 80 °C or two conditions at the lower two temperatures, which was in agreement with the other paper types. An unusual curvature in the colour change rate, not observed in other paper types, was noticed for Whatman paper. The overall colour change was larger compared to acidic papers or rag paper, but not as large as the colour change of lignin or alkaline paper. This was probably due to its initial white colour, compared to yellow-brown colours of acidic and rag papers. Colour change rates of samples, exposed to AcOH or the combination of both pollutants, were approximately the same and very similar to the rate of the Whatman control sample set.

The colour change graph at 70 °C looks very similar to the one obtained for *DP* change (Figures 7.9 and 7.10), indicating a strong correlation between chemical degradation of cellulose and colour change in Whatman paper. This is in agreement with the findings of Rosenau et al. [152], where they identified primary chromophores, which originate from cellulose degradation. These were mainly dihydroxybenzoquinones, polyphenols and hydroxyacetophenones, i.e. conjugated compounds, which explains their colouration. The differences between results, obtained for Whatman paper, and those of real historic papers could therefore possibly be attributed to additives in real papers.

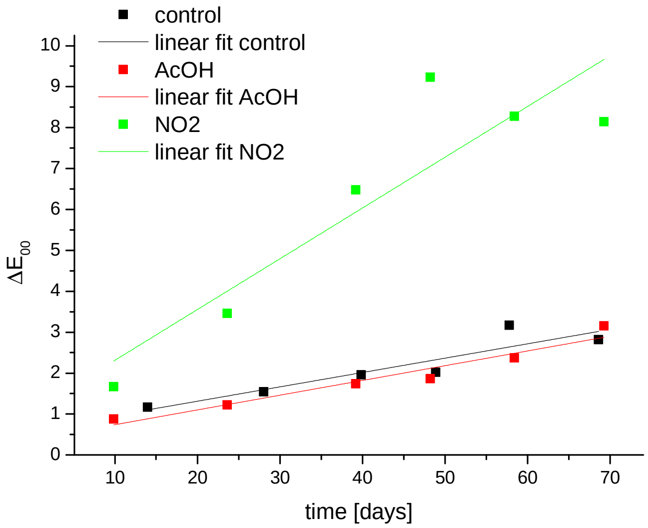


Figure 7.9: Colour change rates of paper sample W at three different conditions at 70 °C, 43% RH.

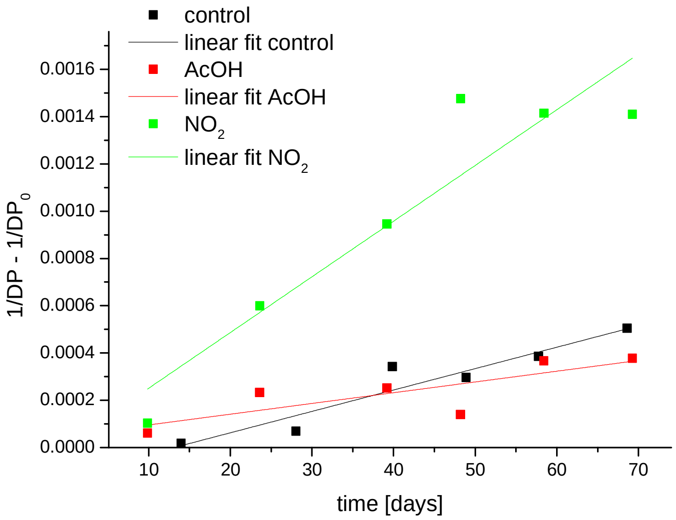


Figure 7.10: Chain scission rates of paper sample W at three different conditions at 70 °C, 43% RH.

Data scatter for Whatman paper was unusually high at 60 °C, especially for samples, exposed to 1000 ppb NO_2 ($R^2 = 0.50$). The overall colour change was comparable to that of rag paper. Acidic papers changed colour to a lesser degree, possibly due to a different initial colour, whereas alkaline and lignin-containing papers are more prone to colour change.

The increase in the rate of colour change due to NO_2 exposure was most likely the result of additional cellulose degradation, caused by NO_2. Since Whatman paper does not contain any optical brighteners, no reactions of NO_2 other than with the cellulose chains were expected. Similarly no increase in the chain scission rate due to AcOH is reflected in no increase in the rate of colour change.

Unlike for chain scission, all intercepts, obtained from colour change linear regressions, were positive. They were mostly low ($\Delta E_{00} < 1$), but were significantly increased in samples, exposed to NO_2. This was observed in nearly all paper types at all temperatures. This observation indicates that colour change in accelerated degradation experiments is a linear process only after the initial equilibration stage, where fast changes in colour occur. This is much more pronounced in the presence of NO_2.

Colour change rates at three temperatures, relative to the colour change rate of the control sample set, are shown in Figures 7.11.-7.16.

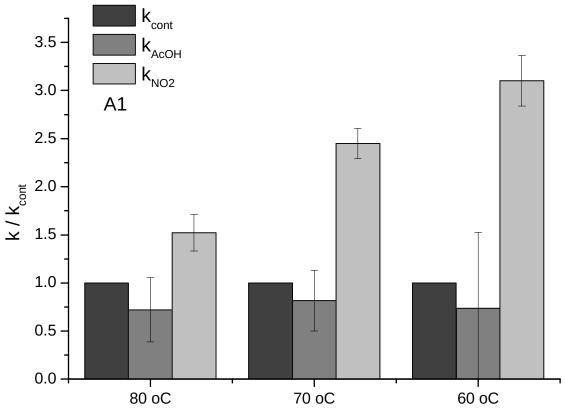


Figure 7.11: Colour change rates of acidic paper 1 relative to the control (k/k_{cont}).

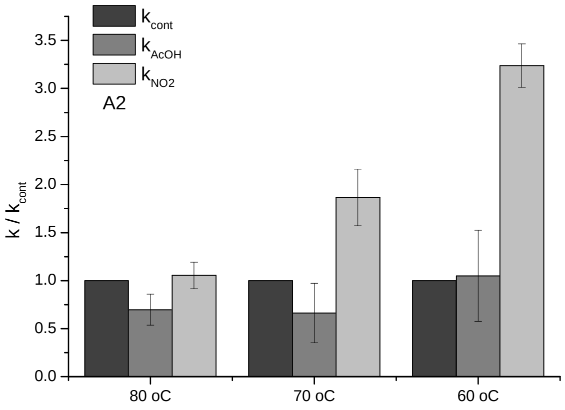


Figure 7.12: Colour change rates of acidic paper 2 relative to the control (k/k_{cont}).

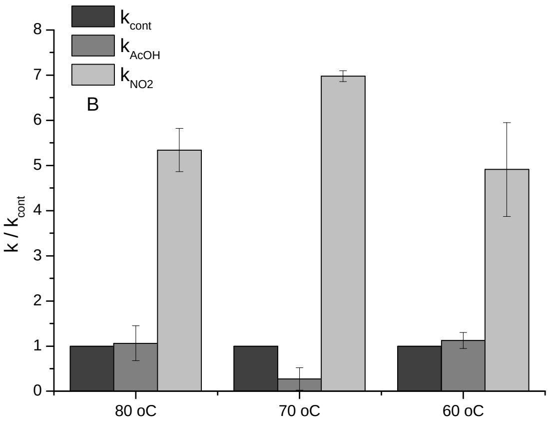


Figure 7.13: Colour change rates of alkaline paper relative to the control (k/k_{cont}).

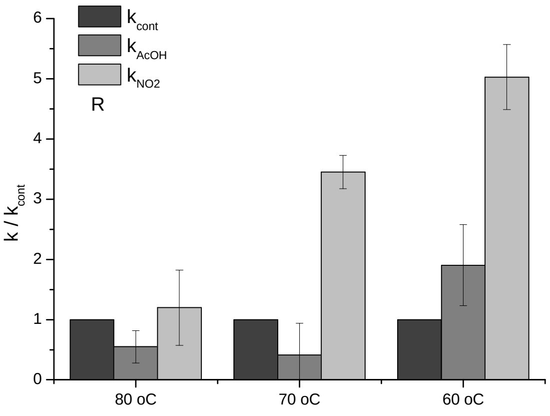


Figure 7.14: Colour change rates of rag paper relative to the control (k/k_{cont}).

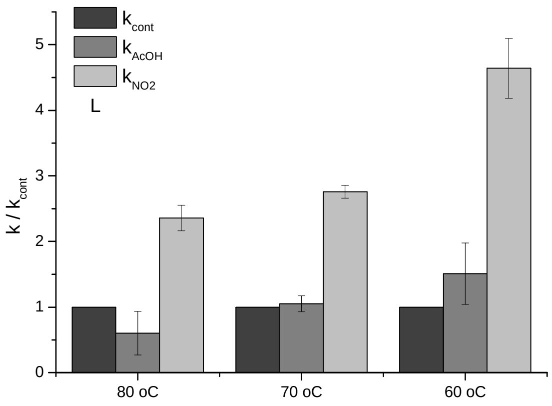


Figure 7.15: Colour change rates of lignin-containing paper relative to the control (k/k_{cont}).

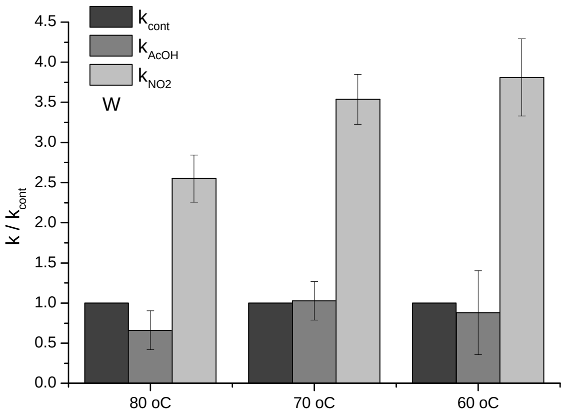


Figure 7.16: Colour change rates of Whatman paper relative to the control (k/k_{cont}).

Similar to chain scission rates the relative importance of pollutant effects on colour change rates changed with temperature, at least in the case of NO_2. The effect of NO_2 increased with decreasing temperature in an approximately linear fashion, whereas the effect on chain scission rates seemed more exponential (at least for samples A1, A2 and W). Experiments at three temperatures, however, are not enough to make solid conclusions on the linear / exponential behaviour of relative effects in temperature dependence. At 80 °C the effect of NO_2 was much less obvious, possibly due to more pronounced thermal degradation / colour change, which decreased at lower temperatures. This assumption can be made if the effect of pollutants is assumed to be additive, which is a simplification of the actual process.

As noted earlier, AcOH had no effect on colour change of most papers, the colour change rates were even marginally smaller compared to the control in some cases. This, however, was also due to data scatter, as the differences are mainly within uncertainty intervals.

The linear trend of increasing NO_2 effect with decreasing temperature, seen in most paper types, was not observed for alkaline paper. The acceleration of degradation due to NO_2 seemed independent of temperature, with the largest effect actually noticed at 70 °C. As mentioned earlier, it is possible that an additive (possibly optical brightener), used in this modern paper, reacted with NO_2, producing yellow-brown chromophores. This would be in agreement with the very limited observed chemical degradation (chain scission). These reactions do not seem to be temperature dependant, possibly because the reaction between NO_2 and the finite reservoir of sensitive molecules (i.e. optical brightener) is fast.

7.2.3. pH change

The pH of paper was expected to decrease during the degradation process [29,153]. To investigate this, the pH of unaged (i.e. artificially aged, to some degree all the papers were degraded or 'aged' before the experiment had started as real historic papers were selected for the experiments) paper samples were compared to the pH values after the experiments. The results for acidic paper 1 are shown in Figure 7.17.

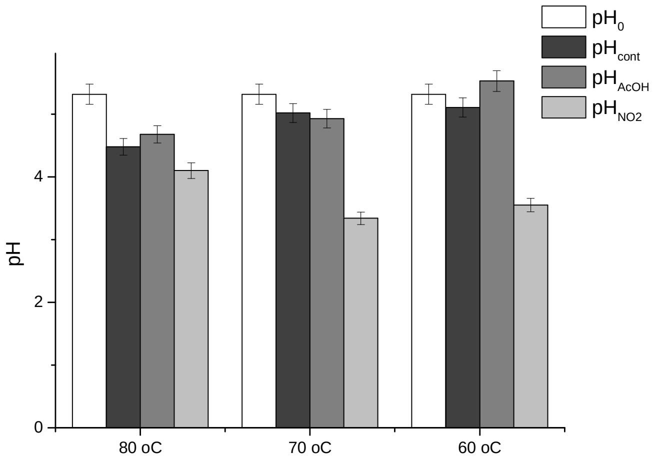


Figure 7.17: Cold extraction pH of the paper sample A1 before and after the experiments at all three temperatures.

A significant decrease in the pH of paper, exposed to 1000 ppb NO_2, was observed at all three temperatures. At the lower two temperatures the pH decreased by approximately 2 units, representing an increase in H_3O^+ concentration by two orders of magnitude. With H_3O^+ playing an important part in acid-catalysed hydrolysis, which is the predominant degradation mechanism in acidic paper, such an increase significantly affects the degradation rate [22]. This is in agreement with the results discussed earlier, where degradation rates were significantly increased in the presence of NO_2. The pH of control samples decreased as well, which was expected, as it is known that pH generally decreases during the degradation process. Unlike NO_2, AcOH did not contribute to the decrease in pH, which corresponds with a minimal contribution of AcOH to the degradation rate. It is however somewhat surprising, as the paper was directly exposed to volatile acid. The difference between pollutant-induced pH changes could be attributed to the difference in pK_a values. As mentioned before, NO_2 can form nitrous (HNO_2) and nitric (HNO_3) acid with water in paper, which both have lower pK_a values compared to AcOH (3.4, -1.4 and 4.75 respectively). This means they dissociate easier, contributing more H_3O^+ to the overall acidity. This suggests that introducing some additional AcOH into already acidic paper has a smaller effect on the H_3O^+ concentration compared to the 'background' degradation process, influenced by T and RH and represented here by the control sample set.

Although the fibre composition of acidic paper 2 is quite different to that of acidic paper 1 (acidic paper 2 was mainly made of cotton), its initial pH was only somewhat higher in comparison, so a similar behaviour was expected. Based on the degradation rate results it was expected that the pH would change the most for samples, exposed to NO_2. pH of acidic paper 2 before and after the degradation experiments are shown in Figure 7.18.

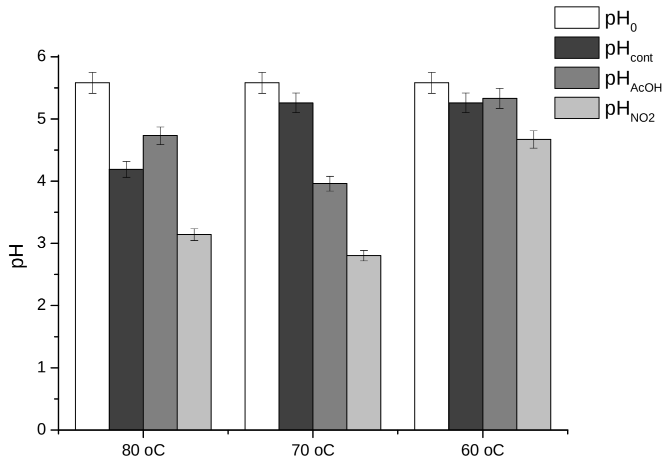


Figure 7.18: Cold extraction pH of the paper sample A2 before and after the experiments at all three temperatures.

NO_2 had the most effect on the pH of paper, in some cases the decrease due to NO_2 was even larger than for acidic paper 1. The effects at different temperatures cannot be compared, as pH is an absolute value, which depends on the duration of the experiment and the extent of degradation taking place. Such a comparison could only be made if the time was taken into account, for example by talking about rates. It is, however, interesting that the change in pH was the smallest at 60°C, as this was not the case for acidic paper 1. The effect of AcOH differed according to temperature. It ranged from a ‘positive’ (i.e. pH decreased less in the presence of AcOH than for the control) to a significant negative effect, suggesting that the difference in pH between AcOH and control samples is a consequence of a random effect rather than a repeatable result. Generally the acidity of control samples did not increase significantly, except in the experiment at 80 °C, where the difference was approximately 1 pH unit. In terms of pH change, acidic papers 1 and 2 behaved very similarly, which was a consequence of their initial pH (below 7 for both) and the absence of an alkaline reserve. Absence of AcOH effect could partly be explained by its volatility and relatively high pK_a, which meant it did not dissociate significantly in paper and could therefore desorb (evaporate) easily at elevated temperatures.

A somewhat different behaviour was expected for alkaline paper due to a significantly higher initial pH value. Results of the pH measurements are shown in Figure 7.19.

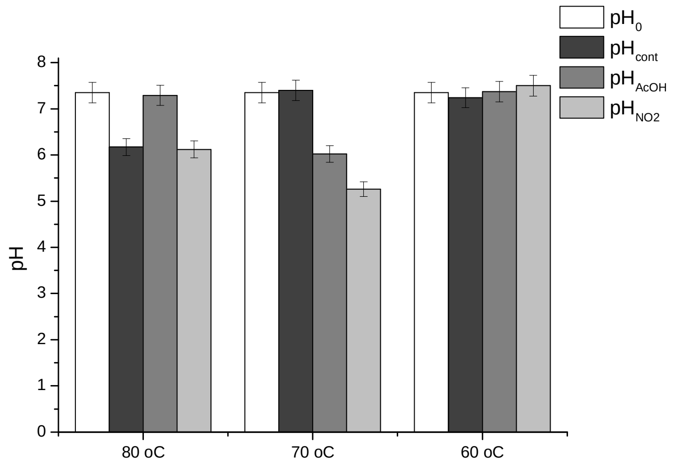


Figure 7.19: Cold extraction pH of the paper sample B before and after the experiments at all three temperatures.

The results at different temperatures differ significantly. At 60 °C there was no change in pH for any of the samples, even NO_2 had no effect. The situation was different at the higher two temperatures, where the pH of paper exposed to NO_2 decreased by 1 – 2 units. At 80 °C the pH of the control sample decreased by the same amount, indicating that the decrease was actually not pollutant related, but a product of the *T*- and RH-induced degradation process. The situation at 70 °C was again different, as the pH of the control did not change at all, whereas the pH of the samples exposed to NO_2 decreased by 2 units, pointing towards the opposite. The behaviour of samples, exposed to AcOH, was equally sporadic. At 80 °C there was no change in pH, despite the fact that the pH of control samples did decrease. At 70 °C the opposite occurred, as there was no change in the pH of the control sample, but the pH of AcOH-exposed samples did decrease. This unexpected behaviour could probably be attributed to the paper's alkaline reserve, which might not react in a uniform way or is not equally distributed in the paper (this would cause large uncertainties in pH measurements). Its behaviour might even be temperature dependant as it seems to protect alkaline paper from pH change at 60 °C, but not at higher temperatures. The alkaline reserve was not consumed entirely in all the experiments (especially at 60 °C), which means that only the slower part of the degradation process is modelled here.

Initial pH of rag paper was similar to that of acidic papers. The degradation was, however, considerably slower, which was expected to be reflected in pH change as well. Results of the measurements are shown in Figure 7.20.

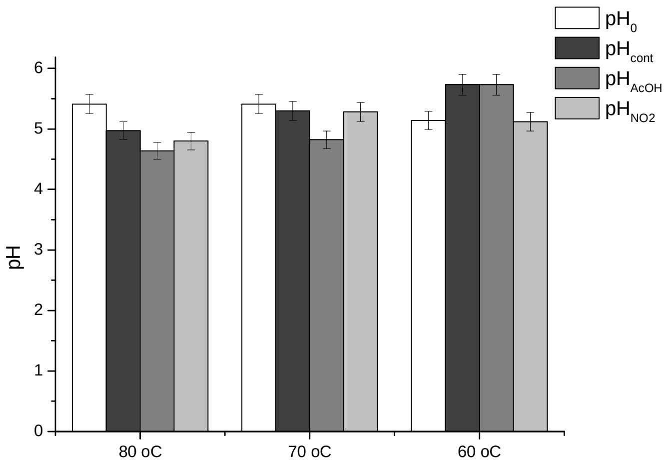


Figure 7.20: Cold extraction pH of the paper sample R before and after the experiments at all three temperatures (initial pH at 60 °C is lower because a different sheet of rag paper was used, see beginning of the Chapter).

The changes in pH were generally smaller compared to the paper types described previously, which is consistent with lower degradation rates. A trend of AcOH having some effect on paper acidity could be observed at 70 °C and 80 °C, but not at 60 °C. At 60 °C, the degradation process (regardless of pollutant presence) did not seem to have an effect on pH at all. The differences were probably due to random errors and inhomogeneity of rag paper, which is generally larger compared to the industrially made papers used in the experiments. Since the AcOH effect could be observed at two temperatures, it is possible that it was a real effect rather than just the consequence of uncertainty. However the differences between control samples and those exposed to AcOH were small and did not seem to affect degradation rates significantly, as no increase due to AcOH was observed at the two temperatures in question.

Initial pH of lignin-containing paper was 5.2, which was similar to acidic paper 1. Lignin-containing paper was also rosin-sized, containing approximately half as much sizing as the acidic papers, described earlier. The results of pH determination are shown in Figure 7.21.

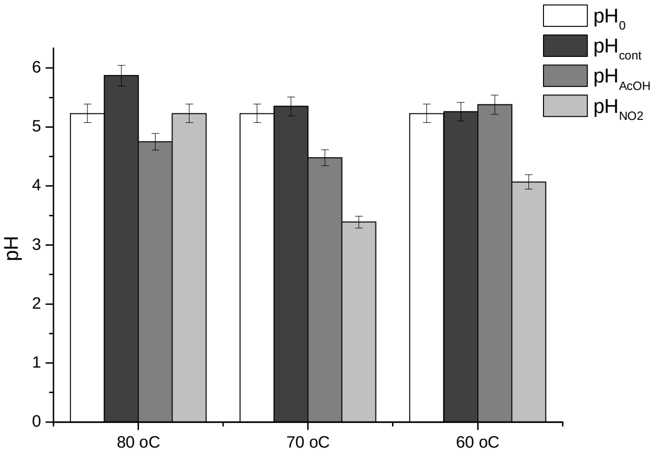


Figure 7.21: Cold extraction pH of the paper sample L before and after the experiments at all three temperatures.

No clear trend across all three temperatures could be observed. The pH of the control did not change during accelerated ageing at either of the three temperatures. This means that pH change in the presence of a pollutant would solely be a result of pollutant-related degradation. The changes observed were however not repeated at all three temperatures, so solid conclusions are difficult to make. NO_2 seemed to have some effect on the pH of lignin-containing paper, as the value decreased significantly at both 70 °C and 60 °C (although no difference was observed at 80 °C). AcOH had a small effect at 80 °C and 70 °C, but not at 60 °C. Generally it seems like the presence of pollutants did have a negative effect on the acidity of lignin-containing paper, which might contribute to the degradation process. However since the effects of NO_2 and AcOH were not observed at all temperatures, further experiments are required to understand the significance of these effects.

Whatman paper (pure cellulose) had an acidic initial pH, which was similar to acidic papers, and a high initial *DP*, similar to alkaline paper. However it did not contain any additives or alkaline reserve, so it was expected to be relatively responsive in terms of pH change. The results are shown in Figure 7.22.

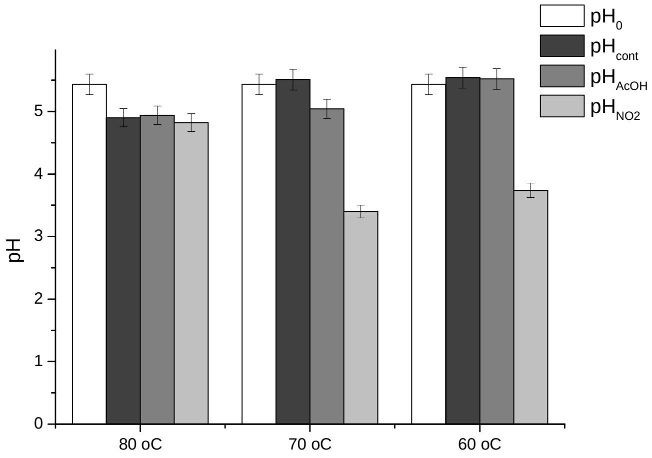


Figure 7.22: Cold extraction pH of the paper sample W before and after the experiments at all three temperatures.

Again there were some differences in the behaviour at different temperatures. Generally the unperturbed degradation process, represented by the control, did not seem to have much effect on the pH of Whatman paper, a small change in pH was only observed at 80 °C. At the highest temperature pH seemed independent of pollutant presence, as the changes were very similar for all three conditions. This was not the case at the lower two temperatures though, where a significant NO_2 effect was observed. No change in pH was observed for the control at 70 °C and 60 °C and the case of AcOH was similar, with only a small effect observed at 70 °C. The behaviour of Whatman paper was similar to that of acidic papers. A difference, however, was that very little change in the pH of the control was observed, whereas small differences in pH were observed for the other two paper types.

Whatman paper has been used extensively to study paper degradation [154]. As pure cellulose it was assumed to reflect the degradation reactions in all paper types, mostly made of cellulose, and because it is commercially produced and widely available, experiments can be repeated and results reproduced. However, how well the behaviour of Whatman paper actually mimics the behaviour of real historic paper is up for discussion, as it is now known that additives can alter the degradation behaviour of paper significantly.

A significant decrease in pH due to NO_2 at 80 °C was only observed for both acidic papers. At 70 °C the pH of all paper types except for rag paper were affected by

NO_2, and at 60 °C both rag and alkaline paper remained unchanged. As noted earlier, the results obtained at different temperatures cannot be compared directly, as the duration of the experiment might have an effect on the pH decrease as well. This is both because the same ‘extent’ of degradation did not occur at all three temperatures and because more pollutant could be absorbed in a longer period of time. Pollutant absorption could also be affected by temperature.

A limited effect of AcOH was observed, as most differences between the control samples and AcOH were not significant and not repeated at more than one temperature for most paper types. A significant effect of AcOH at both 80 and 70 °C was only observed for lignin-containing paper and to a smaller extent rag paper.

7.3. Degradation rates at a lower RH

To test the effect of RH on degradation rates, an experiment was carried out at a low RH, 21%. Chain scission rates of all paper types are shown in Table 7.3.

Table 7.3: Chain scission rates at 80 °C, 21% RH with standards errors and R^2 values. The experiment took 21 days, sampling was done 4 times in equal time intervals for samples A1, A2, B and W and 3 times for sample R.

			intercept		**slope**		
sample	**pollutant conditions**	**T** /°C, **RH** /%	value	st. error	value	st. error	R^2
A1	control	80, 21	1.94E-04	2.03E-05	1.20E-05	1.43E-06	0.96
A2	control	80, 21	1.05E-04	1.94E-05	5.19E-06	1.37E-06	0.82
B	control	80, 21	-8.16E-06	3.10E-06	1.58E-06	2.19E-07	0.94
R	control	80, 21	3.12E-05	1.01E-06	2.44E-06	6.77E-08	1.00
W	control	80, 21	3.50E-05	4.55E-05	2.08E-06	3.21E-06	-0.24

A chain scission rate can be calculated for all five samples, although very little degradation occurred for Whatman and alkaline paper (*DP* was reduced by 11% and 5% respectively, which at least for sample W is significantly less compared to previously discussed experiments). The uncertainties in the Whatman plot were significant as well, possibly due to the same reason. A comparison between chain scission rates, obtained at 21% and 43% RH and 80 °C, is shown in Figure 7.23.

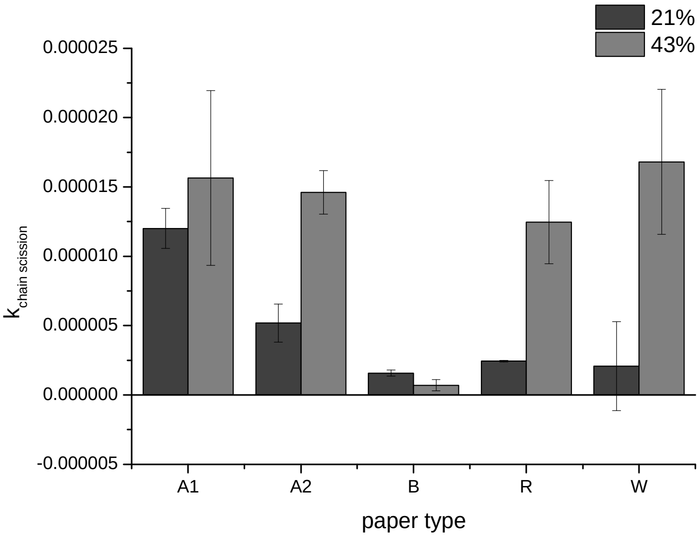


Figure 7.23: Chain scission rates at 80 °C and 21% or 43% RH (error bars represent regression uncertainties).

Chain scission rates for rag and alkaline paper were very low compared to the other paper types or even negligible at 43% RH, discussed earlier, and at the lower RH the rag, alkaline and Whatman samples did not degrade to a significant degree. The *DP* of alkaline paper decreased by only 5% and rag and Whatman paper degraded significantly less compared to the higher RH experiment, the changes could therefore mostly be attributed to measurement uncertainties. This is why the perceived difference in the rates, obtained at different RH values, is so large. Very little difference in degradation rates of Whatman paper at approximately 40 and 20% RH has also been found in the literature [26]. Realistically only the results obtained from acidic and neutral paper showed differences, significant enough to be taken into account. Compared to the degradation rates at 80 °C and 43% RH, the rates, obtained at 80 °C and 21% RH, were lower by a factor of 1.3 and 2.8 for acidic papers 1 and 2, respectively. If the two factors are averaged, a factor of 2 is obtained, suggesting an approximately linear effect of RH, which is in agreement with the results obtained using Sebera's isoperm [54]. Michalski [56], on the other hand, suggested a power law dependence of the degradation rate on the RH, proportional to $RH^{1.3}$. The average of factors for the two paper types, i.e. the linear dependence, was used in further calculations. Further work studying the effect of RH is needed, however, to verify or improve these calculations.

Colour change rates of all paper types are shown in Table 7.4.

Table 7.4: Colour change rates at 80 °C, 21% RH with standards errors and R2 values. The experiment took 21 days, sampling was done 4 times in equal time intervals for samples A1, A2, B, L and W and 3 times for sample R.

sample	pollutant conditions	T /°C, RH /%	intercept value	intercept st. error	slope value	slope st. error	R^2
A1	control	80, 21	7.73E-01	3.33E-01	-9.35E-03	2.35E-02	-0.39
A2	control	80, 21	3.79E-01	6.80E-02	2.12E-02	4.80E-03	0.86
B	control	80, 21	4.90E-01	1.79E-01	2.15E-02	1.27E-02	0.38
R	control	80, 21	3.43E-01	6.73E-03	3.12E-02	4.51E-04	1.00
L	control	80, 21	1.21E+00	8.61E-02	2.23E-02	6.08E-03	0.81
W	control	80, 21	5.16E-01	1.76E-01	2.18E-02	1.25E-02	0.41

Colour change of all but the lignin-containing paper was below 1 ΔE_{00} unit, which means it was not very significant (the average uncertainty, determined in the preliminary experiment, was 0.4 ΔE_{00} units). Because of this, data scatter was significant, which is observed in fairly low R^2 values. This was quite different to the results obtained at 43% RH, where significant colour change was observed in all paper types. This means that relative humidity does have an effect on the colour change of all paper types. A comparison between the colour change rates, obtained at 21% and 43% RH, both at 80 °C, is shown in Figure 7.24.

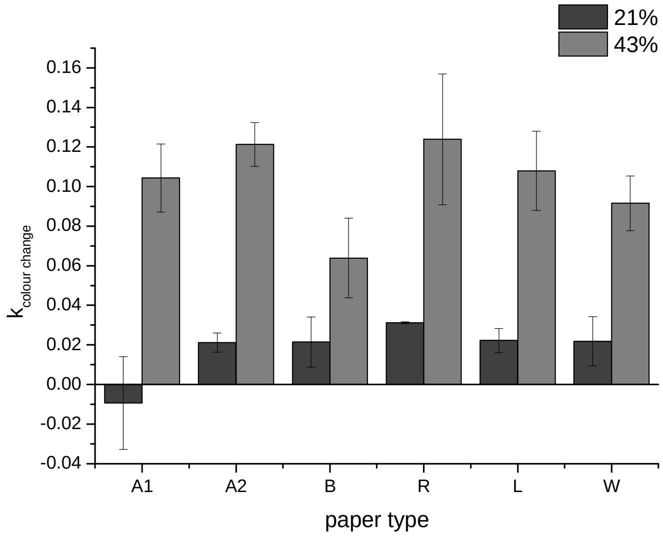


Figure 7.24: Colour change rates at 80 °C and 21% or 43% RH (error bars represent regression uncertainties).

The rates were lower compared to the ones obtained at 43% RH by on average approximate factor of 4, making colour change more RH-dependant than cellulose chain scission. Based on this experiment the effect seems quadratic, with a change in RH of 10% decreasing the rate by approximately a factor of 2. Whether the effect of RH is in fact quadratic or not, however, cannot be concluded based only on this experiment. Little information on the effect of RH on colour change was found in the literature, although a dependence suggestion was made by Michalski [56]. Similarly to the results shown here, he suggested yellowing to be more RH dependent than mechanical strength, with a power of 1.7 ($RH^{1.7}$). More research, however, is needed to understand the colour change and chain scission rate dependence on RH.

7.4. Summary of effects per paper type

Cellulose chain scission of both acidic papers is significantly affected by NO_2. NO_2 also has an effect on the colour of acidic paper, however additional increase in the degradation rate due to NO_2 is smaller for colour change than for chain scission. It should, however, also be pointed out that both acidic papers were considerably more sensitive in terms of chain scission (or DP loss) than colour change. AcOH had no significant effect on either of the processes. Both acidic papers behaved similarly in terms of pH change as well. pH of both decreased during the degradation process; this was observed in the absence of pollutants as well, which means it was a consequence of the degradation process, affected by T and RH. In the presence of NO_2 the pH decreased even more, which could be the result of both additional degradation due to NO_2 and absorption of the pollutant. Similar to chain scission and colour change AcOH had little effect on the pH of acidic paper.

The sensitivity of alkaline paper was opposite to that of acidic paper, as it was much more sensitive to colour change than chain scission. Chain scission of the control sample set and the one, exposed to AcOH, was almost negligible and measurable degradation only occurred in samples, exposed to NO_2. To an extent this can also be observed in pH results, where pH is repeatedly decreased only in the presence of NO_2 (although only at two temperatures). The reason for the paper’s stability is most likely the alkaline reserve, which reacts with acidic pollutants and possible degradation products. Alkaline reserve was probably the reason for unrepeatable pH results as well, as it might not react in a uniform way. Colour change, on the other hand, was extensive in alkaline paper, which indicates that colour change and cellulose chain scission are not necessarily related processes in this paper type and that colour change might be the result of reactions in various additives. Colour change was increased in the presence of NO_2, partly because alkaline reserve increases the absorption of NO_2, whereas AcOH had little effect on the process.

Rag paper is less sensitive to chain scission than acidic papers as well. The process was accelerated by the presence of NO_2, whereas the effect of AcOH is unclear, as the behaviour was different at different temperatures. Low chain scission rates, at least compared to acidic paper, are consistent with small changes in pH. Unusually even the presence of NO_2 did not have a significant repeatable effect on the pH of rag paper, although NO_2 did increase the degradation rate. Partly this could also be attributed to inhomogeneity of rag paper and small samples, used for pH measurements. A similar increase in the rate due to NO_2 was observed for colour change, AcOH on the other hand had little effect on the colour change of rag paper. Overall colour change of rag paper was very similar to colour change in acidic papers, mainly due to similar fibre composition, initial colour and lack of optical brighteners.

Colour change of lignin-containing paper was extensive, especially in the presence of NO_2. A small effect of AcOH on the colour change rate could only be observed at the lowest temperature, however it was not reflected in a change in pH. Overall the pH mainly decreased in the presence of NO_2, which is consistent with the other paper types. Colour change was therefore mainly the result of chromophores, related to lignin, not cellulose degradation.

Similar to acidic papers Whatman paper was very responsive to NO_2, both in terms of chain scission rate and pH decrease, which are closely related. AcOH did not have a significant effect on either, possibly because Whatman paper was acidic and AcOH therefore did not dissociate significantly. Since Whatman paper is made of pure cellulose, colour change results from reactions in cellulose (or between cellulose and a pollutant), and an observation can be made that colour change and chain scission are related processes as well (Figures 7.9 and 7.10). Similar to chain scission (and similar to all other paper types) colour change was most pronounced in the presence of NO_2, indicating a direct reaction between NO_2 and cellulose.

7.5. Uncertainty analysis

Uncertainty intervals were determined as described in Chapter 5, section 5.2.4. The calculated degradation rate uncertainties ranged from 18 to 94% (the highest uncertainty was obtained for Whatman paper), the average was 42% (Table 7.5).

Table 7.5: Overall chain scission rate uncertainties, $\Delta k/k$.

sample	80 °C	70 °C	60 °C
A1 control	0.49	0.34	0.54
A1 AcOH	0.25	0.43	0.42
A1 NO_2	0.42	0.31	0.44
A2 control	0.20	0.25	0.48
A2 AcOH	0.18	0.45	0.34
A2 NO_2	0.20	0.32	0.28
B control	0.66	0.23	0.43
B AcOH	0.41	0.42	0.66
B NO_2	0.37	0.41	0.40
R control	0.34	0.30	0.62
R AcOH	0.25	0.48	0.25
R NO_2	0.79	0.48	0.59
W control	0.40	0.32	0.45
W AcOH	0.76	0.54	0.94
W NO_2	0.24	0.40	0.33

Uncertainties for rates of colour change were determined similarly to chain scission rate uncertainties, the only difference was in the accuracy of the analytical method, where determining *DP* was replaced with colorimetry. Accuracies of both methods were determined using replicates of the same sample, which means they include the uncertainties from material composition. *DP* measurements were assessed to ±2% and colour measurements to ±1.5%. Rate uncertainties for temperature and concentration dependence were calculated separately for colour change rates.

Overall colour change rate uncertainties were somewhat smaller compared to chain scission rate uncertainties and ranged from 12 to 114% (the highest uncertainty was obtained for alkaline paper). The average rate uncertainty was 37% (Table 7.6).

Table 7.6: Overall colour change rate uncertainties, Δ*k*/*k*.

sample	80 °C	70 °C	60 °C
A1 control	0.26	0.28	0.35
A1 AcOH	0.38	0.47	0.90
A1 NO_2	0.18	0.27	0.27
A2 control	0.18	0.45	0.34
A2 AcOH	0.22	0.32	0.55
A2 NO_2	0.19	0.26	0.20
B control	0.40	0.24	0.22
B AcOH	0.31	0.38	0.23
B NO_2	0.45	0.23	1.14
R control	0.37	0.33	0.42
R AcOH	0.12	0.66	0.74
R NO_2	0.65	0.39	0.58
L control	0.28	0.25	0.55
L AcOH	0.36	0.24	0.30
L NO_2	0.14	0.21	0.29
W control	0.24	0.37	0.37
W AcOH	0.27	0.27	0.56
W NO_2	0.34	0.38	0.51

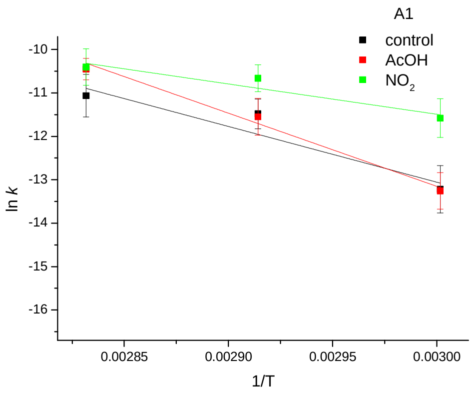
These uncertainties were applied to the Arrhenius plots, which had been created to extrapolate degradation rates from the elevated test condition temperatures to room conditions, as described in section 5.2.5.1. and in the following section.

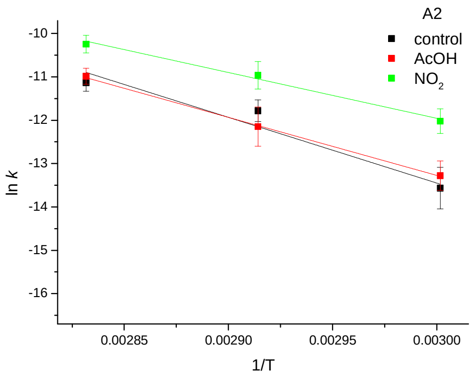
7.6. Arrhenius study

7.6.1. Chain scission

The use of the Arrhenius equation has been discussed thoroughly in the literature, as discussed in Chapter 2. The results, obtained from the experiments presented here, were therefore expected to follow this principle as well.

Arrhenius plots for chain scission rates of all papers are shown in Figure 7.25.


A1
control
AcOH
NO_2
-10
-11
-12
-13
-14
-15
-16
ln *k*
0.00285
0.00290
0.00295
0.00300
1/T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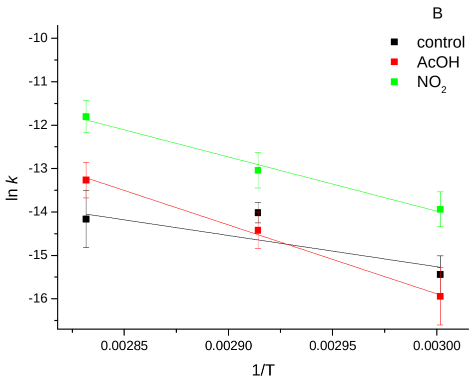
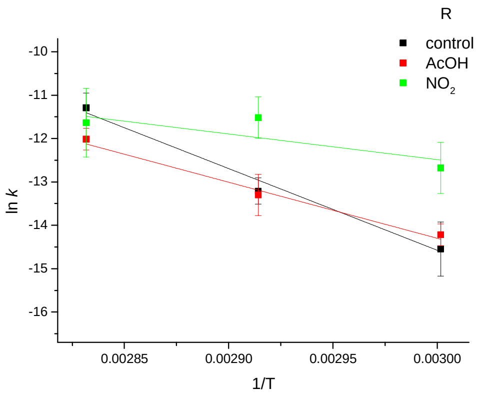
AcOH
NO_2
-10
-11
-12
-13
-14
-15
-16
ln *k*
0.00285
0.00290
0.00295
0.00300
1/T


B
control
AcOH
NO_2
-10
-11
-12
-13
-14
-15
-16
ln *k*
0.00285
0.00290
0.00295
0.00300
1/T


R
control
AcOH
NO_2
-10
-11
-12
-13
-14
-15
-16
ln *k*
0.00285
0.00290
0.00295
0.00300
1/T

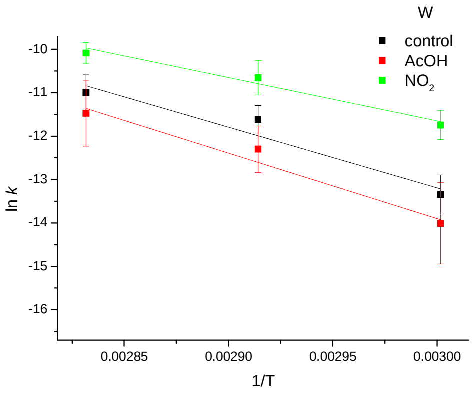


Figure 7.25: Arrhenius plot for rates of chain scission for samples A1, A2, B, R and W.

Taking into account the uncertainty intervals, the plots can be considered to be linear, making extrapolation to lower temperatures possible. The two regressions that stand out due to their poor linearity were obtained for alkaline paper in the absence of pollutants (B control) and rag paper, exposed to NO_2 (R NO_2).

For the alkaline paper the degradation rate at 70 °C was slightly higher than at 80 °C, which seems counter-intuitive. This anomaly was caused by very low (practically insignificant) degradation rates under control conditions, which was especially apparent at 80 °C. Data scatter for control samples at 80 °C was also significant, with $R^2 = 0.3$. With *DP* loss under 3% throughout the experiment, this could be expected, as such small differences are difficult, if not impossible, to determine experimentally. A slope (i.e. degradation rate), obtained under such conditions, would not adequately describe the degradation process, as not enough degradation occurred for the obtained slope to be significant. The rate at 80 °C was therefore discarded from further calculations. Another linear regression for the control set was carried out using only degradation rates, obtained at 70 and 60 °C. The difference between the two lines, obtained for the control, is significant. However in relation to the other two conditions the line obtained, using the lower two temperatures only, is in better agreement with the general degradation process (and the fact that it is generally temperature-dependent) and the results, obtained for the other samples. A steeper slope was expected for the control and that is the case if the data point, representing the rate at 80 °C is omitted. The slope and intercept of this line will therefore be used in further calculations, although unfortunately assessment of prediction uncertainties will not be possible without the standard errors (as only two points were used, standard errors could not be calculated). Ideally the omitted experiment would be repeated on a longer time-scale to allow more degradation to take place, however time limitations prevented this from taking place.

The second case of poor linearity was rag paper, exposed to NO_2. There is an apparent similarity with the control experiment plot for alkaline paper, however there are important differences. Although the point at 80 °C seems to be an outlier, it is less questionable compared to the case discussed above. R^2 of the linear regression was similar to the previously discussed control set of alkaline paper samples ($R^2 = 0.4$), however lower R^2 values were expected for rag paper, as only four instead of six data points were used to obtain degradation rates, which inevitably caused larger uncertainties. Another important difference is that significant degradation occurred in this case, as the *DP* loss throughout the experiment was 35%. This means the degradation rate, obtained for rag paper at 80 °C, was significant and therefore could not be discarded based on the poor linear fit.

Line slopes and intercepts with respective standard errors and R^2 values are shown in Table 7.7.

Table 7.7: Chain scission slopes and intercepts with standard errors, obtained by linear regression.

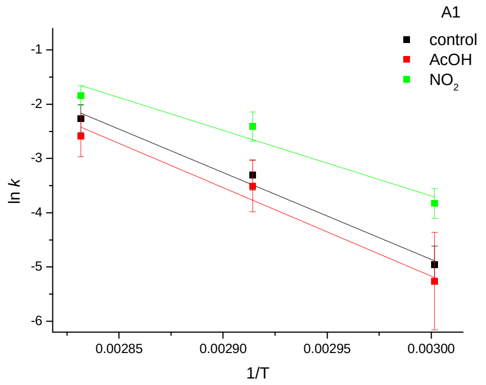
sample	conditions	slope	st. error	intercept	st. error	R^2
A1	control	-12800	3900	30	11	0.85
A1	1000 ppb AcOH	-16900	1900	40	6	0.97
A1	1000 ppb NO_2	-7000	1900	10	5	0.86
A2	control	-15200	3400	30	10	0.91
A2	1000 ppb AcOH	-13400	400	30	1	1.00
A2	1000 ppb NO_2	-10600	1100	20	3	0.98
B 60 °C, 70 °C	control	-16200	-	30	-	-
B	1000 ppb AcOH	-15900	900	30	3	0.99
B	1000 ppb NO_2	-12500	1400	20	4	0.98
R	control	-18800	2000	40	6	0.98
R	1000 ppb AcOH	-12900	1800	20	5	0.96
R	1000 ppb NO_2	-5900	3800	5	11	0.42
W	control	-14000	3200	30	9	0.90
W	1000 ppb AcOH	-15000	2300	30	7	0.95
W	1000 ppb NO_2	-10000	1800	20	5	0.94

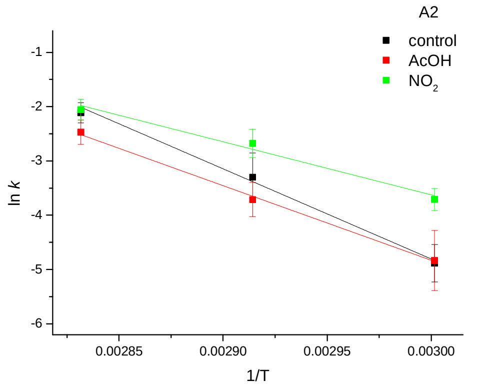
All the linear regressions, besides the two discussed above, have very high R^2 values, mostly above 0.9. The slopes for samples, exposed to NO_2, are generally less steep compared to AcOH and the control. No clear trend regarding the latter two was observed and most differences between the two were within uncertainty intervals.

7.6.2. Colour change

DP loss (cellulose chain scission), described above, was expected to follow the Arrhenius principle. On the other hand, there is no clear reason why colour change would follow the Arrhenius principle, as it can be the result of many chemical reactions taking place in paper and may involve different components of paper in different paper types, such as lignin, optical brighteners etc. It is therefore a much more complex phenomenon. Nevertheless an attempt was made to describe the process of colour change using the linearised form of the Arrhenius equation.

Arrhenius plots for colour change rates of all papers are shown in Figure 7.26.





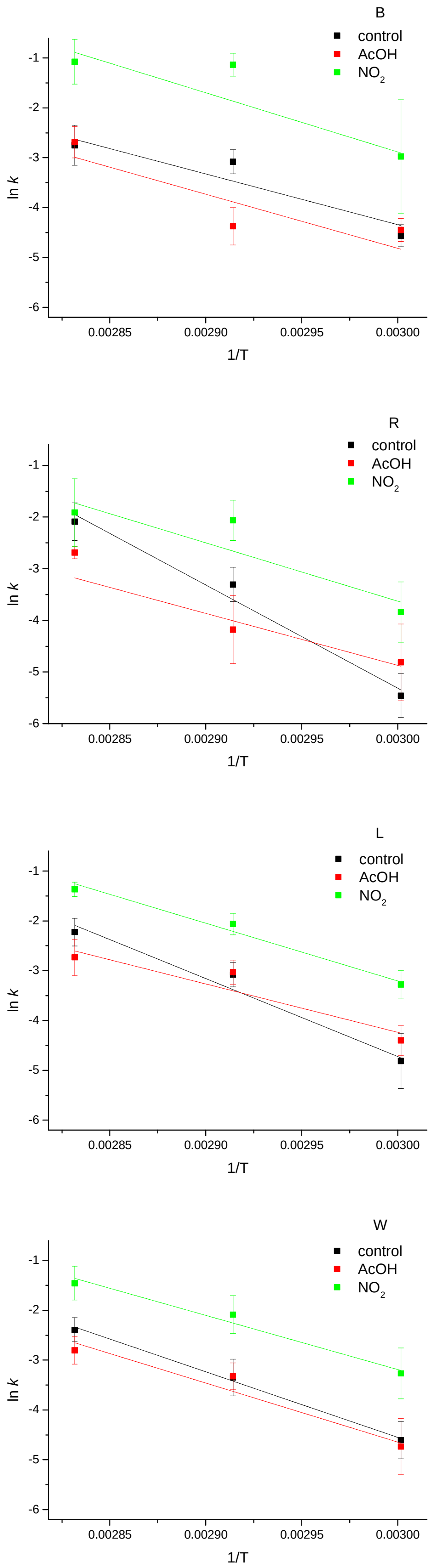


Figure 7.26: Arrhenius plot for rates of colour change for samples A1, A2, B, R, L and W.

Linearity of the plots is comparable, if not better, to that of *DP* loss Arrhenius plots. This finding suggests that activation energies for colour change can be calculated for all paper types, discussed here, and that colour change at lower temperatures can be predicted based on Arrhenius extrapolations of colour change rates.

Arrhenius plots for alkaline paper are not as good as those obtained for acidic papers 1 and 2, suggesting a more complex colour change mechanism or several different mechanisms potentially involving different components of paper, leading to colour change. This was mentioned earlier in this Chapter (section 7.2.2.), where an observation was made that colour change and chain scission do not proceed at a comparable rate in modern alkaline paper and that additives in modern paper might affect the colour change mechanism. However, unlike chain scission rates, which were very low and therefore one determination was discarded, colour change was significant. This means that although the Arrhenius regressions are poorer compared to other paper types and will result in significant prediction uncertainties, they will be used for further calculations.

More data scatter was observed in rag paper in comparison to acidic papers, especially in the case of NO_2 exposure, which will result in larger prediction uncertainties. The same was observed in Arrhenius plots for *DP* loss and can partly be explained by the fact that chain scission (and colour change) rates of rag paper were only determined from four data points instead of six, which meant they were not as well defined as the others.

As *DP* measurements cannot be carried out on lignin-containing paper, the degradation of this paper type was only evaluated in terms of colour and pH change. Colour change results are therefore the only experimental result used for this paper type to be modelled using the Arrhenius equation.

Significant data scatter was observed for both chain scission and colour change of Whatman paper. It seems, however, that this was a consequence of experimental uncertainty, as Arrhenius plots display good linearity regardless. In that sense Whatman paper is similar to the other paper types, as approximately linear plots (however some with larger uncertainties than others) were obtained for both *DP* loss and colour change of all samples.

Line slopes and intercepts with respective standard errors and R^2 values are shown in Table 7.8.

Table 7.8: Colour change slopes and intercepts with standard errors, obtained by linear regression.

sample	conditions	slope	st. error	intercept	st. error	R^2
A1	control	-16000	1800	40	5	0.98
A1	1000 ppb AcOH	-16300	2400	40	7	0.96
A1	1000 ppb NO_2	-12100	2800	30	8	0.90
A2	control	-16600	1300	50	4	0.99
A2	1000 ppb AcOH	-13700	600	40	2	1.00
A2	1000 ppb NO_2	-9800	1400	30	4	0.96
B	control	-10200	2500	30	10	0.79
B	1000 ppb AcOH	-10800	2300	30	18	0.50
B	1000 ppb NO_2	-119	3900	30	11	0.81
R	control	-20000	2700	60	8	0.96
R	1000 ppb AcOH	-10100	3400	30	10	0.79
R	1000 ppb NO_2	-11300	4500	30	13	0.72
L	control	-15600	2300	40	7	0.96
L	1000 ppb AcOH	-9700	3100	30	9	0.81
L	1000 ppb NO_2	-11600	1600	30	5	0.96
W	control	-13200	800	40	2	0.99
W	1000 ppb AcOH	-11800	2500	30	7	0.92
W	1000 ppb NO_2	-10900	1600	30	5	0.96

The regression coefficients are mainly above 0.9, with a few exceptions, discussed above (alkaline and rag paper). This means extrapolations to lower temperatures are reliable and predictions at room conditions can be made for all paper types, even lignin-containing paper, which was not assessed in terms of chain scission.

For most paper types the slopes, obtained for colour change, were steeper compared to slopes, obtained for chain scission, indicating that colour change is more temperature-dependent than chain scission. This also indicates a different reaction mechanism taking place along cellulose chain scission. The only paper type where chain scission slopes were significantly steeper than colour change was alkaline paper. Lack of temperature-dependence in colour change of contemporary alkaline paper was already discussed earlier in this Chapter (section 7.2.2.).

The slopes and their standard errors, described above, were used to calculate activation energies, described in the following section.

7.7. Activation energies

Activation energy is the measure of temperature dependence of the reaction rate, the higher the E_a, the more temperature dependent the degradation rate k. The activation energy is affected by the mechanism of the reaction, whereas the pre-exponential factor of the Arrhenius equation A is affected by humidity, pH and the physical structure of cellulose. Both E_a and A also depend on the property, measured to follow paper degradation (i.e. specific process which is being followed), paper composition and the origin of cellulose [4].

According to the linearised form of the Arrhenius equation the line slope represents activation energy, divided by the gas constant R (8.314 J/mol K).

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A. \qquad (61)$$

Activation energies and their uncertainty intervals for different samples and pollutant conditions were calculated from the slopes and their uncertainty intervals, shown in the previous section. Values, obtained for chain scission, are shown in Table 7.9.

Table 7.9: Activation energies for chain scission, obtained from the Arrhenius study (uncertainty interval for B control could not be determined as the Arrhenius slope was based on two points only).

sample	**conditions**	E_a **/kJ/mol *chain scission***
A1	control	107 ± 31
A1	1000 ppb AcOH	140 ± 16
A1	1000 ppb NO_2	58 ± 16
A2	control	126 ± 28
A2	1000 ppb AcOH	111 ± 3
A2	1000 ppb NO_2	88 ± 9
B	control	135
B	1000 ppb AcOH	132 ± 8
B	1000 ppb NO_2	104 ± 12
R	control	157 ± 17
R	1000 ppb AcOH	107 ± 15
R	1000 ppb NO_2	49 ± 31
W	control	116 ± 27
W	1000 ppb AcOH	125 ± 19
W	1000 ppb NO_2	83 ± 15

If all results were combined regardless of the paper type and experimental conditions, the average activation energy would be 109 kJ/mol, although the uncertainty interval would be extensive. Activation energies have been determined in several studies reported in the literature [4,6,22,154,155]. Experiments were carried out on different paper types (although predominantly model papers) and under different conditions, so results cannot be compared in a straightforward way. Emsley and Stevens [6] reviewed the literature to find a correlation between *DP* data and degradation kinetics for experiments, carried out between 90 and 290 °C. Data was obtained using Kraft paper (delignified wood pulp paper, consisting of almost pure cellulose with a low lignin content), paper and cotton in a variety of conditions (dry insulating oil, oil with up to 4% H_2O, air or nitrogen). Data was plotted according to the Arrhenius equation and overall activation energy was determined to be 111 ± 6 kJ/mol (95% confidence). Although the experimental results, analysed by Emsley and Stevens [6], were obtained at much higher temperatures compared to the experiments described here, on different paper types and under different environmental conditions, the agreement between the activation energies is very good, with almost identical means. Activation energies, determined by Zou et al.

[22], are in the same range, with 104 ± 3 kJ/mol determined for bleached bisulphite pulp and 111 ± 4 kJ/mol and 113 ± 5 kJ/mol for two bleached Kraft pulps. The samples they used had somewhat lower pH values compared to the ones used in the experiments described above (pH $\approx$ 4), but are comparable to the most acidic samples (acidic paper 1 and Whatman paper). The average E_a values, obtained for these two types by averaging all different conditions, are 102 and 108 respectively, which again is in good agreement with the published results. Kaminska and Shahani [4] determined a broader range of activation energies, depending on the property used to determine degradation rates, paper composition and the ageing experiment itself. Activation energies of real papers were measured by Strlič et al. [155]. They determined the E_a of acidic paper to be between 90 and 100 kJ/mol, whereas the E_a of contemporary alkaline was found to be higher, approximately 120 kJ/mol. The trend (acidic papers having a lower E_a than alkaline) is therefore similar to the results, obtained in these experiments, although the determined values were lower.

Significantly lower activation energies, determined for samples exposed to NO_2, suggest a difference in the degradation mechanism, although some authors argue that a change in the degradation mechanism would result in non-linearity of the degradation process [25], which was not observed in these experiments. The significant difference in E_a, however, could be the result of oxidative degradation due to NO_2. Typically, lower activation energies are observed for oxidation reactions and higher for hydrolyses [156], which suggests a significant contribution of oxidation to the degradation process. Oxidation is mainly thought to proceed at a significant rate in neutral or alkaline papers [26], although those were not the samples with the largest decrease in E_a. This is because the process actually measured is chain scission, not oxidation. Oxidation is usually followed by rearrangement and hydrolysis, which only then leads to chain scission. The largest activation energy decrease due to NO_2 exposure was observed in rag and acidic paper, although it should be pointed out that uncertainty intervals were significant for those two paper types as well. Since degradation in the presence of NO_2 proceeded 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 differences between activation energies determined under control conditions and AcOH exposure are mostly insignificant when uncertainty intervals are taken into account. The only significant difference can be observed for rag paper.

Activation energies so far have mostly been determined based on mechanical properties or *DP* measurements [4,6]. Since Arrhenius plots, described in the previous section, were found to be linear for colour change as well, activation energies for colour change could be calculated. Results are shown in Table 7.10.

Table 7.10: Activation energies for colour change, obtained from the Arrhenius study.

sample	conditions	E_a /kJ/mol *colour change*
A1	control	133 ± 15
A1	1000 ppb AcOH	136 ± 20
A1	1000 ppb NO_2	101 ± 24
A2	control	138 ± 10
A2	1000 ppb AcOH	114 ± 5
A2	1000 ppb NO_2	81 ± 11
B	control	85 ± 29
B	1000 ppb AcOH	90 ± 52
B	1000 ppb NO_2	99 ± 32
R	control	166 ± 22
R	1000 ppb AcOH	84 ± 28
R	1000 ppb NO_2	94 ± 38
L	control	130 ± 19
L	1000 ppb AcOH	81 ± 26
L	1000 ppb NO_2	96 ± 13
W	control	109 ± 7
W	1000 ppb AcOH	98 ± 21
W	1000 ppb NO_2	90 ± 14

If all paper types and different conditions are combined, the average activation energy yields 107 kJ/mol, however the uncertainty interval is inevitably extensive. An interesting finding is that there is no significant difference between the average activation energies, determined for *DP* loss and colour change, which is in agreement with results by Strlič et al. [155], although their E_a values were lower, similar to chain scission discussed above. This means the colour change E_a, determined here, is also in good agreement with the values, reported in the literature.

Similar to the activation energies determined for chain scission, the ones determined for colour change in the presence of NO_2 are significantly lower compared to the control conditions, although the difference is smaller in colour change E_a, compared to chain scission E_a, for most paper types. This suggests an additional reaction mechanism responsible for colour change, possibly nitration of cellulose. Considering the E_a values for chain scission and colour change are similar, the two processes could be related. This was observed for all paper types except contemporary alkaline paper, where activation energies determined under all three conditions were within the same range (taking into account calculation uncertainties). A significant difference between activation energies, determined under control conditions and exposure to AcOH, can be observed for neutral, rag, lignin and Whatman paper, where E_a under AcOH exposure was consistently lower.

7.8. Extrapolation of degradation rates to room conditions

7.8.1. Room temperature

Arrhenius plots, described above, were used to predict degradation rates at 18 °C, as described in Chapter 5, section 5.2.5.1. Rate minima and maxima are shown due to asymmetrical uncertainty intervals. Degradation rates in terms of chain scission at 18 °C and 43% RH are shown in Table 7.11.

Table 7.11: Predicted chain scission rates at 18 °C, extrapolated from Arrhenius plots.

sample	conditions	$k_{DP\mathrm{min}}$ /day^{-1}	$k_{DP\mathrm{max}}$ /day^{-1}	k_{DP} /day^{-1}
A1	control	1.2E-09	5.4E-08	8.1E-09
A1	1000 ppb AcOH	4.8E-10	3.4E-09	1.3E-09
A1	1000 ppb NO_2	1.9E-07	1.3E-06	4.9E-07
A2	control	3.8E-10	1.0E-08	2.0E-09
A2	1000 ppb AcOH	4.2E-09	6.2E-09	5.1E-09
A2	1000 ppb NO_2	3.8E-08	1.1E-07	6.5E-08
B	control	1.7E-10	1.7E-10	1.7E-10
B	1000 ppb AcOH	8.0E-11	2.0E-10	1.3E-10
B	1000 ppb NO_2	1.8E-09	7.6E-09	3.7E-09
R	control	4.8E-11	3.5E-10	1.3E-10
R	1000 ppb AcOH	8.8E-10	5.7E-09	2.2E-09
R	1000 ppb NO_2	4.0E-08	2.1E-06	2.9E-07
W	control	8.3E-10	2.2E-08	4.3E-09
W	1000 ppb AcOH	4.0E-10	4.3E-09	1.3E-09
W	1000 ppb NO_2	4.6E-08	2.8E-07	1.1E-07

Colour change rates, extrapolated to 18 °C are shown in Table 7.12.

Table 7.12: Predicted colour change rates at 18 °C, extrapolated from Arrhenius plots.

sample	conditions	$k_{\Delta Emin}$ /day^{-1}	$k_{\Delta Emax}$ /day^{-1}	$k_{\Delta E}$ /day^{-1}
A1	control	3.0E-06	1.8E-05	7.4E-06
A1	1000 ppb AcOH	1.5E-06	1.5E-05	4.7E-06
A1	1000 ppb NO_2	3.1E-05	5.5E-04	1.3E-04
A2	control	3.2E-06	1.1E-05	6.0E-06
A2	1000 ppb AcOH	1.5E-05	2.8E-05	2.0E-05
A2	1000 ppb NO_2	1.9E-04	7.6E-04	3.8E-04
B	control	2.4E-05	1.0E-03	1.6E-04
B	1000 ppb AcOH	2.7E-06	2.0E-03	7.3E-05
B	1000 ppb NO_2	4.9E-05	2.1E-03	3.2E-04
R	control	2.1E-07	3.3E-06	8.4E-07
R	1000 ppb AcOH	1.9E-05	5.1E-04	9.7E-05
R	1000 ppb NO_2	1.9E-05	2.1E-03	2.0E-04
L	control	3.1E-06	3.1E-05	9.9E-06
L	1000 ppb AcOH	4.2E-05	1.1E-03	2.1E-04
L	1000 ppb NO_2	1.2E-04	5.8E-04	2.6E-04
W	control	2.3E-05	5.3E-05	3.5E-05
W	1000 ppb AcOH	1.6E-05	1.9E-04	5.6E-05
W	1000 ppb NO_2	1.6E-04	8.4E-04	3.7E-04

These degradation rates were used for further calculations, described in the following section.

7.8.2. Realistic pollutant concentrations

Degradation rate minima and maxima, described in the previous section, were used to calculate uncertainty intervals of interpolated rates. Interpolations were made across two orders of magnitude and rates were calculated for pollutant concentrations of 10 and 100 ppb using the calculation, described in Chapter 5, section 5.2.5.2. The rates, determined using the described method, take into account both pollutant-induced degradation and ‘background’ degradation, caused by temperature and RH. Chain scission rates, interpolated to lower concentrations, are shown in Tables 7.13 and 7.14.

Table 7.13: Chain scission rates at 100 ppb, /day^{-1}.

sample	$k_{100\ AcOH}$	$k_{100\ AcOH\ min}$	$k_{100\ AcOH\ max}$	$k_{100\ NO2}$	$k_{100\ NO2\ min}$	$k_{100\ NO2\ max}$
A1	7.4E-09	1.1E-09	4.9E-08	5.7E-08	2.0E-08	1.8E-07
A2	2.3E-09	7.6E-10	9.9E-09	8.3E-09	4.1E-09	2.0E-08
B*	1.7E-10	1.6E-10	1.8E-10	5.3E-10	3.4E-10	9.1E-10
R	3.4E-10	1.3E-10	8.9E-10	2.9E-08	4.0E-09	2.1E-07
W	4.0E-09	7.8E-10	2.0E-08	1.5E-08	5.3E-09	4.8E-08

*control rate for B sample was calculated using data from 60 and 70 °C, see section 7.5.1.

Table 7.14: Chain scission rates at 10 ppb, /day^{-1}.

sample	$k_{10\ AcOH}$	$k_{10\ AcOH\ min}$	$k_{10\ AcOH\ max}$	$k_{10\ NO2}$	$k_{10\ NO2\ min}$	$k_{10\ NO2\ max}$
A1	8.0E-09	1.2E-09	5.3E-08	1.3E-08	3.1E-09	6.6E-08
A2	2.0E-09	4.2E-10	1.0E-08	2.6E-09	7.5E-10	1.1E-08
B*	1.7E-10	1.7E-10	1.7E-10	2.1E-10	1.9E-10	2.5E-10
R	1.5E-10	5.7E-11	4.1E-10	3.0E-09	4.5E-10	2.1E-08
W	4.3E-09	8.2E-10	2.2E-08	5.4E-09	1.3E-09	2.5E-08

*control rate for B sample was calculated using data from 60 and 70 °C, see section 7.5.1.

The same assumptions were made for colour change and interpolations were therefore made in the same way. Colour change rates interpolated to lower concentrations are shown in Tables 7.15 and 7.16.

Table 7.15: Colour change rates at 100 ppb, /day^{-1}.

sample	$k_{100\ AcOH}$	$k_{100\ AcOH\ min}$	$k_{100\ AcOH\ max}$	$k_{100\ NO2}$	$k_{100\ NO2\ min}$	$k_{100\ NO2\ max}$
A1	7.1E-06	2.9E-06	1.8E-05	2.0E-05	5.8E-06	7.1E-05
A2	7.5E-06	4.4E-06	1.3E-05	4.3E-05	2.2E-05	8.7E-05
B	1.5E-04	2.2E-05	1.1E-03	1.7E-04	2.6E-05	1.1E-03
R	1.0E-05	2.0E-06	5.4E-05	2.0E-05	2.1E-06	2.1E-04
L	3.0E-05	7.0E-06	1.4E-04	3.5E-05	1.5E-05	8.6E-05
W	3.7E-05	2.2E-05	6.7E-05	6.8E-05	3.7E-05	1.3E-04

Table 7.16: Colour change rates at 10 ppb, /day^{-1}.

sample	$k_{10\ AcOH}$	$k_{10\ AcOH\ min}$	$k_{10\ AcOH\ max}$	$k_{10\ NO2}$	$k_{10\ NO2\ min}$	$k_{10\ NO2\ max}$
A1	7.3E-06	3.0E-06	1.8E-05	8.6E-06	3.3E-06	2.3E-05
A2	6.2E-06	3.3E-06	1.1E-05	9.8E-06	5.1E-06	1.9E-05
B	1.6E-04	2.3E-05	1.0E-03	1.6E-04	2.4E-05	1.0E-03
R	1.8E-06	4.0E-07	8.3E-06	2.8E-06	4.0E-07	2.4E-05
L	1.2E-05	3.5E-06	4.2E-05	1.2E-05	4.3E-06	3.7E-05
W	3.5E-05	2.3E-05	5.5E-05	3.8E-05	2.4E-05	6.1E-05

As the uncertainty intervals for degradation rates used to interpolate degradation rates were asymmetrical, the obtained rates have asymmetrical uncertainty intervals as well. Chain scission and colour change rates, extrapolated to room temperature and interpolated to realistic concentrations, were used to estimate the remaining useful lifetimes, described in the next Chapter.

7.9. Conclusion

Dynamic preliminary experiments gave similar results to steady-state preliminary experiments, NO_2 and AcOH were therefore selected for further experiments at three temperatures. Degradation rates at 80, 70 and 60 °C for both chain scission and colour change of all six paper types were determined and their uncertainty intervals calculated. Degradation rates were significantly higher for samples, exposed to NO_2, but there was no significant difference between degradation rates obtained for AcOH and the control. This was the case for both chain scission and colour change. Degradation rates differed significantly according to paper type, e.g. chain scission rates of acidic paper were significantly higher compared to alkaline paper, whereas the opposite was observed for colour change rates. The rates and their uncertainty intervals were then used to create Arrhenius plots and calculate activation energies. Activation energies differed according to paper type and were significantly lower in the presence of NO_2, suggesting that oxidation plays a noticeable role in paper degradation, in addition to acid-catalysed hydrolysis.

Arrhenius plots were used for degradation rate extrapolations to room conditions and interpolations to realistic pollutant concentrations were carried out. A new approach was introduced for determining degradation rates at realistic pollutant concentrations, where the effects of T and RH are additionally taken into account. This meant that degradation rates for five historic paper types and one model paper (pure cellulose) at realistic archival conditions were determined and could be used for lifetime predictions, described in the following Chapter.

8. Discussion

Degradation rates at realistic environmental conditions were obtained for five representative historic papers and one model paper. They were used to predict the degradation of different paper types under different environmental conditions (different *T*, RH or pollutant concentrations), which forms the basis of the following discussion.

8.1. Remaining lifetime of paper

Handling and display lifetimes were defined as described in Chapter 5 (section 5.3.). Handling and display lifetimes are likely to be significantly different for some paper types, e.g. contemporary alkaline paper containing optical brighteners is prone to colour change, however, it is known to be very stable in terms of *DP* loss [1]. On the other hand, acidic paper is known to be sensitive in terms of its mechanical properties, but might not be as sensitive in terms of colour change.

Uncertainties, obtained from linear regression, described in the Chapter 5 (section 5.2.5.1.), were used to calculate uncertainties in lifetime predictions. To demonstrate the magnitude of prediction uncertainties, handling and display lifetimes with uncertainty intervals at 18 °C and 43% RH are shown in Tables 8.1 and 8.2. Pollutant concentrations in these predictions are 1000 ppb, the same as used in the experiments.

Table 8.1: Predicted handling lifetimes at 18 °C and 43% RH.

sample	conditions	t_{hand} /yr	$t_{hand\ min}$ /yr	$t_{hand\ max}$ /yr
A1	control	520	78	3476
A1	1000 ppb AcOH	3283	1244	8662
A1	1000 ppb NO_2	9	3	22
A2	control	2590	495	13563
A2	1000 ppb AcOH	1006	822	1231
A2	1000 ppb NO_2	79	46	135
B	control	45848	45848	45848
B	1000 ppb AcOH	62693	39680	99054
B	1000 ppb NO_2	2145	1050	4381
R	control	61759	22865	166816
R	1000 ppb AcOH	3589	1411	9132
R	1000 ppb NO_2	28	4	201
W	control	1785	344	9269
W	1000 ppb AcOH	5846	1772	19288
W	1000 ppb NO_2	67	27	167

Table 8.2: Predicted display lifetimes at 18 °C and 43% RH.

sample	conditions	t_{disp} /yr	$t_{disp\ min}$ /yr	$t_{disp\ max}$ /yr
A1	control	5581	2284	13639
A1	1000 ppb AcOH	8646	2671	27992
A1	1000 ppb NO_2	316	75	1328
A2	control	6808	3624	12792
A2	1000 ppb AcOH	2018	1486	2741
A2	1000 ppb NO_2	108	54	217
B	control	262	40	1733
B	1000 ppb AcOH	566	21	15404
B	1000 ppb NO_2	128	20	834
R	control	48878	12357	193346
R	1000 ppb AcOH	424	81	2215
R	1000 ppb NO_2	209	20	2207
L	control	4155	1313	13155
L	1000 ppb AcOH	193	38	989
L	1000 ppb NO_2	156	71	343
W	control	1181	772	1806
W	1000 ppb AcOH	732	215	2493
W	1000 ppb NO_2	112	49	256

Although uncertainty intervals are significant, the results were not rounded up due to the asymmetrical nature of the uncertainties, which is the consequence of symmetrical regression uncertainties in the logarithmic degradation rate calculations. 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 [48,157]. 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. Using the Arrhenius model is also still the best available method for determining low-T degradation rates.

As the pollutant concentrations in the two tables above are much higher than they would be in realistic conditions, lifetime predictions were made for lower concentrations, using interpolated degradation rates. Realistic concentrations, 100 ppb AcOH and 10 ppb NO_2, were used. Handling lifetimes are shown in Table 8.3, uncertainty intervals for each predicted lifetime will be shown later in the text.

Table 8.3: Predicted handling lifetimes at 18 °C and 43% RH. Lifetimes, predicted for realistic pollutant concentrations and a pollutant-free environment and are shown in bold.

sample	**$t_{handling}$ /year**			
	c_{poll} = 1000 ppb	c_{poll} = 100 ppb	c_{poll} = 10 ppb	c_{poll} = 0 ppb
A1 control	-	-	-	**520**
A1 AcOH	3283	**568**	525	-
A1 NO_2	9	74	**325**	-
A2 control	-	-	-	**2590**
A2 AcOH	1006	**2238**	2550	-
A2 NO_2	79	619	**1965**	-
B control	-	-	-	**45848**
B AcOH	62693	**47114**	45972	-
B NO_2	2145	15092	**38086**	-
R control	-	-	-	**61759**
R AcOH	3589	**23566**	53146	-
R NO_2	28	277	**2660**	-
W control	-	-	-	**1785**
W AcOH	5846	**1918**	1797	-
W NO_2	67	502	**1422**	-

Predicted lifetimes are expected to increase as pollutant concentrations are decreased. For AcOH exposure, however, the opposite can be observed for acidic, alkaline and Whatman paper. The reason for that is not an actual positive effect of AcOH, but prediction uncertainty due to the experimental uncertainties. In those three cases the samples exposed to AcOH degraded somewhat less than the control samples, which resulted in lower degradation rates, although the differences were very small and in most cases hardly significant (as discussed in the previous Chapter, section 7.2.1.). When interpolations to lower pollutant concentrations are made, this results in a negative factor in the concentration article of the equation, resulting in a seemingly 'positive' effect of a higher concentration. The effect of AcOH at 1000 ppb is significant in the case of acidic paper 2 and rag paper, although when extrapolated to realistic conditions (100 ppb) the effect becomes insignificant at least for the A2 sample. The lifetime of rag paper would still be shortened by 100 ppb AcOH, although the prediction is still several millennia, so this is realistically of little concern [158].

The effect of NO_2 is more extensive, although it decreases significantly when extrapolated to lower concentrations. At 10 ppb a significant effect can only really be observed for acidic paper 1 and rag paper, although the predicted lifetime of rag paper is again several millennia. Significance of the differences in predicted lifetimes will be discussed later in the text.

Display lifetimes are shown in Table 8.4.

Table 8.4: Predicted display lifetimes at 18 °C and 43% RH. Lifetimes, predicted for realistic pollutant concentrations and a pollutant-free environment and are shown in bold.

	$t_{display}$ /year			
sample	c_{poll} = 1000 ppb	c_{poll} = 100 ppb	c_{poll} = 10 ppb	c_{poll} = 0 ppb
A1 control	-	-	-	**5581**
A1 AcOH	8646	**5786**	5601	-
A1 NO_2	316	2092	**4783**	-
A2 control	-	-	-	**6808**
A2 AcOH	2018	**5502**	6650	-
A2 NO_2	108	945	**4202**	-
B control	-	-	-	**262**
B AcOH	566	**277**	264	-
B NO_2	128	237	**260**	-
R control	-	-	-	**48878**
R AcOH	424	**3934**	22814	-
R NO_2	209	2009	**14666**	-
L control	-	-	-	**4155**
L AcOH	193	**1363**	3449	-
L NO_2	156	1167	**3308**	-
W control	-	-	-	**1181**
W AcOH	732	**1113**	1174	-
W NO_2	112	605	**1078**	-

Display lifetimes in a pollutant-free environment are several millennia for all, except for the alkaline and Whatman paper. AcOH only has some effect on rag and lignin-containing paper, although similar to handling lifetime the display lifetime of rag paper is several millennia even at 100 ppb AcOH. Lignin-containing paper at the same conditions would reach a lifetime of over 1000 years. Although it initially seems like NO_2 has a significant effect, the effect decreases at lower concentrations. At 10 ppb very little effect can be observed, even the effect on alkaline paper, which has the shortest predicted lifetime, is insignificant. Some effect at 10 ppb can be observed for most paper types, although their predicted lifetimes are several millennia even in the presence of NO_2.

Handling and display lifetimes of all paper types with uncertainty intervals are shown in Figures 8.1 – 8.6.

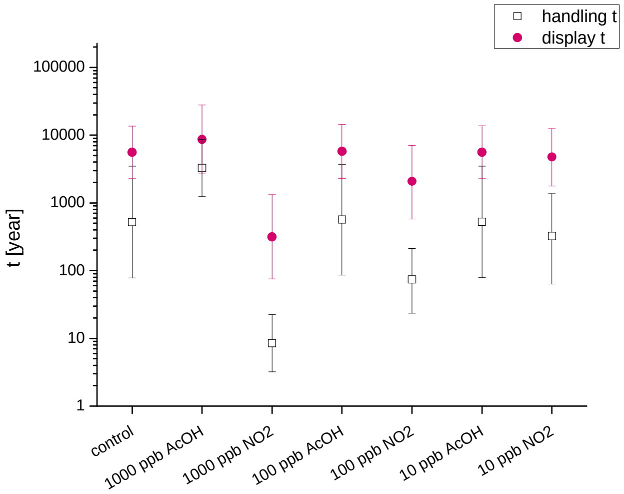


Figure 8.1: Predicted lifetimes of acidic paper 1 at 18 °C and 43% RH.

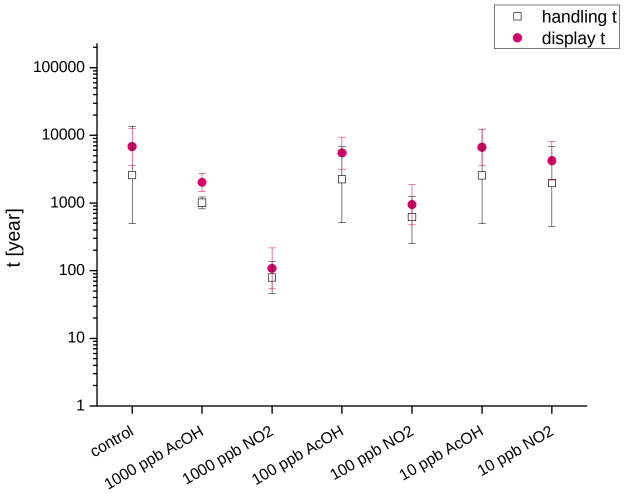


Figure 8.2: Predicted lifetimes of acidic paper 2 at 18 °C and 43% RH.

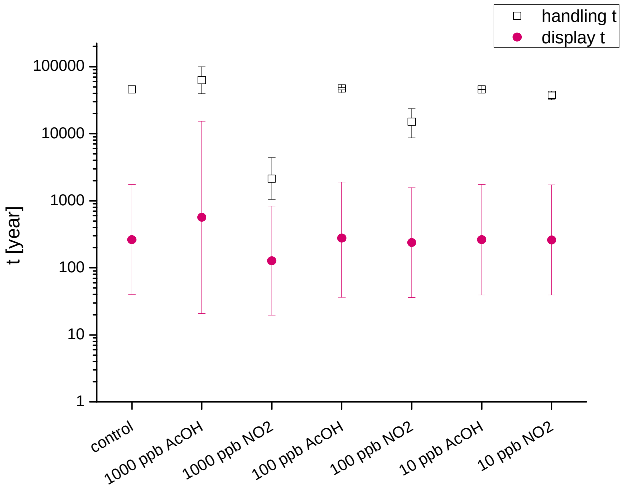


Figure 8.3: Predicted lifetimes of alkaline paper at 18 °C and 43% RH.

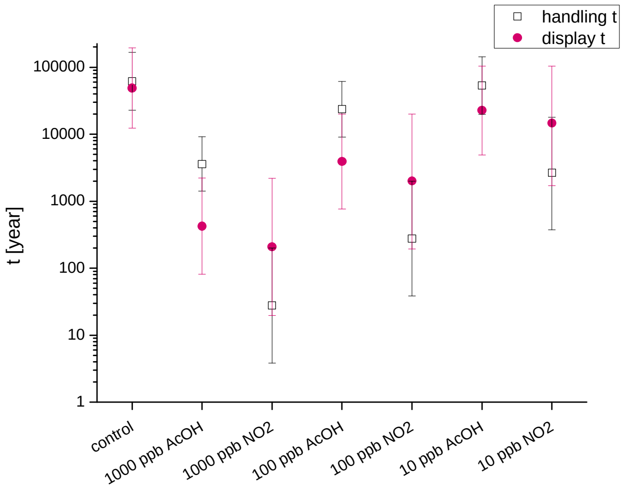


Figure 8.4: Predicted lifetimes of rag paper at 18 °C and 43% RH.

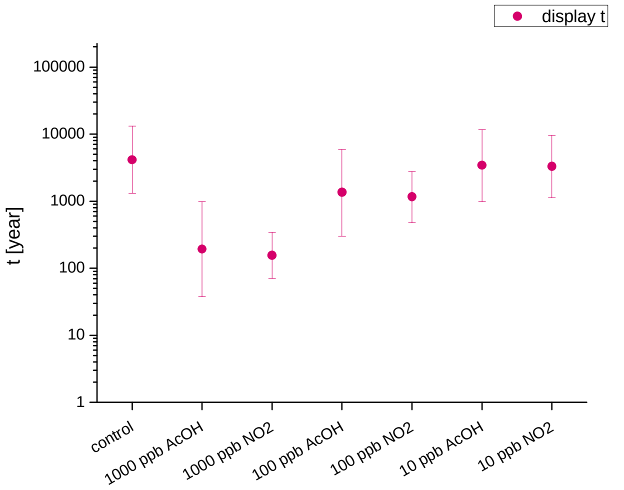


Figure 8.5: Predicted display lifetimes of lignin-containing paper at 18 °C and 43% RH.

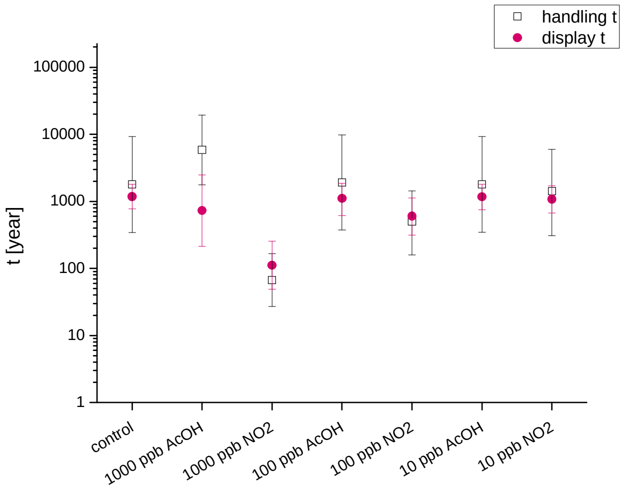


Figure 8.6: Predicted lifetimes of Whatman paper at 18 °C and 43% RH.

Predicted handling lifetimes of acidic paper 1 are significantly shorter than predicted display lifetimes, which was expected based the paper's initial pH and *DP*. It has been shown previously, although in the case of photo-induced degradation, that little change in colour does not necessarily mean significant degradation did not take place [110], and apparently this can be the case in accelerated degradation in the dark as well. The effect of NO_2 on the handling lifetime is significant at high concentrations. At a realistic concentration of 10 ppb a small effect can still be observed, however it no longer seems very significant as the predicted lifetime is well within the uncertainty interval of the lifetime, predicted under control conditions (i.e. no pollutants). A concentration of AcOH, typically found in repositories (100 ppb), is not reflected in a significant effect on the handling lifetime either. A very similar trend can be observed for display lifetimes, although they are significantly longer in comparison, several millennia. The effect of the two pollutants at realistic concentrations is not significant in the case of display lifetimes either.

The difference between predicted handling and display lifetimes of acidic paper 2 is less apparent, indicating better mechanical stability of acidic paper 2 compared to 1. Display lifetimes are, however, still longer by several millennia, although the handling lifetime, predicted for unpolluted conditions, is approximately 2000 years. The effect of both pollutants at the highest concentration is significant (although much less so for AcOH), although this changes when the concentration is decreased. 100 ppb of AcOH do not have an effect on either handling or display lifetime of acidic paper 2. Although the mean predicted lifetime for a realistic concentration of NO_2 is somewhat shorter both for handling and display (Tables 8.3 and 8.4), the effect is not significant when the uncertainty intervals are taken into account. It should also be noted that predicted lifetimes are over 1000 years even in the presence of pollutants at typical repository concentrations.

The opposite trend can be observed for alkaline paper, as predicted display lifetimes are much shorter compared to handling lifetimes. Contemporary alkaline paper is very stable in terms of mechanical properties, which is also due to its alkaline reserve. Once the alkaline reserve is consumed the paper degradation will probably continue at a faster rate, as it will become acidic. As shown in the previous Chapter, where pH measurements were discussed (section 7.2.3.), the alkaline reserve was not consumed entirely in all the experiments (as evidenced by pH measurements), which means that only the slower part of the degradation process is modelled here. In reality the lifetimes would therefore probably not be quite as long (e.g. 40000 years). However even in the presence of pollutants in realistic concentrations, alkaline paper would still reach handling lifetimes of several millennia (uncertainty intervals cannot be seen on the graphs due to the scale). Display lifetimes of alkaline paper are significantly shorter compared to the other paper types, as the predicted lifetime is less than 500 years even in the absence of pollutants. However the lifetime would not be significantly shortened by realistic concentrations of AcOH or NO_2.

So far rag paper is the only paper type with similar display and handling lifetimes, which are also the longest of all the paper types discussed here (several 10000 years in the absence of pollutants). The effects of both pollutants on predicted handling lifetime are significant even at low concentrations, although the effect of AcOH is smaller. Similarly display lifetime is affected both by 100 ppb AcOH and 10 ppb NO_2. Although this is the only paper type where even low pollutant concentrations have a significant effect, it is also clearly the most stable one, both in terms of chain scission and colour change. Lifetimes would still reach several millennia regardless of pollutant presence, which means that realistically pollutants are probably not a significant threat to rag paper.

A significant effect of both pollutants on lignin-containing paper can be observed at the highest concentration, 1000 ppb. Similar to all other paper types the effects become insignificant as the concentration is decreased, at 10 ppb the predicted lifetimes are approximately the same as if the samples were not exposed to pollutants. A small effect of 100 ppb AcOH can be observed, however, the uncertainty interval of the prediction and the control are overlapping. This means that a negative effect of AcOH at realistic concentrations cannot be predicted with certainty from the results, presented here.

Predicted handling and display lifetimes of Whatman paper are in the same range, similar to rag paper. The lifetimes of this paper type, however, are significantly shorter. Aside from alkaline paper, Whatman is the only paper type with shorter display lifetimes compared to handling lifetimes, which might be due to the initial white colour of both paper types. The effect of AcOH is insignificant at all concentrations, whereas the effect of NO_2 is significant at 1000 ppb, but decreases as the concentration is decreased. At 10 ppb NO_2 no significant effect on either handling or display lifetime of Whatman paper can be observed.

Handling and display lifetimes, predicted at realistic pollutant concentrations (100 ppb AcOH and 10 ppb NO_2), are within prediction uncertainties of the control samples for all paper types, used in the experiments. Prediction uncertainties, however, are significant, which is expected for predictions, resulting from Arrhenius studies.

8.2. Pollutant doses and thresholds

8.2.1. Concepts

The concept of doses will be defined on the basis of pollutant effect, as pollutant effects are where doses are most commonly used, both in health and material studies. The concept of dose will, however, be discussed in more general terms later in this section.

The results, described in the previous section, indicate that in archival conditions pollutants are not as much of a threat to paper-based objects as previously thought [108]. This, however, does not mean that pollutants should be discarded as a possible threat in all situations, as some environments might be significantly more polluted, possibly with different pollutants to those studied here, or some materials more sensitive (e.g. acidic paper, affected by NO_2). This highlights the need for pollutant doses or safe thresholds to be defined.

The concept of doses was first introduced in studies of environmental pollution in relation to health issues. Exposure and dose became widely used concepts and are used to describe the impact of environmental pollution on biological and ecological targets, both human and non-human [159]. In the past decades the concept was extended to non-living targets, such as objects of cultural heritage significance [73].

Generically (and theoretically) exposure is the contact of a target with a pollutant and dose is the presence of a pollutant inside a target. However in order to define these concepts precisely, other parameters need to be specified, such as time frame, the target, the pollutant, the medium (i.e. the environment of the target), the route, and the exposure boundary [159]. Depending on the time frame a distinction can be made between instantaneous exposure, temporal exposure profile, peak exposure and average exposure and consequently similar distinctions could be made for doses.

In environmental and health studies a target is defined as any biological or ecological entity occupying space [159]. A target has an external surface, which separates the target from the environment, and the part of the external surface, where the penetration can occur, is defined as exposure boundary. Pollutant concentration should be homogeneous throughout the exposure boundary, otherwise the boundary needs to be divided in smaller areas with uniform concentrations. Considering this, a target might have more than one exposure boundary. In applying these definitions to material studies a target would be an object or a material, in paper degradation studies this could be a sheet of paper, a book or a stack of papers. The exposure boundary would be the surface area in contact with the pollutant and one can easily imagine more than one exposure boundary in a realistic situation, where documents are stored in an archival repository. For example if a target was a bundle of 100 documents, two separate exposure boundaries could be defined. The first and last page would represent the first boundary, as they would be exposed to VOCs, migrating directly from the neighbouring sheets, and the top of the bundle would be the second, as VOC concentrations here are likely to be lower, however other pollutants could also be present, e.g. NO_2.

The pollutant and the medium need to be defined carefully too [159], although this is perhaps less problematic in material or heritage studies than it is in relation to health issues (e.g. very different toxic properties of chromium(VI) and chromium(III)). In the case of paper degradation due to pollution, the medium would generally be air, although it could also be the water, absorbed in paper, into which the pollutants might dissolve and possibly hydrolyse. As discussed in the previous Chapters this could be the case with NO_2 and AcOH, as NO_2 hydrolyses to form nitrous and nitric acid (and further to nitrate) and AcOH dissociates in water.

As mentioned earlier, ‘exposure’ is a concept meaning ‘physical contact of the pollutant with the target’ but it can be expressed in different ways. The most commonly used approaches are average, integrated and peak exposure, where the first two are relevant for chronic health effects and the latter for acute toxic effects

[159]. Integrated exposure is measured in ‘concentration-time’ units (e.g. ppm·h) and the other exposures are measured in the same units as concentration. Parallels with material degradation can be drawn here, as average and integrated exposure affect the overall rate of degradation [117], whereas peak exposure (especially at very high pollutant concentrations) might result in different degradation mechanisms, compared to those taking place at low concentrations [101]. In material studies, integrated exposure could be applied in the concentration range where the reciprocity principle holds, i.e. where a certain extent of pollutant exposure causes a proportional amount of damage. This would be the case for some material/pollutant interactions, where T and RH do not play such an important role (such as silver tarnishing). However, the applicability to paper degradation is not as clear, as factors other than pollutants are likely to contribute significantly to paper degradation during long-term storage.

The dose is generally defined as the presence of a pollutant inside the target, however different types of doses are considered in health terminology. These are intake dose, eliminated dose, net dose and accumulated dose [159]. The intake dose is the penetration of the pollutant into a target via an exposure boundary, and the total quantity of the pollutant penetrated in a certain period of time is known as the integrated intake dose (mass per unit time). However in living organisms the pollutant might not stay absorbed in the target, as apart from the pollutant reacting and therefore causing damage some of it can be excreted, metabolised or neutralised by repair mechanisms, therefore losing its damaging effects. The net dose is therefore the net quantity of a pollutant absorbed inside the target and remaining potent (i.e. it can react and therefore cause damage) during the defined time interval, in other words the difference between the intake dose and the eliminated dose [159].

The amount of pollutant, eliminated from the system, is referred to as eliminated dose, integrated eliminated dose being the total quantity eliminated in a certain period of time. Here difficulties with applying this approach to materials and objects are encountered, as they lack the biological activity of living organisms. Materials like paper cannot eliminate the pollutants from their ‘system’ by exhalation or metabolism, so the eliminated dose can be zero. It has been shown, however, that some pollutants (VOCs in particular) are desorbed from paper and other materials

[148], so some elimination could potentially happen, but would be difficult to quantify. This might be a drawback of applying the concept of pollutant doses to material studies, as obviously many biological processes, which might be well known for different organisms, do not have a parallel process in material degradation. On the other hand the concept could possibly be applied in a simplified way, which would not require a quantitatively determined eliminated dose.

If a simplification was made that materials do not eliminate pollutants, once they were deposited, the net dose would equal the intake dose. This might hold for pollutants reacting with paper at high rates, e.g. O_3, SO_2 or NO_2. However it is known that some pollutants, e.g. VOCs, are also emitted from paper [78,86,148,149], and emission consists of two different processes. One is a chemical process, where small molecules break away from long cellulose chains during the degradation process [86], and the other is a physical process, where pollutants adsorbed onto the material are re-emitted [148]. This is known as primary and secondary source behaviour and the distinction between the two processes is very difficult to make experimentally [160]. In the biological meaning of an eliminated dose only the physical process would have to be considered. With this in mind it is very hard to define eliminated doses for materials (paper in particular), unless the definition of eliminated dose for materials included both primary and secondary source behaviour. In that case eliminated dose would have to be defined as the difference between emitted and produced dose (Equation 66):

$$ED(t_0,t_1) = EmD(t_0,t_1) - PD(t_0,t_1), \tag{66}$$

where *ED* is eliminated dose, *EmD* is emitted dose, resulting from the physical process, and *PD* is produced dose, resulting from a chemical process. If the object produces more of the pollutant than is emitted the eliminated dose would be negative, meaning it would contribute to the total accumulated dose.

Accumulated dose, besides the intake and eliminated dose, also considers the initial accumulated dose, which is the amount of pollutant inside the target at the beginning of the time period (Equation 67):

$$AD\ (t_1) = AD_0(t_0) + ID(t_0, t_1) - ED(t_0, t_1) =$$

$$AD_0(t_0) + ID(t_0, t_1) - EmD(t_0, t_1) + \ PD(t_0, t_1), \tag{67}$$

where *AD* is the accumulated dose, i.e. the amount of pollutant available for reactions (and therefore damage), AD_0 is the initial accumulated dose, *ID* is the intake dose and *ED* is the eliminated dose. As a theoretical concept this could be applied (particularly as some of the terms might be negligible), however in practice most of the terms, especially AD_0 and *ED*, are difficult to determine, at least for some material-pollutant systems.

The reason the concept of pollutant doses is useful is that pollutants cause damage. The response to pollutant exposure by those affected (this might be the population subjected to pollution or the person in charge of a sensitive collection) is often emotional rather than rational, which can lead to arbitrary ‘rules of thumb’ that function as simplified decision-making strategies [161]. But as Paracelsus already discovered nearly 500 years ago: “Poison is in everything, and nothing is without poison. The dosage makes it either a poison or a remedy.” [162], which became a foundation for modern toxicology. Generally the harm, a toxic substance (e.g. pollutant) causes, is a function of dose and the relationship between exposure and the effect, it has on the target’s health, is represented by a dose-response curve. In health studies different shapes of dose-response curves are known for different pollutant-target systems: non-threshold dose response curves, threshold dose-response curves, hormetic dose-response curves, concave dose response curves and convex dose response curves (Figure 8.7) [161].

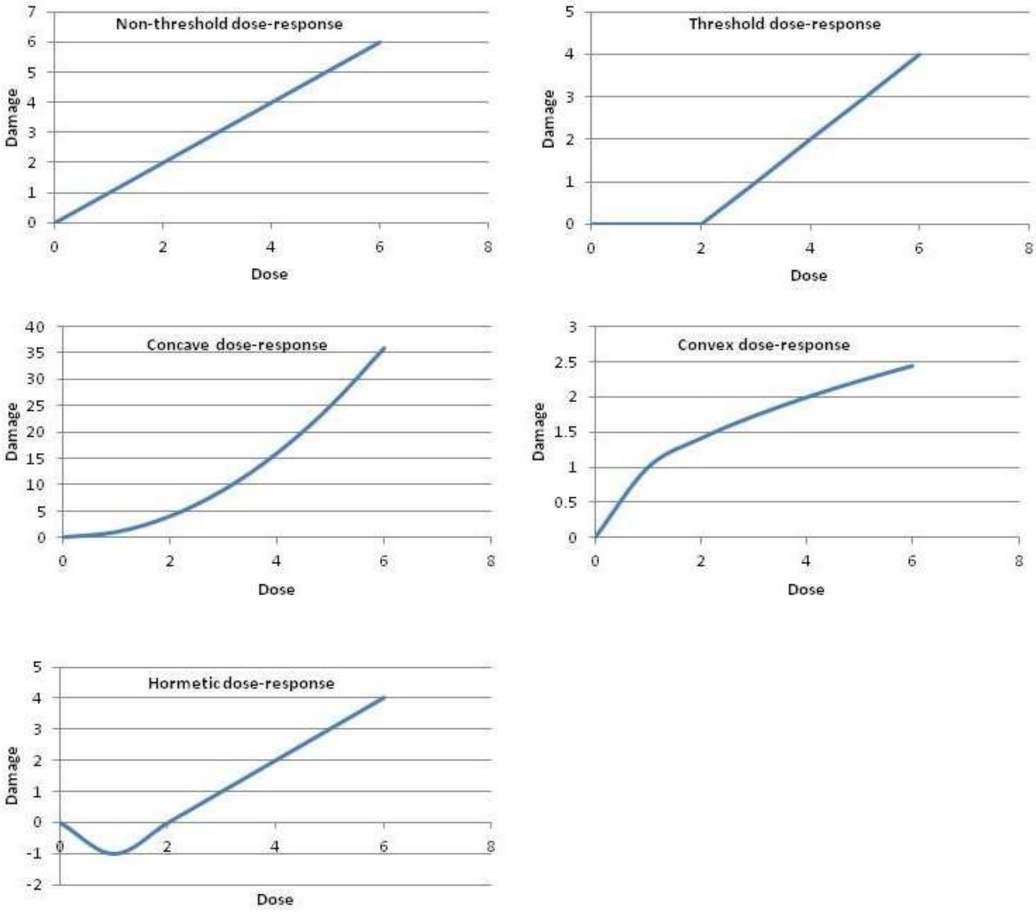


Figure 8.7: Some typical dose response curves (values on the axes selected arbitrarily).

Non-threshold, concave and convex dose-response curves all represent relationships, where the effect (i.e. harm or damage) is directly proportional to exposure, and even ‘small’ exposures have an effect, meaning there is no pollutant threshold, under which exposure would be safe. When the relationship is represented by a threshold dose-response curve, there is a safe exposure limit, and when it is represented by a hormetic one, low exposure is even beneficial to the wellbeing of the target. It is generally perceived in the toxicological community that the linear threshold model (top right) represents the risks of exposure to non-carcinogens and the linear non-threshold model (top left) to carcinogens [163], although the hormetic model is proving to be more and more important in the last decade. Studies are showing it may even outperform the two linear models, it might have just been overlooked because of its distinct features (initial beneficial effect) appear in the low-dose range, commonly omitted in experiments [164,165]. The applicability of hormetic curves in material studies is an interesting idea, as they might apply to metal corrosion, where for some metals a thin layer of a metal oxide might be seen as beneficial to a metal object, as it provides protection from further corrosion (e.g. patina on copper objects) [166].

Threshold dose-response relationships assume safe pollutant exposures (i.e. pollutant exposures that do not cause a measurable negative effect), which are common in biological systems (organisms), as firstly they are constantly being renewed and repaired and secondly they have the ability to process and eliminate some pollutants from their system (by metabolising) [167]. As mentioned earlier, non-living materials, such as paper, do not have the ability to metabolise pollutants, which are therefore absorbed in the material itself, nor can they repair themselves. If there is little or no elimination from the material it seems unlikely that a safe threshold concentration could be defined, as the pollutant deposit would increase (and continue increasing) with time. However even if elimination is possible, it is difficult to quantify and distinguish from emission, following chemical reactions within the material. With that in mind it seems like non-threshold, concave and convex dose-response curves are most likely to describe relationships between pollutants and materials. On the other hand this only applies if an assumption is made that any changes, even very small, can be detected. Since this depends significantly on the property measured and technique used, it could even be said that thresholds or doses depend on the limit of detection of the measurement method. The shape of the curve depends on the system in question, so careful material studies are needed in order to obtain damage (dose-response) functions, which describe the relationship.

Threshold or threshold dose could however be replaced by ‘loss of fitness for purpose’ dose as the ‘amount’ of pollution, that leads to material failure, rather than a measurable change (as in the definition of a threshold dose) in a material property (e.g. cellulose polymerisation, Figure 8.8). This would change the perception that a safe dose leads to no change in the material; the change would be accumulating until the point of failure, which would be reached when the ‘loss of fitness for purpose’ dose was achieved. However if this approach is to be implemented one has to make a decision on what the point of material failure for respective objects is, such as DP = 300 for paper if it is to be handled safely (if the purpose is handling). Different doses could then be determined for different purposes and purposes would need to be well defined, as a dose for an object to be displayed safely (with no handling) could be significantly larger than a dose for the same object to be handled safely. Similar dose-response curves (linear plateau or 'hockey-stick' curves) can be found in the health literature, where the cut off point is when the mortality rate reaches 1 [167].

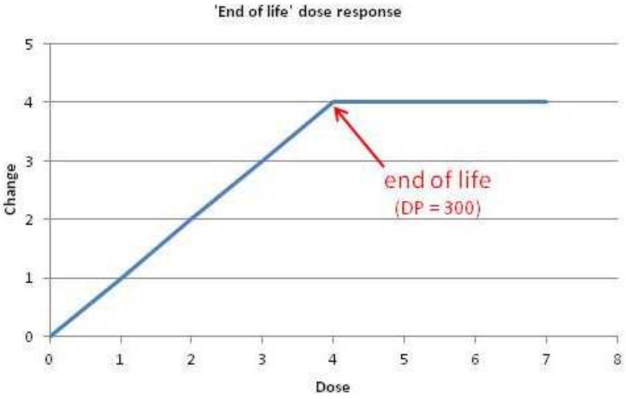


Figure 8.8: 'Fitness for purpose' dose-response function, where the point of loss of 'fitness for purpose' is material failure (values on the axes selected arbitrarily).

An important point is that this approach includes an assumption, that pollutant exposure is the main cause of degradation, as 'loss of fitness for purpose' is directly related to pollutant dose. This, however, is not necessarily the case in long-term storage of archival documents, where *T* and RH have a significant effect as well, as shown in the first section of this Chapter.

An alternative way of defining pollutant thresholds would be to define a threshold as the concentration of a pollutant, at which the effect of the pollutant becomes significant, compared to the other effects, such as those of *T* and RH. The contribution of the concentrations under the threshold to the overall degradation process would therefore be statistically insignificant.

As indicated earlier, an important issue in applying the concept of pollutant doses to materials is how to determine the actual doses. When a material is exposed to a certain concentration of a pollutant it needs to be determined how much of it is actually deposited into the material itself as the deposition velocity might depend on relative humidity (depending on the material's affinity to water and the properties, especially polarity, of the pollutant in question [168,169]), temperature [170], material properties etc. With living organisms intake doses can be calculated using biological properties and models (e.g. using breathing rates and rates of pollutant uptake [171]), whereas for materials deposition velocities would have to be known or estimated in order to determine doses.

In this sense it might be more practical to operate with pollutant concentrations and exposure times in relation to effect, eliminating absorption from the equation. Obviously, different doses for different materials would have to be defined, as absorption rates and material responses vary according to material, but it might be worth simplifying absorption to a constant. This way it could be omitted, when referring to the same material as the one used to determine the threshold dose. The danger of using doses, however, is that they might be used outside the linear response range, which would lead to invalid results. The response of the material to the stressor could therefore be over- or under-estimated, depending on the shape of the response curve. The problem with this is that without actually testing the exact situation, it cannot be known whether the predicted response is too high or too low. High pollutant concentrations, for example, could lead to both situations. Pollutants could react with each other rather than only with the material, so assuming linearity would be over-estimating the response. On the other hand high pollutant concentrations could also lead to a change in mechanism, possibly to a more damaging one, for example at high concentrations SO_2 could hydrolyze and oxidise to very acidic H_2SO_4, which would then react with the material. In this case the response could be under-estimated if linearity was assumed.

Another issue, as mentioned previously, is that pollutants are not the only factor determining the rate of paper degradation. This means that defining a dose as a constant product of concentration and time, which has a constant effect, might lead to significant errors in estimating the extent of degradation, as the ‘background’ degradation (the effect of T and RH, or the degradation taking place regardless of pollutant presence) would be neglected.

The practice in preventive toxicology has been to determine a critical level of dose or a no-effect level, assuming the exposure was adequately long. Then a standard value of dose or concentration would be obtained by introducing an additional ‘safety factor’ (such as 1/10 – ten times less) [172]. This approach could easily be adopted in preventive conservation, but only if the no-effect level was replaced by no-failure level, meaning that degradation is actually taking place, but it has not accumulated to the point of material failure or the point of loss of fitness for purpose. Alternatively a ‘safe’ level (i.e. threshold or no-effect dose) could be defined mathematically, by determining a pollutant concentration, where its contribution to the degradation rate is no longer statistically significant.

In toxicity studies effects are studied depending on the time frame of their appearance, so one can distinguish between short-term, medium-term (several days/weeks) and long-term (several years) studies [172]. Mathematical equations describing these various effects are different, the reason being the different chemical and toxicological properties of the chemicals in question. For a limited number of compounds the toxic effect depends on the external concentration and the duration of the exposure:

$$E_0 = c_E t, \tag{68}$$

where E_0 is the constant measure of minimum exposure, required to produce an effect. This is known as Haber’s Law. The more general equation, which also takes into account the variability of concentration in time, is:

$$E_0 = \int_0^t c_E\,(t)dt. \tag{69}$$

Equations 68 and 69 describe the dependence of the effect on the absorbed dose, when the exposure is not long enough for the elimination process to take place and absorbed dose is proportional to external concentration [172]. In health studies this means that exposure is too short for metabolic processes to be taken into account. If transferred to material studies, this could represent a situation, where exposure is too short and reactions too fast for desorption to take place. However, whether or not this is also applicable to long exposures (even if reaction rates are significantly higher than desorption rates) remains to be determined. Material response could change over time, e.g. once all the reactive sites are exhausted and the material is fatigued it will respond differently than a new material where all the reactive sites are free.

A possible more important argument against the applicability of this equation to long-term exposure is that significant ‘background’ degradation, influenced by *T*, RH and paper composition, will take place as well. The difference between doses, used in the health literature, and those, that might be applicable to heritage, is that health literature describes effects (i.e. diseases), which would not occur had the pollutant (or stressor) not been present. Material (e.g. paper) degradation on the other hand will occur whether or not the material is exposed to pollutants. The main difference therefore lies in the concept, as in health studies the goal is to determine whether or not a disease (parallel to degradation in material studies) will appear, and in heritage (or material) studies the existence of the degradation process is not questionable. The material will degrade during long-term storage regardless of pollutant presence, although pollutants could accelerate the process. Instead of concentration and time product resulting in a constant 'amount' of degradation, it would be more accurate if the product of degradation rate *k* and time *t* would be taken as a constant:

$$kt = D, \tag{70}$$

where D is a constant (certain 'amount' of degradation). An approximation can be made that the degradation rate consists of two contributions, one dependent on the pollutant concentration and the other dependent on all other factors:

$$kt = \left(k_{T,RH,pH} + k_{pollutant}\right)t = \left(k_{T,RH,pH} + m_{T,RH,pH}c_{pollutant}\right)t = D, \tag{71}$$

where $k_{T,\ RH,\ pH}$ is the degradation rate of a specific paper type at a given temperature and relative humidity and $m_{T,\ RH,\ pH}$ is a coefficient, describing the rate's dependence on pollutant concentration. Again this depends on *T*, RH and paper type. This was the approach, used in the previous Chapter to interpolate pollutant effects to concentrations lower than the ones used in the experiments (section 7.7.2.).

In some cases effects develop slowly over time and do not only depend on an increase in concentration. In such cases it is necessary to model the accumulation of micro damage until the change becomes significant enough for a macro effect to be observed [172]. As mentioned earlier in terms of threshold and loss of fitness for purpose doses, a similar example in material studies might be found in paper degradation. The paper's mechanical strength decreases slowly with decreasing degree of polymerisation (*DP*), until *DP* reaches a limiting value (*DP* = 300) when mechanical strength is lost and the object cannot be handled safely anymore. It should, however, be noted that a distinction cannot be made between the degradation, caused by pollutants, and the degradation, caused by all the other factors, mentioned above.

An area of heritage and material studies, where the concept of doses has been applied widely, is light damage. A dose of light is defined as light intensity, multiplied by time, providing the law of reciprocity holds in the specified range [173]. An important use of the reciprocity principle is micro-fading tests. Although they were originally designed as light-fastness tests, used to relate a material to a fading reference material, they are now being interpreted as predictive tests for changes, caused by light exposure [174,175]. This is done by illuminating (and therefore causing damage to) a very small area of the actual object. However where accurate predictions of fading rates are needed, reciprocity should be checked, as it can fail for more sensitive objects, such as photographic prints [175] or at high light intensities [176]. In order for predictions based on this approach to be accurate, light should also be the main degradation factor, significantly more important compared to e.g. T or RH.

The dose concept can be a handy tool for assessing the effects of stressors on material degradation, as introduced by Tétreault in the case of pollution [73]. This concept however only takes into account the effect of a specific pollutant, which might only be applicable to some specific material/pollutant systems (such as silver tarnishing mentioned earlier). All other effects on long-term storage of objects are neglected in this approach, therefore it could be very useful to extend the concept to other environmental factors, such as temperature and RH.

In other fields different types of doses are already in use, for example heat dose, which has been defined in different ways, but generally by specifying the temperature and time of heating [177]. Heat dose has also been re-defined by introducing energy dose (in relation to tumor destruction) [178], which, if simplified, is defined in a similar way to pollutant dose (Equations 68 and 69). Another possibly useful concept, which might have parallels in heritage science, was developed to assess the potential risks of thermal effects of a fetal ultrasound [179]. The thermal dose index (TDI) is based on the thermal index (TI), which is well known in the field of health studies, however it also takes into account the duration of the exposure to the ultrasound. It is defined as:

$$TDI = \frac{(4)^{TI}t}{N}, \tag{72}$$

where t is time and N is a normalizing factor, chosen so that examinations when $TDI < 1$ (meaning examinations can be performed without thermal risk) will not cause adverse effects (in this case $N = 64$ min). Another ultrasound-related study has been carried out to compare two approaches for predicting tissue damage in relation to exposure time. The first is a thermal dose:

$$t_{43} = \int_0^t R^{T(\tau)-43} d\tau, \tag{73}$$

where R is the number of minutes, needed to compensate for a 1 °C change either above ($R = 0.5$) or below ($R = 0.25$) the breakpoint, which in this case is 43 °C. t_{43} is a dose, representing the time it would take for the same effect to be reached at 43 °C [180,181]. Of course the reference temperature and the R values are arbitrary values, chosen according to the type of damage and tissue, but this might be a useful concept in heritage. It would however be fairly complicated to implement, as a decision would have to be made on the reference temperature and R values would have to be determined for specific materials or material groups. The second approach is an intensity-time product:

$$It^m = D, \tag{74}$$

where D is a tissue-dependent damage threshold, I is the average acoustic intensity, t is time and m is an exponent typically around 0.5, determined from experimental data (similar to the previous example) [181,182]. The study determined that in a practical range of intensity values and times both approaches give comparable results [181]. From a material point of view this is interesting because the doses calculated using Equations 73 and 74 are, in effect, doses of different ‘stressors’ (temperature and acoustic intensity), yet they describe the same process and give approximately the same results.

Another interesting example is vibration dose value, defined by the equation:

$$dose = \sum_i [a_i^m t_i], \tag{75}$$

where a is frequency weighted acceleration (measure for vibration magnitude) of the vehicle i and t is exposure time [183]. The relative importance of acceleration and exposure depends on the value of m (they are equal when $m = 1$).

All these approaches to some extent use arbitrary values, determined from experimental data, although what they have in common is that the dose is generally defined as the ‘magnitude/amplitude of stress’ multiplied by exposure time, which gives the dose of ‘stress’.

Most long-term degradation processes are complex and therefore cannot be described using only one ‘stressor’. It would therefore be more accurate if other factors of degradation were included as well, and therefore the product of degradation rate and time would be seen as a constant instead of the product of concentration and time (i.e. if the ‘stress’ was actually degradation rate). Unfortunately, however, degradation rates are more complex and difficult to determine than pollutant concentrations.

An assumption, which could simplify lifetime estimations, is prioritisation of effects. In some cases pollution is the most significant damaging factor (e.g. lead in the presence of AcOH), whereas in others temperature and relative humidity have much more effect and pollution could be neglected. In terms of doses (i.e. stress multiplied by time) the effect of temperature could be described as:

$$t_1 e^{-\frac{E_a}{RT_1}} = t_2 e^{-\frac{E_a}{RT_2}}, \tag{76}$$

where t_1 and t_2 are times at temperatures T_1 and T_2, E_a is the activation energy and R is the gas constant. This equation could be used to estimate lifetimes of alkaline paper, as it is fairly insensitive to changes in relative humidity in terms of *DP* loss [26]. For acidic papers, however, RH would have to be included into the equation. In a relatively narrow RH range, typically found in archival repositories, the RH effect on chain scission is approximately linear and the effect of temperature and RH can be described as:

$$t_1 RH_1 e^{-\frac{E_a}{RT_1}} = t_2 RH_2 e^{-\frac{E_a}{RT_2}}. \tag{77}$$

The equations, described above, could be useful for assessing handling lifetimes. Display lifetimes, on the other hand, are not linearly dependent on RH. There is indication of a quadratic effect, so display lifetimes could be estimated using the equation:

$$t_1 RH_1^2 e^{-\frac{E_a}{RT_1}} = t_2 RH_1^2 e^{-\frac{E_a}{RT_2}}. \tag{78}$$

As pointed out earlier in the text, careful material-stressor relationship studies would be needed to determine dose-response functions, as a certain ‘dose of stress’, which would not lead to the point of material failure (end-of-life) for one object type, might be ‘fatal’ to another.

For paper degradation, pollutant concentration thresholds need to be determined in order to prioritise effects. As mentioned earlier, this could be done mathematically by determining at what concentration the contribution of pollutants becomes insignificant. In Equation 71 the degradation rate is simplified to having two separate contributions, although realistically pollutant effect is likely to be T and RH dependent. As an approximation, however, the degradation rate can be written as:

$$k = k_{T,RH,pH} + k_{pollutant} = k_{T,RH,pH} + m_{T,RH,pH} c_{pollutant}. \tag{71}$$

If the second term is significantly smaller than the first one, it could be neglected when determining the rate. Strictly mathematically this would be the case if the second term was two orders of magnitude smaller than the first one, i.e. the threshold would be 1%. Realistically, however, temperature and relative humidity are not strictly controlled to the set value, so the uncertainty in the first term (T- and RH-dependant degradation rate) is larger than 1%. This means that the contribution of a pollutant to the overall degradation rate would only become significant if it was larger than the uncertainty in T and RH control. Pollutant thresholds can therefore be calculated as the concentration, at which the pollutant contribution becomes larger than the uncertainty in T and RH. The reference T and RH point for threshold calculation was 18 °C and 43% RH and the uncertainties were 1 °C and 10% RH. These values were determined in environmental monitoring at the Nationaal Archief and have been described in Chapter 4. Thresholds were calculated as:

$$m_{T,RH,pH}c_{pollutant} = k_{T+\Delta T,RH+\Delta RH,pH} - k_{T,RH,pH} \tag{79}$$

$$c_{pollutant} = \frac{k_{19\,^0C,53\%\,RH} - k_{18\,^0C,43\%\,RH}}{m_{T,RH,pH}}. \tag{80}$$

The m coefficients need to be determined experimentally. This was done when degradation rates were interpolated in the previous Chapter (section 7.7.2.), so the coefficients are given for 18 °C and 43% RH. The coefficients and pollutant thresholds, calculated according to Equation 80 for the purpose of handling, are shown in Table 8.5.

Table 8.5: Handling threshold concentrations of AcOH and NO_2 (where negative values were obtained, they were replaced by no effect).

sample	m_{AcOH} /day^{-1}ppb^{-1}	m_{NO2} /day^{-1}ppb^{-1}	c_{AcOH} /ppb	c_{NO2} /ppb
A1	-6.78E-12	4.85E-10	no effect	7
A2	3.12E-12	6.30E-11	300	15
B	-4.66E-14	3.53E-12	no effect	24
R	2.11E-12	2.89E-10	33	0
W	-2.98E-12	1.10E-10	no effect	18

Calculated threshold concentrations for some paper types are low, especially for rag paper. This approach to calculating threshold concentrations does not take into account the length of predicted lifetimes, only the relative contribution of pollutant-accelerated degradation. For rag paper this is very apparent, as the contribution of pollutants might be significant, however the predicted lifetimes are still several millennia, regardless of pollutant presence, as shown in the previous section. AcOH has almost no effect, so threshold concentrations can only be calculated for acidic paper 2 and rag paper. The threshold, obtained for acidic paper 2, is above the range of realistic concentrations, meaning that AcOH does not represent a significant risk in an average archival environment. The thresholds for NO_2 on the other hand are much lower, in some cases below 10 ppb, which is a realistic concentration for an archival repository. As explained this would not be problematic for rag paper, due to very long predicted lifetimes. Similarly for alkaline, Whatman and acidic paper 2 this level of NO_2 is unlikely to be problematic. The only paper type, where NO_2 might realistically be problematic, is acidic paper 1, where the predicted lifetime is approximately 500 years with no pollutants present. However as discussed in the previous section, the differences between the control and very low pollutant concentrations are too small to be predicted accurately, considering significant prediction uncertainties.

Coefficients and pollutant thresholds obtained for the purpose of display are shown in Table 8.6.

Table 8.6: Display threshold concentrations of AcOH and NO_2 (where negative values were obtained, they were replaced by no effect).

sample	m_{AcOH} /day^{-1}ppb^{-1}	m_{NO2} /day^{-1}ppb^{-1}	c_{AcOH} /ppb	c_{NO2} /ppb
A1	-2.61E-09	1.23E-07	no effect	50
A2	1.43E-08	3.74E-07	357	14
B	-8.39E-08	1.65E-07	no effect	678
R	9.60E-08	1.96E-07	8	4
L	2.03E-07	2.53E-07	40	32
W	2.13E-08	3.32E-07	1262	81

Similar to the handling thresholds, the thresholds obtained for the purpose of display are the lowest for rag paper. Predicted lifetimes of rag paper were, however, the longest of all paper types (several 10000 years) even in the presence of pollutants, which means pollutants are not realistically a threat to this paper type. AcOH thresholds are in the realistic concentration range or above for alkaline and Whatman paper and AcOH has no effect on the colour of acidic paper. Even where a threshold can be calculated (acidic paper 2, rag and lignin-containing paper), predicted display lifetimes were over 1000 years, which should be taken into account when discussing safe pollutant levels.

8.2.2. Comparison of different dose approaches

It was argued above that assuming the product of concentration and time is a constant (and therefore causes a constant ‘extent’ of degradation) would underestimate the overall observed degradation taking place in long-term storage by neglecting the degradation, caused by temperature and relative humidity. To quantitatively compare both approaches, lifetime predictions, based on both, were calculated.

The *c·t=const* approach does not usually include temperature extrapolation, as experiments are mostly performed at room temperature and accelerated degradation is caused by increased pollutant concentrations. To be able to compare this approach with the one, used in this research, the degradation rates, obtained at 1000 ppb of each pollutant, were extrapolated to 18 °C. Interpolation to lower concentrations was then done in two different ways (see Appendix B for an example of calculation):

a) Using $c \cdot t = const$, where the degradation rate is interpolated between 0 and the rate at 1000 ppb,
b) Using $k \cdot t = (k_{T,RH,pH} + k_{pollutant}) \cdot t = const$, where the degradation rate is interpolated between the rate of the control (i.e. in the absence of pollutants) and the rate at 1000 ppb.

Average handling lifetimes (without uncertainty intervals, which are shown in Appendix D), predicted using both approaches, are shown in Tables 8.7 and 8.8. The figures are not rounded up due to asymmetrical uncertainty intervals. **a** and **b** in the columns are corresponding with a) and b) above.

Table 8.7: Handling lifetimes, predicted at 18 °C, 43% and 100 & 10 ppb AcOH, using both approaches.

	a	**b**	**a**	**b**
sample	**$t_{100\ AcOH}$ /yr**	**$t_{100\ AcOH}$ /yr**	**$t_{10\ AcOH}$ /yr**	**$t_{10\ AcOH}$ /yr**
A1	32831	568	328315	525
A2	10056	2238	100563	2550
B	626933	47114	6269326	45972
R	35892	23566	358925	53146
W	58457	1918	584566	1797

Table 8.8: Handling lifetimes, predicted at 18 °C, 43% and 100 & 10 ppb NO_2, using both approaches.

	a	**b**	**a**	**b**
sample	**$t_{100\ NO2}$ /yr**	**$t_{100\ NO2}$ /yr**	**$t_{10\ NO2}$ /yr**	**$t_{10\ NO2}$ /yr**
A1	85	74	851	325
A2	789	619	7887	1965
B	21445	15092	214453	38086
R	278	277	2778	2660
W	672	502	6721	1422

Generally the lifetimes, shown in **b** columns, appear significantly shorter. This shows the 'traditional' dose approach (**a**) under-estimates the degradation at low pollutant concentrations, where temperature and relative humidity have a significant effect. Similar to the lifetimes described in the previous section, the lifetimes discussed here have extensive uncertainty intervals. The differences between the two approaches, however, are mainly outside prediction uncertainties and therefore significant. Uncertainty intervals for individual paper types are shown in Appendix D.

Handling lifetimes, predicted using method b, are consistently significantly lower. The greatest agreement between the two methods was observed for 100 ppb NO_2, where the predicted lifetimes are in the same order of magnitude and within prediction uncertainties. The reason is that the effect of NO_2 is very significant at high concentrations and therefore only a small error is made if the other degradation factors (such as T and RH) are neglected. Once the rates are extrapolated to lower concentrations, however, the relative importance of 'background' degradation becomes significant and the under-estimation made by not taking this into account increases. The only paper type, where there is relatively good agreement between the predictions at the lower NO_2 concentration, is rag paper, which demonstrates its general stability towards T- and RH-induced degradation. Some overlap between uncertainty intervals of both methods at 10 ppb NO_2 was also observed for the other paper types (with the exception of alkaline paper). However the differences between the approaches, are still relatively large.

In terms of AcOH exposure the disagreement is significant (by several orders of magnitude). This is a consequence of AcOH causing very little additional degradation compared to T and RH. This means that when the handling lifetime is calculated from the $c \cdot t = const$ formula, it is greatly over-estimated, as the samples exposed to AcOH actually degraded mainly from T and RH, i.e. the 'background' degradation, which is not taken into account.

Average display lifetimes (without uncertainty intervals), predicted using both approaches, are shown in Tables 8.9 and 8.10.

Table 8.9: Display lifetimes, predicted at 18 °C, 43% and 100 & 10 ppb AcOH, using both approaches.

sample	a $t_{100\ \mathrm{AcOH}}$ /yr	b $t_{100\ \mathrm{AcOH}}$ /yr	a $t_{10\ \mathrm{AcOH}}$ /yr	b $t_{10\ \mathrm{AcOH}}$ /yr
A1	86462	5786	864619	5601
A2	20183	5502	201827	6650
B	5655	277	56551	264
R	4241	3934	42411	22814
W	1933	1363	19332	3449
L	7322	1113	73223	1174

Table 8.10: Display lifetimes, predicted at 18 °C, 43% and 100 & 10 ppb NO_2, using both approaches.

sample	a $t_{100\ \mathrm{NO2}}$ /yr	b $t_{100\ \mathrm{NO2}}$ /yr	a $t_{10\ \mathrm{NO2}}$ /yr	b $t_{10\ \mathrm{NO2}}$ /yr
A1	3156	2092	31562	4783
A2	1080	945	10799	4202
B	1279	237	12789	260
R	2086	2009	20864	14666
W	1561	1167	15611	3308
L	1121	605	11210	1078

Similar to handling lifetimes the display lifetimes predicted using both methods appear significantly different. The differences between **a** and **b** increase as the concentration decreases, which is unsurprising, as pollutant exposure might not be the critical factor in degradation or colour change at low pollutant concentrations. Uncertainty intervals of both predictions for individual paper types are shown Appendix D.

Similar to the handling lifetime the greatest agreement between approaches **a** and **b** was observed at 100 ppb NO_2. The difference between the approaches, however, is larger than for the handling lifetime, as fairly good agreement was observed only for acidic paper 2 and rag paper. Predictions differ most for the alkaline, Whatman and lignin-containing papers, which were the most prone to colour change. This indicates that the relative contribution of NO_2 to colour change is even smaller than to *DP* loss. Similar to handling lifetimes the predictions differ even more for AcOH exposure, which did not contribute significantly to colour change of most paper types. The differences are larger at lower concentrations, where the relative contribution of pollutant-induced change is smaller compared to other factors. The difference between the two approaches is outside uncertainty intervals, especially for AcOH exposure. The exception is for 100 ppb NO_2, where the greatest agreement was observed, and the overlap between uncertainty intervals is relatively small.

As discussed in the previous section, prioritisation of effects on the degradation process could simplify lifetime estimations. Prioritisation, however, is only possible when one degradation factor is dominant, otherwise significant prediction errors can be made. Lifetime predictions, discussed here, show that a high concentration of a very damaging pollutant, such as NO_2, could be an example, where prioritisation is possible. At 100 ppb NO_2, 18 °C and 43% RH the effect of the pollutant on chain scission is predominant, so only small errors would be made by not taking into account the 'background' T- and RH-induced degradation. As soon as the concentration is decreased, the other degradation factors become significant and can no longer be neglected without risking significant over-estimation of lifetimes. The same would be true of a less damaging pollutant at high concentrations, such as AcOH. The $c \cdot t = const$ approach can therefore only be used safely at high concentrations of pollutants, which cause significant degradation. In a typical archival environment, however, no pollutant is present in a high enough concentration for this approach to be applicable, as was shown in Chapter 4 where environmental monitoring at the Nationaal Archief was discussed.

8.3. Environmental management options

Different preservation options for paper-based collections have been employed in the past decades, from purely environmental strategies such as cold-storage or extensive filtration to interventive measures, such as deacidification. Assessing the benefits of such measures in a quantitative way can provide information about what measures are the most effective and most beneficial to the collection.

Although assessing lifetimes in the way described in the previous sections is only possible for papers with a known initial *DP* or colour and a well-defined degradation rate, the results obtained in this study can be applied in a wider sense. The samples, selected for the experiments were selected to represent typical documents, found in an archival or library collection. In most Western repositories 70-80% of collections are acidic [1], prone to degradation, which are represented here by two fairly acidic samples (A1 and A2) of different fibre compositions. Lignin-containing groundwood paper is also very common and known to be fairly unstable, especially in terms of colour change, and this part of archival collections has been represented by the lignin-containing sample L. These three samples all date from the first half of 20th century, which is when papers of the poorest quality were produced, due to a significant increase in demand. All archival collections generally include significant amounts of rag paper, which is known to be relatively stable in comparison [1]. To test this stability a rag sample produced in 19th century (R), was also used in the experiments. Contemporary alkaline sample B, produced in mid-1990's, was used to represent modern paper, containing alkaline reserve, which improves the paper's durability by reacting with acidic degradation products and pollutants. Lastly Whatman filter paper was added as the only model paper, representing pure cellulose. Much previous paper degradation research has been carried out on Whatman paper, so inclusion of this sample means the results are comparable. Further reason to use Whatman paper was the reproducibility of results. The samples were selected to represent the most common paper types in an archival collection, allowing the results to be used to demonstrate degradation trends and general behaviour of real paper-based collections.

8.3.1. Decreasing the temperature

According to the Arrhenius principle chemical reactions proceed at a slower rate at lower temperatures. This of course means that paper degradation is decelerated at lower temperatures, making low temperatures an effective preventive conservation measure.

A decrease in temperature by 2 °C was selected as a reasonable measure to prolong the lifetime of the collection, so the degradation rates were extrapolated to 16 °C as well. All lifetimes were calculated at 16 °C and 43% RH and the average predictions at realistic pollutant concentrations (100 ppb AcOH and 10 ppb NO_2) at both 18 and 16 °C are shown in Table 8.11 (handling lifetimes) and Table 8.12 (display lifetimes) to allow direct comparison.

Table 8.11: Predicted handling lifetimes at 18 and 16 °C and 43% RH. Predictions are made for no pollutants and realistic concentrations of AcOH and NO_2.

sample	$t_{handling}$ /year					
	18 °C			**16 °C**		
	0 ppb	**100 ppb AcOH**	**10 ppb NO_2**	**0 ppb**	**100 ppb AcOH**	**10 ppb NO_2**
A1	520	568	325	706	772	417
A2	2590	2238	1965	3713	3178	2738
B	45848	47114	38086	67445	69262	55114
R	61759	23566	2660	96607	33543	3096
W	1785	1918	1422	2488	2676	1941

On average decreasing the temperature by 2 °C would prolong the lifetime of paper by approximately a factor of 1.4. There are, however, some differences, especially between different conditions, due to differences in E_a. Lifetimes of papers, exposed to NO_2, are therefore increased by a somewhat smaller factor than the control lifetimes, where activation energies are higher. Under control conditions there are also some differences between the paper types, as for example rag paper is more affected by temperature changes than acidic paper.

Table 8.12: Predicted display lifetimes at 18 and 16 °C and 43% RH. Predictions are made for no pollutants and realistic concentrations of AcOH and NO_2.

sample	$t_{display}$ /year					
	18 °C			**16 °C**		
	0 ppb	**100 ppb AcOH**	**10 ppb NO_2**	**0 ppb**	**100 ppb AcOH**	**10 ppb NO_2**
A1	5581	5786	4783	8165	8469	6895
A2	6808	5502	4202	10099	8009	5833
B	262	277	260	334	353	331
R	48878	3934	14666	78545	5073	20300
L	4155	1363	3308	6027	1786	4697
W	1181	1113	1078	1614	1513	1466

Similar to handling lifetimes the display lifetimes would be extended by approximately a factor of 1.4 if the temperature was decreased by 2 °C. As the activation energies determined for handling and display were similar (section 7.6.), this was expected. Again a somewhat smaller increase in lifetimes can be observed for samples, exposed to NO_2, and some differences between paper types can be appreciated (e.g. rag paper would be more affected by temperature change than alkaline paper). Predictions for individual paper types will be discussed in the following paragraphs, calculations for acidic paper 1 are shown in Figure 8.9.

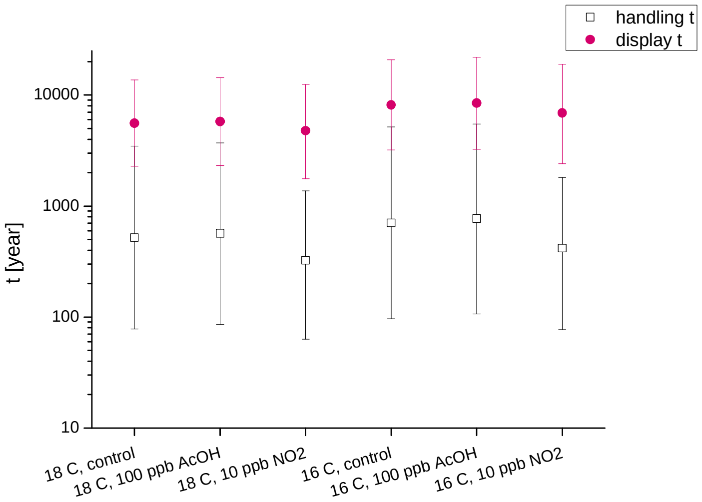


Figure 8.9: Predicted handling and display lifetimes of acidic paper 1 with uncertainty intervals at 18 and 16 °C and 43% RH. Predictions are made for no pollutants and realistic concentrations of AcOH and NO_2.

Although average lifetime predictions seem to show clearly, that lifetimes are extended, when temperature is decreased by 2 °C, this in not quite as obvious when uncertainty intervals are taken into account and the lifetimes are plotted on a logarithmic scale. Unfortunately predictions, based on Arrhenius studies at three temperatures (and on real historic papers), generally have large uncertainty intervals, which means that all smaller effects are not going to appear significant. The predictions can, however, still be used to assess trends and at least to indicate (if not predict) the behaviour of paper under different temperature and pollutant conditions.

Firstly it must be pointed out that all handling lifetimes are within the uncertainty intervals of the control at 18 °C, as are the display lifetimes. The difference between the temperatures, however, can be appreciated. By decreasing the temperature by 2 °C, the handling lifetime of acidic paper 1 under control conditions is extended to approximately 700 years, which is a significant improvement. The effect of the temperature decrease on the sample, exposed to 10 ppb NO_2 is somewhat smaller compared to completely removing the pollutant. If display lifetime is considered, decreasing the temperature had a larger effect than removal of pollutants, as the predicted lifetime for acidic paper 1, exposed to 10 ppb NO_2 at 16 °C is longer than the lifetime under control conditions at 18 °C. AcOH had no effect on acidic paper, so a temperature decrease would, of course, be more beneficial compared to AcOH removal.

Acidic paper 2 benefits from reducing the temperature slightly more than acidic paper 1, which is due to a higher activation energy, determined for this sample. Even the samples, exposed to pollutants (both AcOH and NO_2), would reach longer handling lifetimes than the control, if the temperature was decreased by 2 °C. This is not entirely the case with display lifetimes, as the control lifetime at 18 °C is a bit longer than the lifetime at 16 °C and 10 ppb NO_2, although the predictions are quite similar. 100 ppb AcOH on the other hand has less effect on the display lifetime than a 2 °C temperature difference.

Activation energies, determined for *DP* loss of alkaline paper, were higher compared to most other paper types, so a 2 °C temperature difference would extend its handling lifetime significantly and would have more effect than completely removing realistic concentrations of pollutants. Although considering the length of predicted handling lifetimes, even pollutants are not a particular threat. Display lifetimes are very different, reaching only approximately 250 years at 18 °C. Decreasing the temperature would improve that, extending the lifetime by approximately 100 years for all three conditions. Similar to the handling lifetime, display lifetime is more positively affected by a temperature decrease of 2 °C than complete removal of pollutants, as realistic pollutant concentrations of AcOH and NO_2 have very little effect on contemporary alkaline paper.

The unusual results, obtained for rag paper, are due to significant differences in activation energies, obtained under different pollutant conditions. While the activation energies for both *DP* loss and colour change, determined under control conditions, were the highest of all paper types (157 and 166 kJ/mol, respectively), the E_a values, obtained for samples exposed to NO_2, were amongst the lowest (49 and 94 kJ/mol). This means that although the degradation rate is highly temperature dependant at control conditions, a 2 °C temperature decrease would not make a significant difference if the paper was exposed to pollutants (AcOH or NO_2). This implies that removing pollutants is more beneficial to rag paper than decreasing the temperature, although it should be noted that both handling and display lifetimes, predicted for rag paper, are several millennia long even in the presence of pollutants.

Whether significant preservation measures are necessary for rag paper is therefore debatable.

Activation energies, determined for lignin-containing paper, differ according to pollutant conditions as well, although in this case the lowest E_a was obtained for samples, exposed to AcOH. A decrease in temperature by 2 °C would extend the display lifetime of lignin-containing paper slightly more than if the paper was completely protected from NO_2. AcOH in realistic conditions, on the other hand, would still have more effect compared to the control at 18 °C. Even the worst 'starting' scenario (100 ppb AcOH at 18 °C and 43% RH) would, however, lead to a display lifetime of approximately 1500 years.

The differences between activation energies of Whatman paper are not as significant as for some other paper types, which means that a change in temperature has a similar effect on samples under all three conditions. Handling lifetime of Whatman paper, exposed to 10 ppb NO_2 at 16 °C, would be approximately the same as the lifetime of the control at 18 °C, meaning that complete removal of pollutants would have the same effect as decreasing the temperature by 2 °C. In terms of display lifetime a larger beneficial effect of a lower temperature can be observed, as predicted lifetimes would be longer at 16 °C regardless of pollutant presence.

Lowering the temperature by 2 °C, although beneficial in all cases, does not have the same effect on all paper types. The magnitude of the effect depends on the activation energy of the degradation reaction, as the lower the E_a, the less the process is temperature dependent. In terms of handling lifetime decreasing the temperature by 2 °C generally has a similar effect as complete removal of all pollutants[3], which is only theoretically possible. The effect of a lower T is only smaller for acidic paper 1, where the difference between a lower temperature and no pollutants would be approximately 100 years. NO_2 would have a much larger effect on rag paper, however predicted handling lifetimes would still be several millennia. In terms of display lifetimes decreasing the temperature has a larger positive effect on most papers compared to complete removal of pollutants. A different trend can be observed for acidic paper 2, where lifetime in 10 ppb NO_2 at 16 °C is somewhat shorter compared to the control at 18 °C, and for rag paper, where the difference is

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[3] Pollutants investigated in this study, NO_2 and AcOH.

much larger. However predicted display lifetimes of both are still several millennia long.

8.3.2. Air filtration

Air filtration was introduced in several heritage institutions as a means of improving the preservation of paper-based collections [72]. Although it was justified to introduce air purification with the historically high levels of pollution in mid 20th C, the benefits of this measure need to be assessed according to current pollutant concentrations. To assess the effect of air filtration, pollution data collected at the Nationaal Archief was used. NO_2 concentration was measured in two repositories, one equipped with an air filtration unit and one without it (see Chapter 4). The average concentrations, obtained in both repositories, were used in lifetime predictions (section 4.3.3.). As semi-quantitative analysis of AcOH in the two repositories gave results, incompatible with concentrations published in the literature [87,105], they were not used for lifetime predictions. A rough estimation, based on measurements, carried out at the Swiss National Library, is that AcOH concentration is reduced by 20-30% if a new chemical filtration unit is installed [94]. This was used to assess the benefit of air filtration in terms of AcOH. The concentrations, used for predictions, are shown in Table 8.13.

Table 8.13: Pollutant concentrations with and without air filtration (AcOH concentrations based on approximate estimations).

filtration	c_{NO2} /ppb	c_{AcOH} /ppb
YES	70	0.3
NO	100	8.9

Similar to predictions, discussed in the previous section, all lifetimes under different pollutant conditions are within uncertainty intervals of the control and in most cases prediction uncertainty intervals are actually much larger than differences between pollutant conditions. The results could, however, still be useful to observe trends and estimate the effects. Predicted lifetimes are shown in Tables 8.14 and 8.15.

Table 8.14: Handling lifetimes with and without air filtration.

	t_{handling} /year				
	18 ^{o}C, 43% RH			**18 ^{o}C, 43% RH, filtration**	
sample	**0 ppb**	**100 ppb AcOH**	**8.9 ppb NO_2**	**70 ppb AcOH**	**0.3 ppb NO_2**
A1	520	568	339	553	511
A2	2590	2238	2021	2333	2566
B	45848	47114	38843	46727	45569
R	61759	23566	2989	28934	37058
W	1785	1918	1456	1876	1771

Table 8.15: Display lifetimes with and without air filtration.

	t_{display} /year				
	18 ^{o}C, 43% RH			**18 ^{o}C, 43% RH, filtration**	
sample	**0 ppb**	**100 ppb AcOH**	**8.9 ppb NO_2**	**70 ppb AcOH**	**0.3 ppb NO_2**
A1	5581	5786	4863	5723	5553
A2	6808	5502	4395	5838	6684
B	262	277	260	273	262
R	48878	3934	15950	5432	45682
L	4155	1363	3387	1707	4124
W	1181	1113	1089	1132	1177

AcOH has no effect on either handling or display lifetime of acidic paper 1, air filtration therefore has no positive effect in that respect. It does, however, have some effect on the degradation, caused by NO_2. Both handling and display lifetimes would be shorter in the repository without air filtration. In comparison to the repository with air filtration, the handling lifetime would be shorter by a third, approximately by 200 years. The display lifetime would also be decreased, but would still reach almost 5000 years. Whether a difference of several 100 years is significant, when even the lifetime under the least favourable conditions is several millennia, depends on the stakeholders' decision. There is no significant difference between the filtered repository results for both AcOH and NO_2, and the control.

Similar to acidic paper 1 very little difference between the repositories with and without air filtration can be observed for acidic paper 2, exposed to AcOH, both in terms of handling and display lifetime. Some effect of air filtration can, however, be seen for NO_2, as there is no difference between the filtered repository and the control, but a shorter lifetime is predicted for the non-filtered repository. This is the case for both handling and display lifetimes. The difference is approximately 300 years for handling lifetime, although even the shorter predicted lifetime (at the higher NO_2 concentration) is over 1500 years. The difference in the display lifetime is larger, however the lifetimes are much longer as well, with several millennia even for the higher concentration of NO_2.

Air filtration has no effect on alkaline paper in terms of display lifetime, which is much shorter for alkaline paper compared to the other paper types. Predicted lifetimes under all four pollutant conditions are approximately the same as for the control. A significant positive effect of air filtration can be observed for handling lifetime, as NO_2 seems to have a significant effect even at very low concentrations. Even though the effect is significant, the predicted lifetime in the non-filtered repository reaches several 10000 years. Realistically when predictions are this long a 20% difference in lifetimes when comparing a filtered and non-filtered environment is probably not very important. Taking this into account, air filtration does not have a significant positive effect on contemporary alkaline paper.

A positive effect of air filtration on handling and display lifetimes of rag paper can be observed both in terms of NO_2 and AcOH accelerated degradation. Even in the filtered repository the lifetimes would not reach that of the control, predicted in the absence of pollutants. Although the benefits of air filtration seem significant in this case, even the shortest of all predicted lifetimes (handling, when exposed to 8.9 ppb NO_2) is approximately 2000 years, which should be taken into account when assessing the beneficial effects of air filtration.

For lignin-containing paper the effect of AcOH is larger than the effect of NO_2, so air filtration might have some effect in reducing the AcOH concentration. The difference between the repositories with and without air filtration, however, is not very significant compared to the difference between the filtered repository and the control. At 100 ppb AcOH, assumed for a repository without air filtration, lignin-containing paper would reach a display lifetime of over 1000 years. In terms of NO_2 accelerated degradation the filtered repository performs as well as the control. The lifetime in the non-filtered repository is reduced by approximately 700 years, however still reaching over 3000 years.

There seems to be no significant difference between repositories with and without air filtration in terms of display lifetimes of Whatman paper. Some benefits of air filtration can be observed in terms of the effect of NO_2 on the handling lifetime, as the predicted lifetime in the repository without air filtration is a few centuries shorter. It would, however, still be over a millennium long, as would all the display lifetimes.

It should be highlighted, that all the differences discussed above, are within the prediction uncertainties of the control sample. It is therefore difficult to say that the predicted differences are significant, although unfortunately that is usually the case with Arrhenius studies on real historic materials [48]. To assess, whether air filtration contributes significantly to the preservation of a collection, a decision should be made on acceptable lifetimes a collection is expected to achieve. If, for example, the goal is a millennium, most paper types would achieve it regardless of pollutant presence, both in terms of handling and display lifetime. The only exceptions are the display lifetime of alkaline paper and handling lifetime of acidic paper. Air filtration has no effect on the display lifetime of alkaline paper, as predicted lifetimes are roughly the same for all pollutant conditions and the control. The only case, where air filtration could realistically have a beneficial effect (if all lifetimes over 1000 years are assumed to be acceptable), is the handling lifetime of acidic paper, which is predicted to increase by approximately two centuries in the repository with air filtration, at 18 °C and 43% RH.

8.3.3. Decreasing the RH

Decreasing relative humidity as a preservation measure was already thoroughly described by Sebera, when he introduced isoperms [54]. He assumed a linear dependence of the degradation rate on the RH, which received some criticism and revision [55]. Although this relationship might hold in the approximately linear middle part of the water sorption curve, this might not be the case for all paper types. Results from the experiment carried out at a low RH (section 7.3.), show that chain scission in acidic samples (both with pH between 5 and 6) are affected by change in RH, as the degradation rates at a lower RH were significantly decreased.

Decrease factors of 1.3 and 2.8 were obtained for the two acidic papers. To assess the behaviour of a mildly acidic paper, the factors 1.3 and 2.8 were averaged, which gave a factor of 2. This is consistent with the factor, obtained by assuming a linear effect of RH on acidic papers (43% / 21% ≈ 2).

Since the lifetime of paper is linearly dependent on the degradation rate, an approximation can be made that it is also in linear dependent on relative humidity, providing the assumption on the rate being linearly dependent on RH is correct. Handling lifetimes were therefore assessed using Equation 77, described in section 8.2.1.

Lifetimes were calculated for acidic papers, rag and Whatman, but not for alkaline paper, as it is thought to be generally insensitive to RH changes in the investigated RH range. Rag and Whatman paper were assumed to be similarly RH-dependent to acidic papers based on their similar pH, although unfortunately insufficient degradation occurred in the experiment described previously (section 7.3.) to confirm that.

A decrease in RH of 5% was selected as a reasonable preservation measure, which could be possible to implement. The average handling lifetimes at 18 °C and 38% RH, calculated at realistic pollutant conditions (100 ppb AcOH and 10 ppb NO_2) are shown in Table 8.14, together with predicted lifetimes at 18 °C and 43% RH to allow direct comparison. The figures are not rounded up due to asymmetrical uncertainty intervals. An assumption was made that pollutant-affected degradation rates retain the same linear dependence as the rates under control conditions.

Table 8.16: Predicted handling lifetimes at 18 °C, 43% RH and 18 °C, 38% RH. Predictions are made for no pollutants and realistic concentrations of AcOH and NO_2.

	$t_{handling}$ /year					
	18 °C, 43% RH			**18 °C, 38% RH**		
sample	**0 ppb**	**100 ppb AcOH**	**10 ppb NO_2**	**0 ppb**	**100 ppb AcOH**	**10 ppb NO_2**
A1	520	568	325	589	643	368
A2	2590	2238	1965	2931	2532	2223
R	61759	23566	2660	69886	26667	3010
W	1785	1918	1422	2020	2171	1609

A 5% reduction in RH does not achieve much additional preservation. Especially for samples other than A1, which were already predicted to have lifetimes longer than a millennium, such an increase seems insignificant, although the difference in lifetime is the same for all paper types percent-wise. Considering the significant prediction uncertainties already discussed, such an increase in lifetime seems insignificant. If the beneficial effects of decreasing relative humidity were to be comparable to the previously described temperature decrease, the change in RH would have to be much larger.

An average increase in predicted lifetime, if the temperature was decreased by 2 °C, was by a factor of 1.4, as discussed in section 8.3.1. For the same factor to be achieved by decreasing RH, a decrease of 13% would be required, taking the RH level to approximately 30%.

As discussed in the previous Chapter (section 7.3.), colour change of all paper samples was significantly affected by RH. Although experimental data was insufficient to find whether the relationship between RH and ΔE_{00} is actually quadratic, this relationship was assumed, as it was also in relatively good agreement with the relationship, suggested by Michalski [56], $k\ \alpha\ \mathrm{RH}^{1.7}$. Lifetimes were therefore calculated using Equation 78, described in section 8.2.1. These assumptions are approximate and more experimental data is needed to either confirm or discard them. As no other colour change rate dependence on relative humidity was found in the literature, this was used to make approximate predictions. Average lifetimes, corresponding to an RH decrease of 5% at realistic pollutant conditions, are shown in Table 8.15. Predicted lifetimes at 18 °C and 43% RH are shown as well to allow direct comparison.

Table 8.17: Predicted display lifetimes at 18 °C, 43% RH and 18 °C, 38% RH. Predictions are made for no pollutants and realistic concentrations of AcOH and NO_2.

	$t_{display}$ /year					
	18 °C, 43% RH			**18 °C, 38% RH**		
sample	**0 ppb**	**100 ppb AcOH**	**10 ppb NO_2**	**0 ppb**	**100 ppb AcOH**	**10 ppb NO_2**
A1	5581	5786	4783	7147	7409	6125
A2	6808	5502	4202	8718	7046	5380
B	262	277	260	336	355	332
R	48878	3934	14666	62587	5037	18780
L	4155	1363	3308	5321	1745	4236
W	1181	1113	1078	1512	1425	1380

Based on the assumption, described above, display lifetimes would be significantly prolonged if the RH was decreased by 5%. However for most paper types, the realistic benefit of that is not as clear, as the lifetimes were predicted to be over a millennium even at the original RH level. A significant improvement can, however, be appreciated for alkaline paper, where lifetimes at the lower RH are predicted to be approximately 500 years, which is approximately a century longer than at 43% RH. The effect of a 5% RH decrease on display lifetimes is similar to a 2 °C decrease for most paper types, although it is somewhat smaller for paper types with the lowest colour change rates (acidic papers and rag). The effect on the most sensitive alkaline paper is comparable.

8.3.4. Comparing the effects of different measures

Of the three possible preservation measures, described above, decreasing the temperature seems to be the most effective. Of course the effectiveness depends on how much the temperature is decreased and how much energy (and resources) would be required for such a decrease. A similar effect could be achieved by reducing the RH, although the difference in RH would have to be much larger (this is due to a linear versus exponential effect of RH and T, respectively), at least in terms of DP loss, i.e. handling lifetimes. The effects on display lifetimes are more comparable, as the effect of RH is assumed to be approximately quadratic (section 7.3.). To visually compare all measures, graphs were created for each paper type separately. The graphs show predicted lifetimes under control conditions (no pollutants) and when exposed to realistic concentrations of AcOH and NO_2, where NO_2 concentration was taken from the environmental monitoring results, described in Chapter 4. The starting points are lifetimes, predicted at 18 °C, 43%, with no air filtration, and different environmental management options are compared to that point. As shown in the previous sections, the effects of all preservation measures are likely to fall within prediction uncertainties of the control samples, which is unavoidable when using the Arrhenius approach. Therefore the plots below are made without uncertainty intervals.

Predicted handling lifetimes of acidic paper 1 are shown in Figure 8.10.

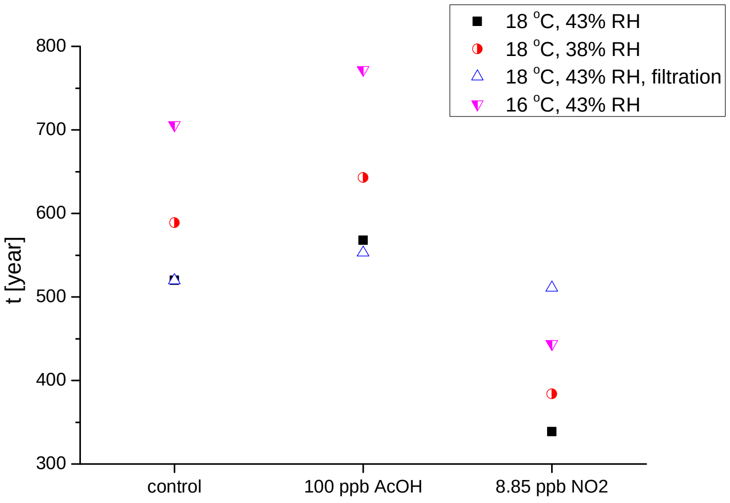

Figure 8.10: Predicted handling lifetimes of acidic paper 1 with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

In terms of the control and the samples, exposed to AcOH, the most beneficial effect can be observed for the decrease in temperature. This is not surprising, as AcOH had no effect on the degradation of acidic paper and the control was not exposed to pollutants at all. More interesting is the case of samples at the NO_2 concentration, measured in the repository without air filtration. Filtration has the most effect as nearly all NO_2 is removed (the concentration, measured in the repository with air filtration, was only 0.3 ppb). The preservation effect is therefore larger compared to the decrease in temperature by approximately 100 years. In order for the same effect to be achieved only by decreasing the temperature, the difference in temperature would have to be significantly larger, approximately 4 °C (T would have to be decreased to 13 °C).

Predicted handling lifetimes of acidic paper 2 are shown in Figure 8.11.

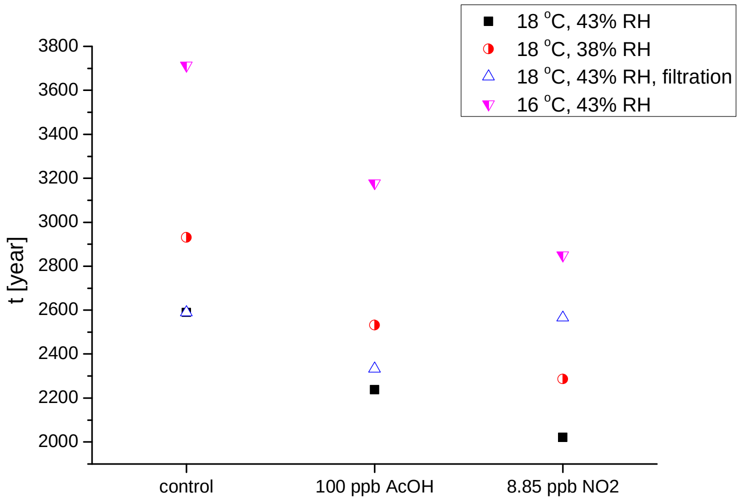

Figure 8.11: Predicted handling lifetimes of acidic paper 2 with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

The effects of different measures are not entirely the same for acidic papers 1 and 2. Again a decrease in temperature seems most beneficial for the control and AcOH exposure, however, in this case it would have the most effect on the lifetime, predicted for NO_2 exposure as well. The effect is larger than complete removal of pollutants, as acidic paper 2 was less affected by NO_2 than acidic paper 1. Decreasing the RH has less effect than air filtration for NO_2 exposure, but would be more beneficial in terms of AcOH exposure. AcOH, however, is not very critical and even with no additional preservation measures acidic paper 2 would reach a handling lifetime of approximately 2000 years in the worst case, shown in the graph.

Predicted handling lifetimes of alkaline paper are shown in Figure 8.12.

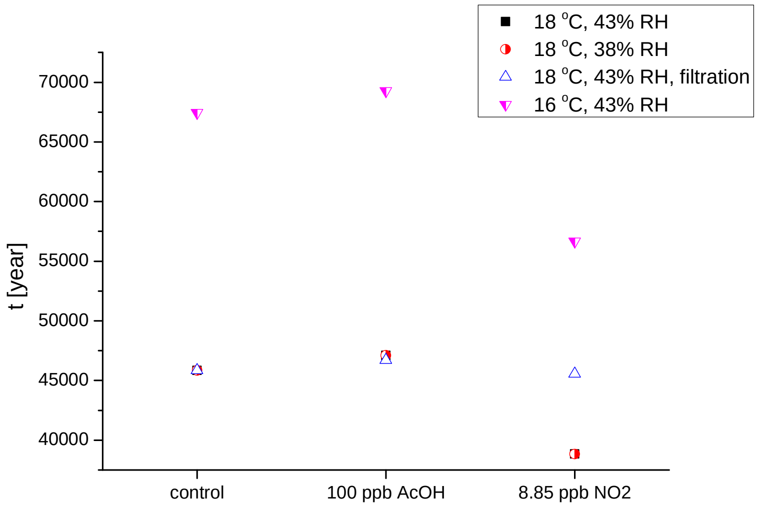

Figure 8.12: Predicted handling lifetimes of alkaline paper with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

It was assumed that a small RH change in the range discussed has no effect on the stability of alkaline paper, so no benefits of decreasing the RH are shown on the graph. Filtration has a beneficial effect in terms of NO_2 exposure, as predicted lifetime with air filtration is the same as that of the control. No effect of AcOH was observed, so filtration would have no effect in that sense. Decreasing the temperature has a much larger beneficial effect with lifetimes under all three conditions being significantly increased. However even if no preservation measure is taken, the lifetime of alkaline paper would be several millennia, so realistic benefits of the preservation measures discussed are debatable.

Predicted handling lifetimes of rag paper are shown in Figure 8.13.

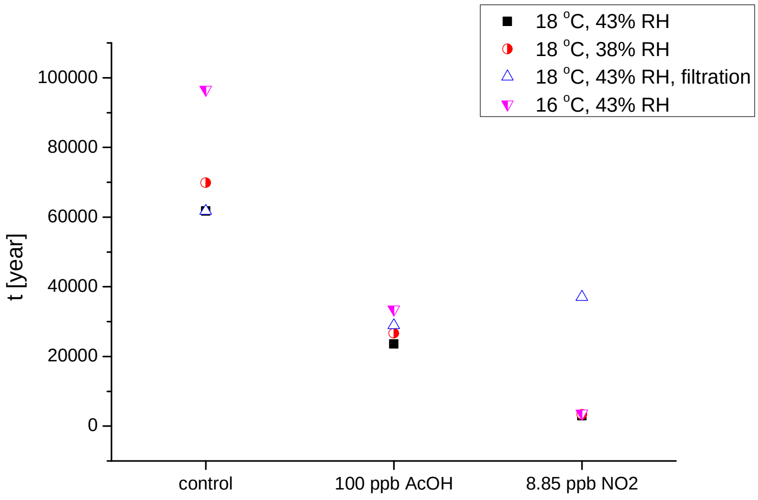

Figure 8.13: Predicted handling lifetimes of rag paper with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

Interestingly decreasing the temperature would have very little effect as well, especially in comparison with air filtration, when NO_2 induced degradation is considered. A lower temperature has more effect compared to air filtration in terms of AcOH, but the difference is very small, and therefore insignificant. A similar observation can be made for a lower RH at all three conditions. It should, however, be pointed out that rag paper would reach very long handling lifetimes (several millennia) even without additional preservation measures, i.e. at 18 °C, 43% RH and no air filtration.

Predicted handling lifetimes of Whatman paper are shown in Figure 8.14.

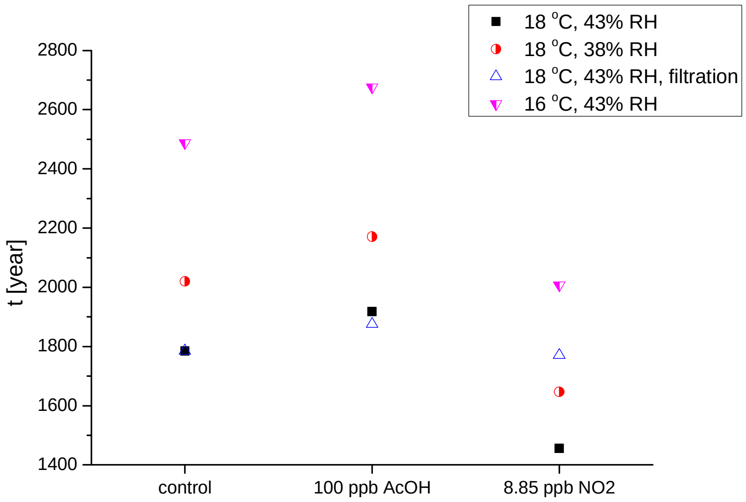

Figure 8.14: Predicted handling lifetimes of Whatman paper with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

Different preservation measures would have a very similar effect on Whatman paper as those on acidic paper 2. This means that decreasing the temperature by 2 °C would have more beneficial effect than air filtration. Filtration would, however, be preferable to decreasing the RH by 5%, at least in terms of NO_2 induced degradation. No negative effect of AcOH was observed, so air filtration would have no effect in that sense. Even with no additional preservation measures, Whatman paper has a predicted handling lifetime of approximately 1500 years.

It was shown that for most papers decreasing the temperature by 2 °C would be more beneficial than air filtration. Different observations were only made for acidic and rag paper, where rag paper would reach incredibly long handling lifetimes regardless of pollutant presence. All samples, but the acidic, would reach lifetimes of over 1500 years, so realistically acidic paper is possibly the only paper type, where preservation measures are needed. Although decreasing the temperature would have a significant beneficial effect, it would have to be decreased by 4 °C to reach the same preservation effect as removing NO_2.

Similar assumptions, used for predicting handling lifetimes, were made for display lifetimes. The comparative graphs are therefore plotted in the same way.

Predicted display lifetimes of acidic paper 1 are shown in Figure 8.15.

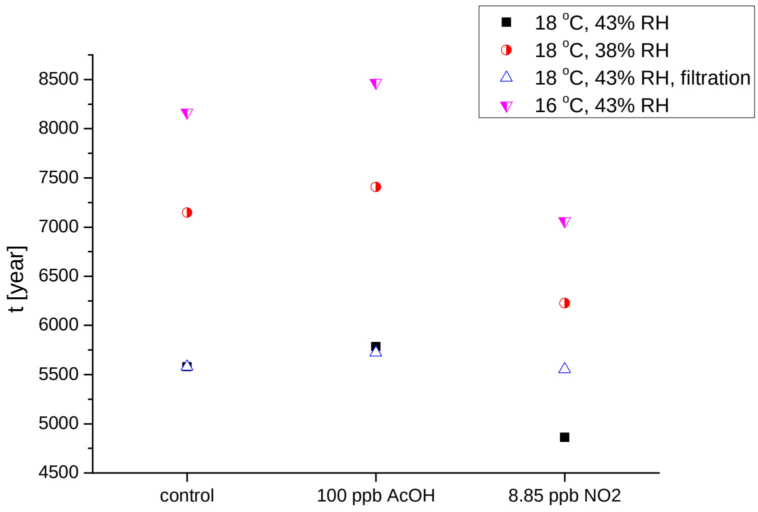

Figure 8.15: Predicted display lifetimes of acidic paper 1 with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

Display lifetimes of acidic paper 1 would be most positively affected by decreasing the temperature. Decreasing the RH would have a significant positive effect as well, as would to some extent air filtration. Although air filtration would eliminate the negative effect of NO_2, it would not have as much effect as the other two measures, which would increase the lifetimes beyond the predicted lifetime of the control. All predicted display lifetimes, however, are several millennia.

Predicted display lifetimes of acidic paper 2 are shown in Figure 8.16.

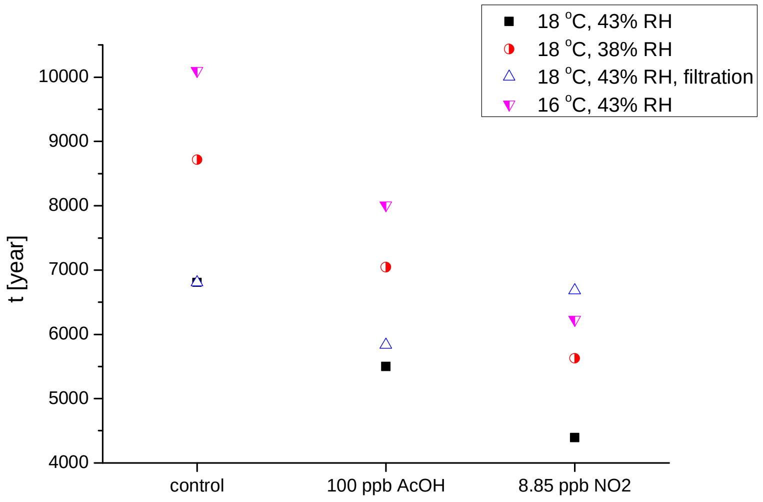

Figure 8.16: Predicted display lifetimes of acidic paper 2 with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

The predicted behaviour of acidic paper 2 is significantly different to acidic paper 1. Air filtration seems to be the most effective preservation measure, especially when NO_2 exposure is considered. As the negative effect of AcOH is considerably smaller, the benefits of air filtration are insignificant in terms of AcOH. Significant positive effects of decreasing the temperature or RH can be observed, although neither of the two measures would have quite as much effect on paper, exposed to NO_2, as air filtration. Similar to acidic paper 1 all predicted display lifetimes are several millennia, even if no additional preservation measure is taken.

Predicted display lifetimes of alkaline paper are shown in Figure 8.17.

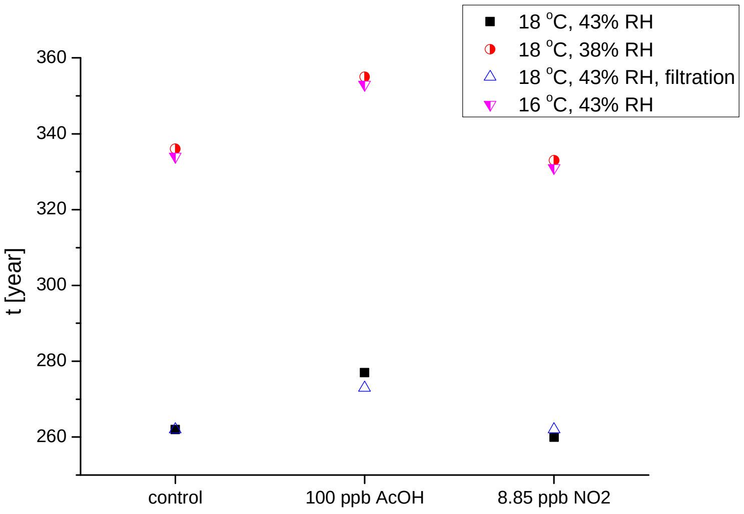

Figure 8.17: Predicted display lifetimes of alkaline paper with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

Predicted lifetimes of alkaline paper are significantly shorter compared to the other paper types. Air filtration would have a very small positive effect, increasing the lifetime to the prediction made for the control sample. The other two preservation measures, however, would have a significantly larger beneficial effect. Both a *T* and RH decrease would extend the lifetime to approximately 500 years. The effect of a *T* decrease is slightly greater, although when prediction uncertainties are considered the difference between the two measures is insignificant. With alkaline paper being the most sensitive one in terms of colour change, it seems like a 2 °C *T* decrease or a 5% RH decrease would be the most beneficial preservation option.

Predicted display lifetimes of rag paper are shown in Figure 8.18.

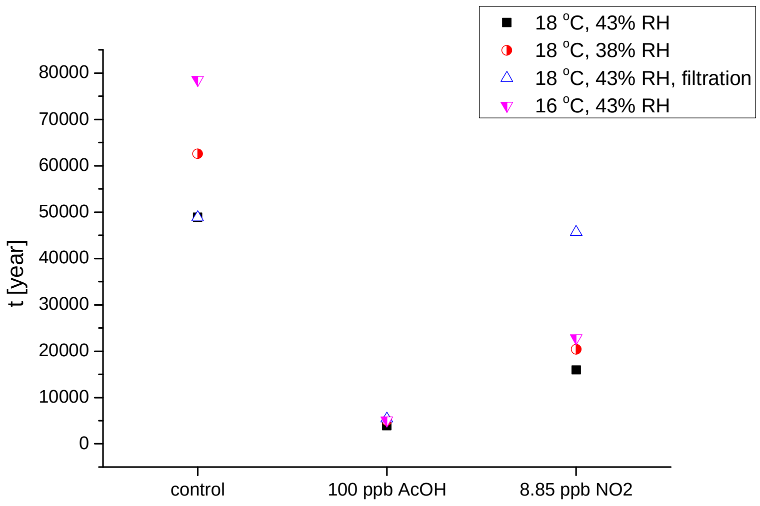

Figure 8.18: Predicted display lifetimes of rag paper with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

Similar to acidic paper 2 air filtration would have the most beneficial effect on rag paper. For the paper, exposed to NO_2, the benefits would be greater compared to decreasing T or RH, which would have a relatively small effect compared to the other paper types. The effect of AcOH on the display lifetime of rag paper is atypically large and would not be affected significantly by any preservation measure. It should, however, be taken into account that even the shortest predicted display lifetime (100 ppb AcOH at 18 °C, 43% RH) is approximately 4000 years, which means additional preservation measures are not necessarily needed.

Predicted display lifetimes of lignin-containing paper are shown in Figure 8.19.

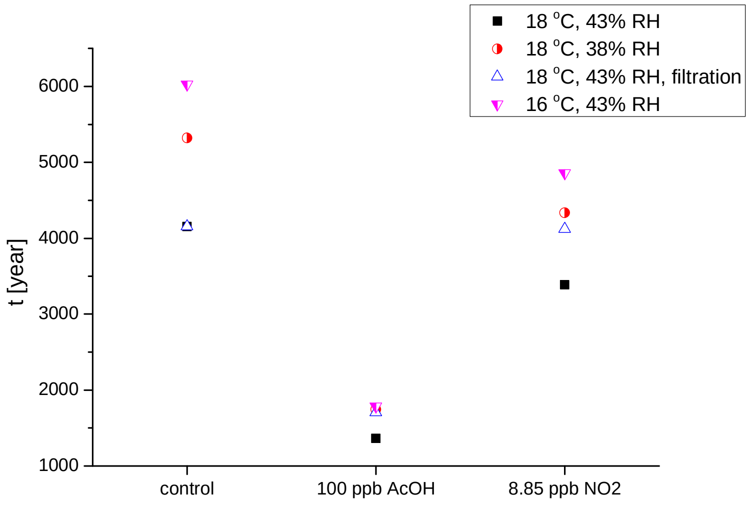

Figure 8.19: Predicted display lifetimes of lignin-containing paper with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

Similar to rag paper a significant effect of AcOH can be observed, however the lifetimes, predicted for lignin-containing paper are significantly shorter. Both *T* and RH decrease have a positive effect on the predicted lifetimes, although the effect of *T* is slightly larger (when 2 °C and 5% are compared). Air filtration would have a significant beneficial effect as well. The differences between the measures are well within prediction uncertainties. Although display lifetimes of lignin-containing paper are amongst the shortest of all studied paper types, they still reach over 1000 years.

Predicted display lifetimes of Whatman paper are shown in Figure 8.20.

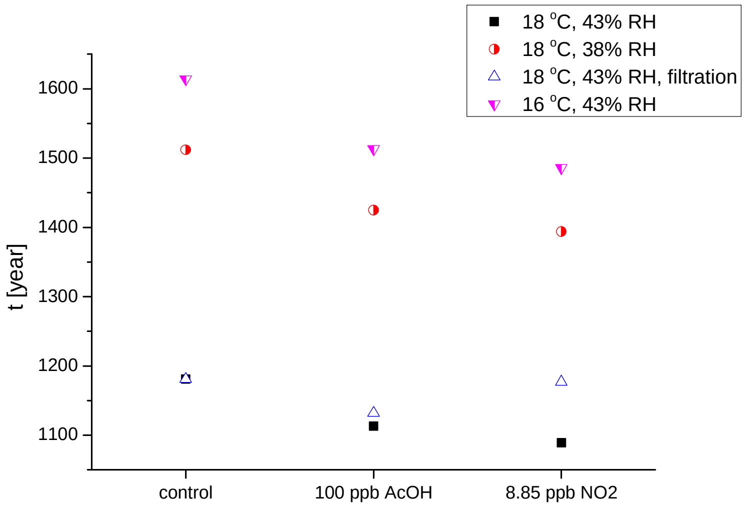

Figure 8.20: Predicted display lifetimes of Whatman paper with different preservation measures. The reference at 18 °C, 43% RH and no filtration is shown in black.

The effects of preventive measures on Whatman paper are similar to the predicted effects on alkaline paper. Air filtration would have some positive effect, increasing the lifetime to the level of the control (i.e. eliminating negative effects of NO_2 and decreasing negative effects of AcOH). Temperature and relative humidity decrease, however, would have significantly more beneficial effect, prolonging the predicted lifetime by several centuries. The difference between the hypothetical *T* and RH decrease is relatively small.

Similar to handling lifetimes the display lifetimes would, in most cases, be most affected by a decrease in temperature by 2 °C, although a decrease in RH by 5% would give very similar results. Acidic paper 2 and rag paper, on the other hand, would benefit most from air filtration, reducing the negative effect of NO_2. Predicted lifetimes of the two, however, are several millennia long.

Overall the results for handling and display lifetimes are not entirely the same, as the most sensitive paper in terms of chain scission (i.e. acidic paper) would benefit most from air filtration, and the most sensitive one in terms of colour change (i.e. alkaline paper) would be more affected by a decrease in *T* or RH.

8.3.5. Assessment method for paper-based collections

Environmental conditions normally found in an archival repository, are usually not extreme enough for one degradation factor to have a predominant affect on paper degradation. Although this is fortunate in terms of collection preservation, it makes assessing beneficial effects of different preservation measures somewhat more complicated.

An important degradation factor, which should be taken into account as well, is the type of paper itself. Papers differ according to initial pH and their composition and that has an effect on how resistant to degradation factors the paper is. This could be seen from the very different lifetime predictions for different paper types, discussed in the previous sections.

In order to propose a method for assessing the benefits of different measures, some simplifications were made based on the results presented so far. Papers were divided into classes based on their sensitivity and different classes are proposed for different paper properties, as some paper types are more stable in terms of chain scission, but are sensitive in terms of colour change and vice versa (e.g. alkaline and acidic paper, respectively).

Average degradation activation energies were calculated for each class of papers, which can then be used in approximate calculations. As NO_2 is very likely to cause degradation by a different mechanism (oxidation in addition to acid-catalysed hydrolysis) the activation energies for NO_2 exposure were calculated separately. These should be used when the collection is exposed to significant NO_2 concentrations.

In terms of *DP* loss (cellulose chain scission) sensitivity the papers were divided into two classes based on their activation energies, predicted lifetimes under control conditions, starting *DP* values and degradation rates. The more sensitive class I contains acidic papers (and Whatman paper, although for assessments in archival collections this is not really relevant), which all have initial pH values between 5 and 6. The less sensitive class II contains alkaline and rag paper, which have significantly different initial pH values, but are both quite resistant to degradation. Average activation energy for class I is 121 kJ/mol, which should be used for calculations only if the collection is not exposed to a significant concentration of NO_2. A lower activation energy was determined for degradation, affected by NO_2, 73 kJ/mol. Average activation energies, determined for class II were approximately 10 kJ/mol higher, 133 kJ/mol in the absence of NO_2 and 77 kJ/mol for NO_2 exposure.

As activation energies and rates (and therefore predicted lifetimes) differed even more in terms of colour change, the papers were divided into three classes. The most sensitive class I contains alkaline and Whatman paper, the less sensitive class II contains both acidic papers and lignin-containing paper and the least sensitive class III contains only rag paper. The average activation energies are 96 kJ/mol for class I, 122 kJ/mol for class II and 125 kJ/mol for class III. Interestingly the classes differ much less in terms of NO_2 exposure, as the average activation energies for all three are between 93 and 95 kJ/mol. The summary is given in Table 8.16.

Table 8.18: Sensitivity classes with average activation energies.

	samples		**E_a /kJ/mol**		**$E_{a\,NO2}$ /kJ/mol**	
class	*DP*	ΔE_{00}	*DP*	ΔE_{00}	*DP*	ΔE_{00}
I	A, N, W	B, W	121	96	73	95
II	B, R	A, N, L	133	122	77	93
III		R		125		94

As discussed previously, lifetime or effect assessment, if simplified, differs according to environmental conditions the collection is subjected to. If it is exposed to high concentrations of very damaging pollutants, such as NO_2, a simple dose approach, suggested by Tétreault [73] can be used without risking significant prediction errors. This could be done both for handling and display lifetimes for all three classes of paper. It is, however, only suggested to do so in concentrations above 100 ppb, where the effect of the pollutant is much greater compared to the effects of T and RH. Such conditions, however, are not commonly found in archival repositories.

This approach cannot be used for pollutants, which cause significantly less damage to paper, such as AcOH. In terms of handling lifetime AcOH effect can be neglected in concentrations up to 300 ppb for all paper types, except rag paper. 300 ppb was calculated to be the significant effect threshold for acidic paper 2 earlier in this

Chapter (section 8.2.1.) and no effect was observed for the other paper types. AcOH concentration, higher than 300 ppb, would not be commonly encountered in archives or libraries [87].

If the collection is exposed to NO_2 concentrations below 100 ppb or AcOH concentrations above 100 ppb the following equation can be used to assess handling lifetimes at different pollutant concentrations:

$$kt = (k_{T,RH,pH} + k_{pollutant})t = (k_{T,RH,pH} + m_{T,RH,pH}c_{pollutant})t = const. \quad (71)$$

To simplify the calculations one k and one m value are given for each class of paper. To avoid underestimation of effects the worst-case-scenario k and m for each class are used. The values at 18 °C and 43% RH for handling lifetimes are shown in Table 8.17.

Table 8.19: k and m values for handling lifetimes for sensitivity classes I and II.

class	samples	$k_{18\ °C,\ 43\%\ RH}$ /year^{-1}	m_{AcOH} /year^{-1}ppb^{-1}	m_{NO2} /year^{-1}ppb^{-1}
I	A, N, W	2.94E-06	1.14E-09	1.77E-07
II	B, R	6.33E-08	7.71E-10	1.06E-07

This approach is applicable to concentrations of NO_2 commonly found in repositories. Once the pollutant concentration-dependent lifetime (or degradation rate) is calculated, it can be adjusted to different temperatures using Equation 76, described in section 8.2.1. Approximate activation energies for each sensitivity class, shown in Table 8.16, can be used for calculations. To include a change in RH, Equation 77 can be used

$$t_1 RH_1 e^{-\frac{Ea}{RT_1}} = t_2 RH_2 e^{-\frac{Ea}{RT_2}}. \quad (77)$$

The assessment method for display lifetimes is slightly different due to different pollutant thresholds, calculated in section 8.2.1, and a different dependence of colour change on relative humidity. Similar to handling lifetimes the simple dose approach ($c \cdot t = const$) can be used for high concentrations of pollutants, which have a significant effect on colour change (such as NO_2 above 100 ppb), although slightly larger errors are expected compared to handling lifetimes. The effect of AcOH on the other hand is not as simple as for handling lifetimes. The thresholds, determined in section 8.2.1, differ significantly according to sensitivity class, as colour change of the most sensitive papers is actually the least AcOH dependent. For class I AcOH can therefore be omitted when the concentration is below 100 ppb (similar to handling lifetimes of all paper types) without significant prediction errors, however for classes II and III it should be taken into account when assessing lifetimes. It is therefore likely that both pollutants will need to be taken into account when assessing display lifetimes. In the absence of experimental data, the simplest mechanism assuming additivity of both effects, is used. No synergistic effect of the two pollutants was observed in the experiments at 80 °C, where samples were exposed to a mixture of NO_2 and AcOH (Chapter 7, sections 7.2.1. and 7.2.2.), so a conclusion was made that a mixture of both pollutants does not cause more degradation than the sum of individual pollutants. The Equation 71 therefore becomes:

$$kt = (k_{T,RH,pH} + k_{pollutant\ 1} + k_{pollutant\ 2})t =$$

$$= (k_{T,RH,pH} + m_1 c_1 + m_2 c_2)t = const. \qquad (81)$$

The lifetimes can then be assessed using Equation 71 or 81 and k and m values, shown in Table 8.18.

Table 8.20: *k* and *m* values for display lifetimes for sensitivity classes I, II and III.

class	**samples**	$k_{18\,°C,\ 43\%\ RH}$ **/year^{-1}**	m_{AcOH} **/year^{-1}ppb^{-1}**	m_{NO2} **/year^{-1}ppb^{-1}**
I	B, W	5.72E-02	7.78E-06	1.21E-04
II	A, N, L	3.61E-03	7.40E-05	1.37E-04
III	R	3.07E-04	3.51E-05	7.16E-05

Following that, the lifetimes can be assessed according to temperature and relative humidity, using a quadratic dependence on the RH, described in section 8.2.1:

$$t_1 RH_1^2 e^{-\frac{E_a}{RT_1}} = t_2 RH_1^2 e^{-\frac{E_a}{RT_2}}. \qquad (78)$$

Although the approaches, described above, are simplifications of actual behaviour of papers, they could be useful in assessing the impact of different environmental conditions. They might seem somewhat more complicated to implement, compared to established dose [73] or isoperm [54] approaches, however they take into account pollutants in a realistic concentration range, *T*, RH and different stability of different paper types, which could be useful when predicting the lifetime of a real archival collection.

8.4. Conclusion

Handling and display lifetimes of all paper types under different realistic temperatures, relative humidity and pollutant conditions were calculated and discussed. Lifetimes, predicted at realistic pollutant concentrations (100 ppb AcOH and 10 ppb NO_2), were found to be within prediction uncertainties of the control samples for all paper types. Uncertainty intervals, however, were significant, which is common in Arrhenius studies. A clear trend of NO_2 causing more paper degradation and reducing paper lifetime compared to AcOH (both in realistic concentrations) was nevertheless observed.

Lifetimes under different hypothetical environmental management options (*T* or RH decrease and air filtration) were discussed. Of the three options presented here, a temperature decrease of 2 °C would be the most beneficial for the majority of paper types. However, this was not the case for acidic paper, where the most beneficial measure was found to be air filtration, which significantly decreases the concentration of NO_2. The same effect could, however, be achieved by a larger temperature decrease, for example using cool storage.

The concepts of pollutant dose and threshold were discussed and a method of calculating both proposed. Pollutant thresholds, at which the effect of pollutants becomes significant compared to the uncertainty in the *T* and RH control, were calculated. For most paper types the thresholds were above concentrations typically found in archival repositories. The two exceptions were acidic paper 1 (in terms of handling lifetime) and rag paper (in terms of both handling and display lifetime). However, rag paper would reach lifetimes of several millennia regardless of pollutant presence.

Lifetimes were calculated using both the ‘traditional’ dose approach ($c \cdot t = const$) and the suggested approach. It was shown that using the traditional pollutant dose approach could result in significant overestimations of lifetimes, as this method does not take into account the degradation, caused by T and RH and should therefore only be used if the pollutant effect can be prioritised over the other effects on paper degradation. Additionally a method for assessing lifetimes of a real archival or library collection, based on different stability towards chain scission or colour change, was proposed.

9. Recommendations for archival storage

Based on the results and discussion, described in the previous two Chapters 7 and 8, recommendations can be made for the long-term storage of paper-based collections. The assessment method, proposed in section 8.3.5., will be used to compare and optimise beneficial effects of different preservation measures on a ‘typical’ collection, found in an archival repository and on the collection, held in the Nationaal Archief. Environmental conditions, typical for an archival repository, are used for predictions, 18 °C and 50% RH ([146], Chapter 4).

9.1. Different environmental conditions in a typical archival collection

A typical archival collection in a Western repository is thought to contain approximately 70% acidic paper [1], which is prone to more rapid degradation. The remaining 30% are more resistant towards degradation (mainly rag paper and possibly contemporary alkaline paper) and therefore cause fewer concerns. Preservation measures are usually employed to prolong the lifetimes of the most sensitive part of the collection [5], which represents the majority of the objects in an archive.

9.1.1. Preservation measures

To investigate the benefit of different preservation measures to a typical collection, the assessment method, introduced in the previous Chapter (section 8.3.5.), is used. As the samples, used in the experiments, were selected to be representative of typical paper types in archival collections, generalization of the results and the assessment method is possible. In terms of handling, 70% of a typical collection could be classified as class I (acidic paper) and 30% as class II (rag and alkaline paper).

If AcOH is assumed to be present in concentrations up to 100 ppb, which is consistent with a recent survey of archives and libraries [87], the effect of AcOH can be neglected in estimations of lifetimes, because as shown in the previous chapters it has a negligible effect. On the other hand, concentrations of NO_2, usually encountered in archival collections, have to be taken into account and the pollutant-affected lifetime should be calculated according to Equation 71, described in Chapter 8. A realistic concentration of 10 ppb has been used for estimations. Acidic papers usually have *DP* values between 500 and 1000 and the two realistic papers, forming class I in this study, had initial *DP*s of 560 and 680 units. The worst case scenario, *DP* = 500, was used in the calculations below. The lifetime of class I papers was also calculated as a range of values, using *DP*s of 500 and 1000 as limits. Pollutant-dependant lifetime at 18 °C and 43% RH was therefore calculated as:

$$kt = (k_{class\ I,18\ ^0C,43\%\ RH} + k_{NO2})t = (k_{T,RH,pH} + m_{T,RH,pH}c_{NO2})t = \frac{1}{300} - \frac{1}{500}$$

$$t = \frac{\left(\frac{1}{300} - \frac{1}{500}\right)}{2.94*10^{-6}\ \mathrm{year}^{-1} + 1.77*10^{-7}\mathrm{year}^{-1}\mathrm{ppb}^{-1}*10\mathrm{ppb}}, \tag{82}$$

which gives a lifetime of 280 years. To estimate the lifetime in the most common archival conditions, however, the lifetime needs to be adjusted to 50% RH, using:

$$t_1RH_1 = t_2RH_2 \Rightarrow 280yr * 43 = t * 50,$$

which gives a lifetime of 240 years.

If the two limit *DP* values for class I are used, lifetimes range between 240 and 430 years. In a rather pessimistic estimation 70% of the collection would ‘survive’ between 240 and 430 years if the temperature was 18 °C, relative humidity 50% and no air filtration was installed. However, this estimation is based on experimental results from only two acidic papers. In reality there are always going to be some objects, which are more prone to degradation and will therefore degrade faster and some, that will degrade slower.

Depending on what the preservation goals of an institution are, or what the archival regulations prescribe, a decision would be required on whether additional preservation measures are needed. This would also depend on what is perceived as acceptable, i.e. how fitness (‘end of life’) thresholds are defined (here *DP* = 300 and ΔE_{00} = 15 were set as limits).

Using the same formula and appropriate *k* and *m* values, the handling lifetime of a class II paper can be calculated. Class II consists of contemporary alkaline and rag paper, which differ in their initial *DP* values. Rag papers usually have lower *DP*s, typically between 1500 and 1800 [53], so a typical rag paper *DP* was selected as the starting point to avoid over-estimation of lifetimes. This was also used because rag papers are typically much more abundant in archival collections than contemporary alkaline paper [184]. A lifetime range, using *DP*s of 1500 and 1800 as limits, was calculated at 18 °C, 50% RH and 10 ppb NO_2. Lifetimes between 2050 and 2150 were obtained, which means 30% of a typical collection would therefore last for two millennia with no additional preservation measures.

Display lifetimes are determined in a similar way, using representative m and k values for each class. A very small percent of a typical archival collection is composed of contemporary alkaline paper, which is the most sensitive in terms of colour change. A survey in the National Archives of Finland [184] revealed only a couple of percent of their collection was composed of contemporary documents. However for estimation purposes and not to underestimate the detrimental effects on the collections, a decision was made to estimate 10% of a typical collection to be class I in terms of colour change sensitivity. Since even lignin-containing paper was classified as class II based on the experiments, the rest of the collection can be assumed to consist of class II and III papers.

For class I paper (10% of the collection) AcOH could be neglected, so the colour change rate can be calculated for 10 ppb NO_2 exposure only. For papers from the other two classes both pollutants need to be taken into account and an assumption was made that the effects are additive (Chapter 8, section 8.3.5.). The display lifetime is therefore calculated from:

$$kt = (k_{class\ II,III,18\ ^{0}C,43\%\ RH} + k_{NO2} + k_{AcOH})t =$$

$$(k_{T,RH,pH} + m_{NO2}c_{NO2} + m_{NO2}c_{AcOH})t = 15 \qquad (83)$$

Estimated lifetime of class I paper is 250 years at 43% RH, which needs to be adjusted to 50% RH using Equation 78 (within the same *T*):

$$t_1 RH_1^2 = t_2 RH_2^2 \Rightarrow 250yr * 43^2 = t * 50^2\ , \qquad (78)$$

which gives a display lifetime of 190 years. This estimation excludes the effect of light, so this lifetime could only be achieved if the objects were mainly kept in the dark, as is common for archival collections.

Fortunately this is limited to approximately 10% of the collection, although unfortunately this is not the paper that is also the most sensitive in terms of handling. Estimated lifetimes for classes II and III are approximately 900 and 2500 years, respectively. The majority of the collection (>90%) would therefore reach at least 900 years (in terms of acceptable colour change) if no additional preservation measures were taken.

With the reference lifetimes at 18 °C and 50% RH calculated, a decision has to be made whether the predicted lifetimes are sufficiently long or not. However, since both handling and display lifetimes of the most sensitive part of the collection are bellow 500 years, some preservation measures probably need to be taken to extend the lifetimes.

Preservation measures can be investigated in two ways:

a) by setting a target lifetime (e.g. 500 years [158]) and calculating what environmental conditions are necessary to reach that target
b) by deciding on a feasible preservation measure (e.g. what decrease in T or RH is achievable) and calculating the resulting lifetime.

A decision on which route to take is up to the stakeholders, as it would depend on a number of factors beyond the scope of this work [5]. Both ways, however, are presented here to demonstrate the approach.

9.1.1.1. Target lifetime

A target lifetime of 500 years for the most sensitive part of the collection (the rest of the collection would reach lifetimes well beyond that) was selected as an example. Lifetimes can be prolonged by decreasing T or RH, or by reducing pollutant concentration, if the effect of the pollutant is significant. The decrease in T or RH, needed for extending the handling lifetime to 500 years, can be calculated using Equation 77 from the previous Chapter (section 8.2.1.) and E_a for class I paper. Here the worst case scenario, using paper with DP = 500, was calculated:

$$t_1 RH_1 e^{-\frac{E_a}{RT_1}} = t_2 RH_2 e^{-\frac{E_a}{RT_2}} \Rightarrow \tag{77}$$

$$240yr * 50 * e^{-\frac{77*\frac{10^3 J}{molK}}{R*291{,}15\,K}} = 500yr * RH_2 * e^{-\frac{77*10^3 J/molK}{RT_2}}.$$

If the temperature was kept at 18 °C, the RH would need to be decreased to 24% in order for the most sensitive part of the collection to reach 500 years. At the same environmental conditions class II (i.e. 30% of the collection) would reach approximately 4300 years.

If the lifetime was controlled by adjusting the temperature, the temperature would need to be decreased to 11 °C (a decrease of approximately 7 °C). The rest of the collection would reach a lifetime of approximately 5100 years under the same conditions.

To see whether the target lifetime can be achieved by employing air filtration to reduce pollutant levels, a theoretical lifetime in a pollutant-free environment can be calculated from Equation 71, with $c_{NO2} = 0$ ppb. The theoretical lifetime is approximately 390 years, which means filtration alone could not ensure the most sensitive papers would achieve a lifetime of 500 years. Therefore additional measures would have to be taken.

Using the equations above it is now possible to calculate environmental conditions at which the lifetime of class I objects would equal 500 years with air filtration installed. The calculated conditions are 15 °C and 50% RH, which means the temperature would have to be decreased significantly, although by 4 °C less than without air filtration. At the same conditions the rest of the collection, classified as class II, would reach a handling lifetime of approximately 30000 years. Similarly a lifetime of 500 years would be achieved at a decreased RH, 38%, and 18 °C.

If the target lifetime for class I objects was set to 1000 years, it could only be reached by further decreasing *T* or RH. Theoretically, providing the linear dependence on RH is still valid in that RH range, it could be achieved by decreasing relative humidity to 12% and maintaining the temperature at 18 °C. In order to reach 1000 years by lowering the temperature alone, it would need to be decreased to 5 °C. Target lifetimes could, of course, also be achieved using a combination of environmental measures, most appropriate for the institution in question. Assuming 95% efficiency of chemical air filtration for removing NO_2, which is realistic considering the measurements in repositories with and without air filtration, showed in Chapter 4, the target of 1000 years could also be achieved using air filtration and either decreasing the RH to 19% or temperature to 9 °C. A summary of possible measures is shown in Table 9.1, although other combinations of environmental conditions can be calculated using the same approach.

Table 9.1: Different preservation options for reaching target handling lifetimes for the most sensitive part of a typical collection.

target lifetime for class I	options **1**	 **2**	 **3**	 **4**
500	18 °C, 24% RH, 10 ppb NO_2	11 °C, 50%, 10 ppb NO_2	18 °C, 38% RH 0.5 ppb NO_2	15 °C, 50% RH, 0.5 ppb NO_2
1000	18 °C, 12% RH, 10 ppb NO_2	5 °C, 50%, 10 ppb NO_2	18 °C, 19% RH, 0.5 ppb NO_2	9 °C, 50% RH, 0.5 ppb NO_2

The same target lifetimes can be set for the purpose of display. The most sensitive part of the collection, estimated to represent ~10%, would achieve a lifetime of 190 years at 18 °C, 50% RH, 10 ppb NO_2 and 100 ppb AcOH. The same target lifetimes can be used, and the impact of preventive measures can be calculated using Equation 78, described in the previous Chapter:

$$t_1 RH_1^2 e^{-\frac{E_a}{RT_1}} = t_2 RH_1^2 e^{-\frac{E_a}{RT_2}} \Rightarrow \tag{78}$$

$$190yr * 50^2 * e^{-\frac{94*\frac{10^3 J}{molK}}{R*291{,}15\ K}} = 500 * {RH_2}^2 * e^{-\frac{94*10^3 J/molK}{RT_2}}.$$

Similar to handling lifetimes, a variety of combinations of measures could ensure the target lifetime is achieved. Unlike for handling lifetime, the concentration of AcOH should be taken into account, at least for sensitivity classes II and III. However to consider the worst case scenario and the maximum effect of all factors, the lifetime of class I was calculated taking into account AcOH as well, although the effect is insignificant. 30% efficiency of chemical air filtration in removing AcOH was assumed, as described in the previous Chapter. Several different preservation options to achieve lifetimes of 500 and 1000 years are shown in Table 9.2.

Table 9.2: Different preservation options for reaching target display lifetimes for the most sensitive part of a typical collection.

target lifetime for class I	**options**			
	1	**2**	**3**	**4**
500	18 °C, 30% RH, 100 ppb AcOH, 10 ppb NO_2	11 °C, 50%, 100 ppb AcOH, 10 ppb NO_2	18 °C, 31% RH, 70 ppb AcOH, 0.5 ppb NO_2	11 °C, 50% RH, 70 ppb AcOH, 0.5 ppb NO_2
1000	18 °C, 22% RH, 100 ppb AcOH, 10 ppb NO_2	6 °C, 50%, 100 ppb AcOH, 10 ppb NO_2	18 °C, 22% RH, 70 ppb AcOH, 0.5 ppb NO_2	6 °C, 50%, 70 ppb AcOH, 0.5 ppb NO_2

As seen from the Table 9.2 above, air filtration alone cannot ensure the target display lifetime will be reached. Filtration in fact has very little effect on display lifetimes, partly due to its inefficiency in removing AcOH. So in order to reach a lifetime of 500 years, temperature or relative humidity would need to be significantly decreased regardless of air filtration (the decrease would actually be approximately the same with or without pollutants).

In terms of achieving a target lifetime of 500 years, the preservation measures for handling and display, involving T or RH decrease, are quite similar. If the temperature or humidity was decreased enough to ensure the majority of the collection could be handled safely for 500 years, the small part of the collection, which is the most sensitive in terms of colour change, would have a long enough display lifetime as well. The same, however, could not be achieved using air filtration alone. The majority of the collection (90%) would reach display lifetimes of over a millennium under each of the conditions, described above.

Deciding on a target lifetime and calculating the required conditions could be a useful tool for archival collection keepers, especially if they are required to follow recommendations or regulations on how long their collection is expected to be preserved into the future.

9.1.1.2. Different preservation measures

This approach might be more useful if an archive or another institution is expected to sustain a collection for ‘as long as possible’ with what is available, e.g. if a certain amount of energy can be consumed to control the environment or a certain amount of funding is available etc. By calculating lifetimes, resulting from these different measures, a decision can be made on the most efficient one.

Unfortunately data on energy consumption of different preventive measures was not available. As it is also likely to differ according to institution, only a theoretical example will be discussed here. For future calculations, however, the theoretical measures can be substituted for those perceived to be the most energy efficient.

Similar to the previous Chapter, where different environmental options were compared for the six paper types (section 8.3.4.), used in the experiments, they are compared for a typical collection according to sensitivity classes. An example for each class is given to facilitate future calculations.

The following measures, chosen arbitrarily, will be compared: temperature decrease of 5 °C, relative humidity decrease of 10% and air filtration with 95% efficiency with respect to NO_2 and 30% efficiency in terms of AcOH. NO_2 and AcOH concentrations without air filtration will be taken as 10 and 100 ppb, respectively, and the starting T and RH conditions are 18 °C and 50% RH, realistic in archival repositories. A 5 °C decrease in temperature is used, as a simple estimation suggested by Michalski [56], is that the lifetime of a collection doubles for every 5 °C decrease. This uses an average E_a of 100 kJ/mol, which is slightly different to the E_a values used here, mainly because different activation energies have been used for different sensitivity classes and pollutant conditions.

The same equations, as used in the previous section, are used here. For handling lifetimes the following equations are used:

$$(2.9 * 10^{-6} yr^{-1} + 1.8 * 10^{-7}\, yr^{-1} ppb^{-1} * 10ppb)t_1 = \frac{1}{300} - \frac{1}{500},$$

$$t_1 * 50 * e^{-\frac{73*10^3 J/mol}{8.314\frac{J}{molK}*291K}} = t_2 RH_2 e^{-\frac{73*10^3 J/mol}{8.314\frac{J}{molK}*T_2}} \qquad \text{(class I)}$$

And

$$(6.3 * 10^{-8} yr^{-1} + 1.1 * 10^{-7}\, yr^{-1} ppb^{-1} 10ppb)t_1 = \frac{1}{300} - \frac{1}{1500},$$

$$t_1 * 50 * e^{-\frac{77*10^3 J/mol}{8.314\frac{J}{molK}*291K}} = t_2 RH_2 e^{-\frac{77*10^3 J/mol}{8.314\frac{J}{molK}*T_2}} \qquad \text{(class II)}$$

Display lifetimes for the three sensitivity classes can be estimated using the following equations:

$$(5.7 * 10^{-2} yr^{-1} + 7.8 * 10^{-6} yr^{-1} ppb^{-1} * 100ppb + 1.2 * 10^{-4}\, yr^{-1} ppb^{-1} 10ppb)t_1 = 15,$$

$$t_1 * 50^2 * e^{-\frac{95*10^3 J/mol}{8.314\frac{J}{molK}*291K}} = t_2 RH_2^2 * e^{-\frac{95*10^3 J/mol}{8.314\frac{J}{molK}*T_2}} \qquad \text{(class I),}$$

$$(3.6 * 10^{-3} yr^{-1} + 7.4 * 10^{-5} yr^{-1} ppb^{-1} * 100ppb + 1.4 * 10^{-4}\, yr^{-1} ppb^{-1} 10ppb)t_1 = 15,$$

$$t_1 * 50^2 * e^{-\frac{93*10^3 J/mol}{8.314\frac{J}{molK}*291K}} = t_2 RH_2^2 * e^{-\frac{93*10^3 J/mol}{8.314\frac{J}{molK}*T_2}} \qquad \text{(class II)}$$

And

$$(3.1 * 10^{-4} yr^{-1} + 3.5 * 10^{-5} yr^{-1} ppb^{-1} * 100ppb + 7.2 * 10^{-5}\, yr^{-1} ppb^{-1} 10ppb)t_1 = 15,$$

$$t_1 * 50^2 * e^{-\frac{94*10^3 J/mol}{8.314\frac{J}{molK}*291K}} = t_2 RH_2^2 * e^{-\frac{94*10^3 J/mol}{8.314\frac{J}{molK}*T_2}} \qquad \text{(class III)}$$

Lifetimes, estimated as shown above, are shown in Table 9.3.

Table 9.3: Handling and display lifetimes (/year) of a collection at different preservation measures.

purpose	sensitivity	**reference** 18 °C, 50% RH, 100 ppb AcOH, 10 ppb NO_2	***T* decrease** 13 °C, 50% RH, 100 ppb AcOH, 10 ppb NO_2	**RH decrease** 18 °C, 40% RH, 100 ppb AcOH, 10 ppb NO_2	**filtration** 18 °C, 50% RH, 70 ppb AcOH, 0.5 ppb NO_2
handling	class I	240	420	300	380
	class II	2000	3800	2600	20000
display	class I	190	370	290	190
	class II	900	1700	2000	1300
	class III	2400	5000	6200	4000

When comparing the beneficial effects of a preventive measure in terms of the handling lifetime, the more sensitive class I represents 70% of a typical collection, whereas in terms of display (i.e. colour change) only 10% is classified as the most sensitive. As mentioned earlier, a 5 °C decrease would not necessarily double the lifetime, at least not in terms of handling. This is due to lower activation energies, determined in the degradation experiments in Chapter 7, compared to the value, used by Michalski [56]. Display lifetimes, on the other hand, would be approximately doubled, as the colour change E_a values were just under 100 kJ/molK. For the majority of the collection a temperature decrease seems like the best option of the three, shown in the table above (Table 9.3). Air filtration would be efficient in terms of handling lifetimes, but would have relatively little effect on display lifetimes, whereas a decrease in RH would be more beneficial in terms of display (due to the assumed quadratic versus linear effect of RH on colour change and chain scission, respectively). Energy (and financial) input of the measures would need to be investigated in order to make a decision on the most appropriate option.

As 30% of the collection, classified as class II in terms of handling sensitivity, would reach lifetimes of several millennia regardless of preservation measures, it might be useful to split the collection into two parts. Stricter environmental control or additional preservation measures could therefore only be used on one part of the collection, which could reduce the overall energy consumption. Most of the collection would achieve display lifetimes of over a millennium if no additional preservation measures were taken, making colour change less of an issue in a typical archival collection. However if display was the main purpose of an institution, light-induced colour change would have to be taken into account as well, which has not been undertaken as a part of the work presented here.

9.1.2. Climate change

The same approach as used in the previous section, where different preservation measures were discussed, can be used to assess the impact of changes in temperature and relative humidity as a consequence of climate change. As the temperature is expected to increase in the future, archives and other heritage institutions might be required to change temperature and humidity settings to values, closer to outdoor conditions, as the energy required to keep them at the current set points becomes too high.

The temperature in Europe is expected to increase by approximately 3 °C on average by the end of the century [185,186]. Predictions have been made for indoor temperatures, for example an idealised unheated room in a historic house is expected to experience an increase in T by approximately 3-4 °C [187]. Currently the annual average temperature is approximately 14 °C, so by the end of the century this would result in an average annual temperature of approximately 18 °C. The temperatures in the repositories of the Nationaal Archief are currently controlled at 18 °C, so it is difficult to predict how an external increase would affect temperatures in archives. However it is possible that the T set point would have to be increased or, perhaps preferably, that more season drift would be allowed. A hypothetical increase in T by 1 °C was used to calculate handling and display lifetimes (Table 9.4).

Assuming no change in the other environmental parameters, predicted handling and display lifetimes of the most sensitive part of the collection would decrease by approximately 20-30 years. The rest of the collection, however, would still ‘survive’ almost a millennium in terms of display and over a millennium in terms of handling.

Table 9.4: Predicted handling and display lifetimes at 19 °C and 50% RH.

purpose	sensitivity	19 °C, 50% RH, 100 ppb AcOH, 10 ppb NO_2 **t /year**
handling	class I	220
	class II	1800
display	class I	160
	class II	790
	class III	2100

A study of the storage facilities of The National Archives (UK), carried out recently [146], showed that seasonal adjustment of *T* and RH set points would have a significant positive effect in terms of energy consumption, saving up to 43% of energy used for environmental control. A positive effect on the collection, based on the isoperm approach, was calculated as well. Suggested temperature set points, resulting from this study, were 16 °C in February, incrementing up to 20 °C in September and then back down to 16 °C by December. Relative humidity settings would change from 35% in February to 55% in September and then back to 35% by December. Although modelling lifetimes at a changing *T* and RH is not as straightforward as the approaches described above, an attempt was made to compare the lifetimes of a typical collection under these conditions to the ones described earlier. Handling and display lifetimes, calculated for conditions, suggested by Hong et al. [146], are shown in Table 9.5. Realistic pollutant concentrations (100 ppb AcOH and 10 ppb NO_2) are assumed.

Table 9.5: Handling and display lifetimes, calculated for changing *T* and RH set points.

purpose	sensitivity	changing T & RH set points **t /year**
handling	class I	290
	class II	2400
display	class I	250
	class II	1200
	class III	3300

Predicted lifetimes for the changing set points are longer in comparison to the ones obtained for 19 °C and 50% RH, which would be the conditions at TNA without changing the set points according to the season. Even the most sensitive part of a typical collection would be safe to handle for almost 300 years, whereas the rest of the collection would 'survive' under these conditions for over a millennium. The display lifetime of the most sensitive theoretical 10% of the collection is somewhat longer, approximately a century compared to stationary conditions of 19 °C and 50% RH. Considering the increased seasonal drift in environmental conditions is also likely to mean significantly reduced energy consumption, it seems like a good solution.

Obviously energy consumption would depend significantly on the type of building, HVAC system and outside *T* and RH conditions, which are beyond the scope of this work. The example above, however, is used to demonstrate that changing temperature and humidity settings according to season could not only be beneficial in terms of energy consumption, but also in terms of collection preservation. When energy consumption should be taken into account in deciding on suitable preservation measures, seasonal drift set points should be considered a valuable option. In colder climates the differences in the winter could possibly be even larger (especially for infrequently accessed materials), saving energy, used for heating, and adding further to the preservation of the collection.

All the calculations above are made to represent a typical archival collection, although the same approach could be used for different paper-based collections, as long what kind of paper the collection consists of is known. Values *k* and *m*, determined for a suitable sensitivity class of paper or even a specific paper type, can be used for calculations in the same way as the calculations above were presented for different parts of a typical collection. For example if a specific collection was composed mainly of rag paper or contemporary alkaline paper, the *k* and *m* values for class II (in terms of handling) would be used and the results would show that the collection would 'survive' several millennia regardless of the conditions. This should be considered when planning preservation measures, as energy or financial resources might be better used elsewhere.

As discussed in the previous Chapter, all the differences between the preservation measures or climate change effects are smaller than prediction uncertainty intervals. Strictly mathematically speaking, this would make most of them insignificant. This, however, cannot be avoided in studies of this nature, where fairly complex experiments are carried out on real historic objects, especially if the experiments are based on the Arrhenius equation. Although the uncertainties of the predictions discussed here are significant, they can still be used to demonstrate trends and compare effects, even if the exact lifetime predictions are not very accurate, as predictions with much smaller uncertainties are not likely to be available.

9.2. Different preservation measures in relation to the collection of the Nationaal Archief

Lifetime predictions, especially in terms of different preservation measures, can also be applied to the collection, held in the Nationaal Archief. The indoor environment in the Nationaal Archief building is strictly controlled, using a separate temperature and relative humidity unit for each repository and an extensive air filtration system. Electrostatic filters are installed to remove particulate matter from outside air, most of which is then passed through a chemical filtration system to remove outdoor generated pollutants as well. The majority of repositories are therefore supplied with chemically filtered air, although a few are supplied with only electrostatically filtered air (‘non-filtered’), as described in Chapter 4. The average temperature is 18 °C and the average RH 50%.

The approach, described in the previous Chapter and the first part of this Chapter, can be used to quantitatively assess the effect of climate control and the extensive filtration system, and to determine which preservation measure might be most beneficial or appropriate for this specific collection.

As described in Chapter 4, 42% of the collection dates from before 1830 and the collection consists of 8% acidic paper, 45% groundwood and 55% rag paper. This makes roughly half of the collection very stable and the other half quite unstable.

Predictions, made in the previous section for a ‘typical’ collection can be used here, except that the ratio between more and less sensitive objects is different, as 45% of the collection could be classified as class I and 55% as class II in terms of handling. In terms of display the collection consists of classes II and III, with apparently negligible amounts of modern materials. Class II and III objects have predicted lifetimes of at least approximately a millennium under all conditions, described in section 9.1.1., when preservation measures were discussed, with ‘the worst’ conditions being 18 °C, 50% RH, 100 ppb AcOH and 10 ppb NO_2.

The current measured conditions in the Archives are 18 °C, 50% RH and 8.9 ppb or 0.3 ppb NO_2, depending on whether the repository is supplied with chemically purified air or not. Under the conditions in the repository without air filtration 45% of the collection would remain safe to handle for the next 250 years. In the repository with air filtration the lifetime would be extended to approximately 380 years. If the temperature was reduced by 5 °C, the handling lifetimes would be extended to 440 years without and 670 years with air filtration. A 10% decrease in RH would prolong the handling lifetimes to 320 and 480 years. This shows that longer lifetimes could be achieved even for the sensitive part of the collection, if the environmental conditions were adjusted. Although air filtration seems like a very effective measure, it should be stressed that similar beneficial effects can be achieved using different preservation measures (for example a 5 °C decrease has a greater effect).

Judging from the results, presented in the previous Chapters and sections above, the part of the collection, consisting of rag paper, can be expected to last very long without much degradation occurring, as predicted lifetimes were several millennia both in terms of handling and display. However it should be pointed out here that lifetimes were predicted for paper only, and rag papers often contain iron-gall ink, which also has a negative effect on paper degradation. The preservation measure, determined to have the most effect on stability of rag paper, is air filtration. Relatively low activation energies, determined for rag paper, mean that decreasing temperature would not have a significant effect on rag paper, as the degradation process is not very temperature dependant.

A significant effect of both AcOH and NO_2 was observed for rag paper, so removing pollutants is bound to have a significant beneficial effect. Pollutant ‘significant-effect’ thresholds, determined in the previous Chapter, are between 0 and 33 ppb for both investigated pollutants, which theoretically means that rag paper will be affected by pollutants in all concentration ranges, commonly encountered in repositories. Only considering thresholds without looking at predicted lifetimes could, however, be misleading. Although low pollutant thresholds indicate that air filtration is necessary, predicted handling and display lifetimes are long even in the presence of pollutants in realistic concentrations. At approximately 8.9 ppb NO_2, which is the concentration measured in the repository without air filtration, 100 ppb AcOH and 18 °C, 50% RH, predicted handling lifetime of rag paper would be approximately 2300 years and the display lifetime nearly 2500 years. This means that the paper itself might not be a particular concern even when exposed to moderate concentrations of pollutants. However the effect of iron-gall inks on the degradation rate is unknown and was beyond the scope of this project.

A decision on managing the environment could therefore mostly be made based on the 45% of the collection, classified as class I, as the other 55% is relatively insensitive to degradation. In terms of slowing down the degradation process, air filtration seems like an effective measure. The same effect could be achieved by decreasing the temperature by 4 °C, so the two measures would need to be compared in terms of the energy and financial input. Since the two parts of the collection seem quite different in terms of stability, dividing the collection into two may be a viable solution.

Unfortunately data on energy consumption of different preventive measures was not available, therefore a quantitative comparison in terms of energy efficiency cannot be made. The reason is that energy consumption at the Nationaal Archief is not metered separately for *T* and RH control or air filtration. Environmental control is made up of a variety of steps, some of which use mutual energy sources (e.g. cooling, dehumidification and air filtration are all electricity powered and therefore cannot be separated, heating is carried out using warm water from a waste incinerator and humidifying uses gas as an energy source), which do not allow simple estimations of how much energy each separate measure would consume. A quantitative comparison of preservation measures in terms of energy efficiency was therefore not possible.

When planning preservation measures and environmental control of the repositories, institutions and even standards [5] are moving away from very rigid guidelines used in the past decades [108], recommending strict *T* and RH control with uniform settings throughout the year and very small allowable fluctuations. Different ways of preserving collections, which would also be more sustainable (or energy efficient) are explored and new solutions are emerging. Adjusting temperature and relative humidity according to outdoor conditions was shown to be a good alternative [146], both in terms of energy consumption and collection preservation, and there have been ideas (or plans) to separate collections according to paper type [188] (for example in The Royal Library of Denmark in Copenhagen). Both of these solutions seem like useful alternatives to current practices for the collection of the Nationaal Archief. Changing *T* and RH set points according to season is worth considering, as the more sensitive part of the collection would definitely benefit from lower temperatures. This would probably also be more energy efficient in the relatively cold winters in The Hague (the average annual temperature outside the Archives building is 12 °C, Chapter 4). Similarly dividing the collection by paper type (which could also be done by year of production, as the older part of the collection is made of rag paper and the newer part is composed of groundwood paper), if at all possible, would be a good solution. This might be a useful measure especially since a very large part of the collection (55%) is quite stable, which means environmental control could be less strict for one half of the collection. Similarly air filtration would be much less necessary for this part of the collection and could possibly be omitted. If energy and funds were saved on half of the collection, they could be used more efficiently for the other half, significantly improving preservation of the most sensitive part of the collection. As described above, handling lifetimes of approximately 500 years would be achieved if air filtration remained in use in the Nationaal Archief building. If filtration was discontinued, the same could still be achieved by decreasing the temperature by 4 °C.

9.3. Conclusion

Using the assessment method, proposed in the previous Chapter, the lifetimes of a typical archival collection, and the collection held in the Nationaal Archief, were calculated. Predictions under different environmental conditions were made in order to demonstrate how to achieve target lifetimes or compare different environmental effects.

The effect of a hypothetical temperature increase on a collection was calculated and a possible energy-saving solution, found in the literature [146], was investigated in terms of handling and display lifetimes. This solution allows seasonal drift of *T* and RH and was found to be significantly beneficial to the collection as well.

Generally air filtration seems to have a significant beneficial effect in terms of handling lifetimes of the most sensitive part of the collection. The same effect could, however, be achieved by decreasing the temperature by approximately 4 °C, which would be more beneficial for the most sensitive documents in terms of colour change. Because a lower temperature for the collection would also mean a colder working environment for the archive employees, this could probably only be employed for infrequently handled materials. Although the Dutch law does not specify a minimum working temperature [189], it is generally perceived that workroom temperature should be at least 16 °C.

10. Conclusions and further work

10.1. Background and research elements

Paper degradation is affected by many different factors, the importance of which depends greatly on the environment the paper is stored in. In this work T, RH, pollutants and paper composition were considered as the most important parameters for long-term archival storage. In order to prolong the lifetime of paper-based objects, archival institutions usually control environmental parameters, however, quantitative assessment of the effect of those measures has been scarce. To investigate them, a collaborative project with the Nationaal Archief (the National Archives of the Netherlands) was carried out, with the aim to provide information on how to optimise preventive measures in their repositories.

To study the effect of polluted environments on paper degradation, six different paper types (five real historic papers of different compositions, initial properties and age, and filter paper, made of pure cellulose linters) were selected for experiments. This is the first study on the effects of pollution on paper, using actual historic paper instead of model samples.

Preliminary experiments where samples were exposed to elevated concentrations of the most abundant pollutants in an archival repository (NO_2, AcOH and formaldehyde), showed that the most harmful pollutants were NO_2 and AcOH. The two were therefore selected for the main experiments.

An Arrhenius study was performed at three temperatures, 80 °C, 70 °C and 60 °C, and 43% RH, which is in a realistic relative humidity range for an archival repository, in order to extrapolate degradation rates to lower temperatures. As the plots were created using only three points (i.e. three temperatures), slope uncertainties were significant, which resulted in significant uncertainties in the predicted degradation rates at room temperature. However, this was expected as Arrhenius studies are known for their extensive uncertainties, especially if conducted on real historic materials. Degradation rate interpolations were also made to realistic pollutant concentrations.

To assess the degradation behaviour of different paper types under conditions resembling those in an archival repository, handling and display lifetimes were proposed. Lifetimes at repository conditions (18 °C and 50% RH) and realistic pollutant concentrations (100 ppb AcOH and 10 ppb NO_2) were calculated for all paper types.

10.2. Outcomes

10.2.1. Predicted lifetimes in archival conditions

Both handling and display lifetimes differ significantly according to paper type. Predictions for both range from a few centuries for the most sensitive paper types (acidic in terms of handling and alkaline in terms display) to several millennia for the most stable ones (e.g. rag paper). In some cases, the predicted lifetimes are shorter than 500 years, which has recently been proposed as a suitable long-term planning horizon for collection management.

The differences between handling and display lifetimes are significant for some paper types (especially acidic and alkaline paper, which behave in the opposite way), suggesting that chain scission and colour change are, at least partly, the results of two different degradation processes. NO_2 had a negative effect on the lifetime of all paper types, which means it cannot be neglected entirely despite extensive prediction uncertainties. A very limited effect of AcOH was observed for most paper types.

10.2.2. Is the concept of dose generally applicable?

It was shown in this work that significant prediction errors can be made by using the simple approach, where the concentration multiplied by time is considered to be constant, while all other degradation parameters are not taken into account. This is the case especially at low (and realistic) pollutant concentrations, which could lead to significant underestimation of degradation. The approach, used here, also takes into account the degradation resulting from T and RH (‘background’ degradation), which contributes significantly to the overall degradation process during long-term storage and when pollutant concentrations are low enough for the effect of the pollutant not to be predominant. This is a novel concept.

This work also introduces a new concept of pollutant thresholds. Thresholds are defined as concentrations of pollutants when their effects become significant compared to uncertainty in *T* and RH control. Determined thresholds are in the concentration range found in an archival repository or above for NO_2, AcOH thresholds on the other hand differ much more. However it should be noted, that these thresholds do not take into account predicted lifetimes, which are in some cases several millennia even in the presence of pollutants. Taking threshold concentrations as the only decision-making criterion, without taking into account the overall stability of paper, can therefore be misleading.

10.2.3. Classification of historic paper according to sensitivity to storage environments

The five real paper types used in the experiments were divided into sensitivity classes based on their behaviour (predicted lifetimes and activation energies). A novel method for estimating lifetimes of each sensitivity class was proposed. The method takes into account the temperature, relative humidity, concentrations of the most abundant pollutants (AcOH and NO_2) and how prone the paper is to degradation, which is a result of its initial *DP*, pH and composition and is reflected in the sensitivity class of the paper type.

According to this method, the handling lifetime of a typical archival collection, composed of approximately 70% sensitive acidic paper and 30% more stable paper (e.g. rag paper), ranges from approximately 250 years for the more sensitive papers with a low starting *DP* (DP = 500) to over a millennium for the more stable paper. Display lifetimes are in the same range, however a much smaller part of the collection (only 10%) is estimated to reach the shorter lifetimes compared to handling, as most of the collection is relatively stable in terms of colour change.

Unlike the currently available methods for estimating collection lifetimes, such as the isoperm approach or the Preservation Calculator by the Image Permanence Institute, the method proposed here includes pollutants as an additional degradation factor, which in some environments makes a significant difference.

10.2.4. Comparative evaluation of preservation measures

As both handling and display lifetimes of the most sensitive parts of the collection were predicted to be less than 500 years, preservation measures to achieve that theoretical target were investigated, using the method, developed in this research. The handling lifetime of 500 years could be achieved by decreasing the RH to 24% or decreasing the temperature to 11 °C or employing chemical air filtration to reduce the NO_2 concentration to values below 1 ppb, combined with either reducing the T to 15 °C or reducing the RH to 38%. The same preventive measures would additionally ensure that display lifetimes of class I objects would reach 500 years. Both handling and display lifetimes of the rest of the collection at those conditions would be over a millennium.

10.2.5. Filtration – yes or no?

Air filtration is very efficient in decreasing the concentration of NO_2, however the beneficial effect differs according to paper type. Acidic and rag paper, which represent a significant part of the collection, were found to be most sensitive towards pollutants and would therefore benefit from air filtration most. It should also be taken into account that rag paper is significantly more stable compared to acidic paper, if any additional degradation by iron gall inks is ignored.

Current air filtration measures prolong the lifetime of the most sensitive acidic paper by approximately 150 years. The same effect could, however, be achieved by other preservation measures, such as decreasing the temperature by 4 °C, decreasing the RH by 14%, or a combination of both.

The available preservation measures should also be discussed in terms of energy consumption and sustainability, in relation to their benefits to the collection. A possible energy saving solution might be dividing the collection into two parts, where the environment in the less sensitive part, composed of rag paper, would have less need for air filtration, and the focus could therefore be on the more sensitive part. Another interesting option is changing the set points according to the season, similar to the study at The National Archives (UK).

It has to be noted that these considerations are relevant for archives in environments with low O_3 concentrations. An important observation is that external NO_2 concentrations in post-industrial environments are decreasing and are therefore likely to be lower in the future. Data in this work can be further used to assess the effect of pollutants in confined environments, where their effect is more pronounced.

10.3. Further work

The biggest issue in the work presented here, are the extensive lifetime prediction uncertainties, arising from uncertainties in the Arrhenius regressions. The quality of regressions could be improved by carrying out additional experiments at different temperatures, which would ensure the Arrhenius plots are created using more than three points. Ideally more sampling points per degradation rate would be added as well, to improve the accuracy of degradation rate determination. Although the samples used in this work were selected to be representative of a real collection, more papers could be studied to improve the results and test the classification and lifetime assessment method, introduced in this work.

The effect of changes in relative humidity was only investigated briefly at one temperature and more experiments are needed to either confirm or disprove the linear dependence of chain scission and the quadratic dependence of colour change. An Arrhenius study at different humidity levels (both lower and higher) would improve the general understanding of its effects, as the relative importance of RH might change with temperature, similar to the effect of pollutants. Similar to relative humidity, pollutant effects were only investigated at one concentration. A linear dependence of the degradation rate on the pollutant concentration was assumed, but should be verified experimentally. Experiments at concentrations below 1 ppm could significantly improve the understanding of pollutant effects in realistic concentration ranges.

The research presented in this thesis could be extended to include different pollutants that can be present in collection environments and which might pose a threat, such as O_3 or particulate matter. These were measured at Nationaal Archief, but not prioritised due to low concentrations. Other degradation processes could also be of interest, such as degradation caused by corrosive inks and light-induced degradation for objects frequently on display.

Materials other than paper could be studied using the approach introduced in this work, as this would provide the required evidence for different types of collections as well. This would validate the approach suggested here and make it more generally applicable to different environments and collections. It could also help reassess preventive conservation measures applied to collections, which are thought to be sensitive towards pollutant-induced damage.

If research was conducted on different material/pollutant systems, the pollutant thresholds proposed in this work could be applied to different collections, which in turn could be used to reassess pollutant guidelines and standards.

It should be stressed that the approach assumes that material composition of collections is known (e.g. mixed collections where different materials are represented) and that the main purpose (handling/display) has been assessed. For informed decisions on whether air filtration is a necessary prevention measure, preliminary research is therefore needed to enable initial prioritisation to take place. Pollutant thresholds are significantly different for deterioration of different material properties, and if the main purpose of a collection was display light exposure should be taken into account. Long-term plans for collections should be investigated and included in the decision-making process, as pollutant thresholds differ significantly according to the desired collection lifetime.

A key limitation of this work was the lack of energy consumption data, which would allow quantitative comparison of preservation measures in terms of the energy and financial input as well. Different preservation measures, compared here in terms of their beneficial effects on the archival collection, could be compared in terms of their costs and energy efficiency, which would differ according to institution. Energy consumption for temperature and relative humidity control could be compared to energy consumption and financial input, required for air filtration. This would inform quantitative cost-benefit analysis, to determine which measure (or combination of measures) would be most beneficial for the collection and at the same time most sustainable.

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Appendix A

Publications and conference presentations

1 Menart, E., de Bruin, G., Strlič, M. Dose-response functions for historic paper. *Polymer Degradation and Stability*, 96 (2011), 2029-2039.

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

3 Menart, E., Strlič, M., de Bruin, G. Damage functions for historic paper. (Liverpool 11-12 July 2011), Macro Group Young Researchers Meeting.(oral presentation)

4 Menart, E., de Bruin, G., Strlič, M. The effect of indoor pollution on historic paper. (London 17-20 June 2012), IAQ, Indoor Air Quality in Heritage and Historic Environments.(oral presentation)

5 Menart, E. Indoor pollution in archival collections. (The Hague 4 October 2012), Research seminar, Nationaal Archief.(oral presentation)

6 Menart, E., de Bruin, G., Strlič, M. Pollution, temperature and humidity control in paper preservation. (Glasgow 10-12 April 2013), Icon PF13, Institute of Conservation. (oral presentation)

7 Menart, E., de Bruin, G., Strlič, M. Historic paper and environment. (London 23 May 2013), Collections Demography Colloquium. (oral presentation)

Appendix B

1. Lifetime calculation: *t*, *t* $_{\text{min}}$, *t* $_{\text{max}}$

Sample A1, handling lifetime, 1000 ppb NO_2

Arrhenius slope: -6976 (S)	Intercept: 9.44 (I)
Slope error: 1884 (Er_S)	Intercept error: 5.50 (Er_I)

(rounded up figures in Table 7.7)

Degradation rate is calculated according to the linearised Arrhenius equation:

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

$$\left(-\frac{E_a}{R}\right) = S = -6976\ \frac{J\ mol\ K}{mol\ J} = -6976\ K$$

$$\left(-\frac{E_a}{R}\right)_{min} = S + Er_S = -5092\ K$$

$$\left(-\frac{E_a}{R}\right)_{max} = S - Er_S = -8860\ K$$

$$\ln A = I = 9.44$$

$$\ln A_{min} = I - Er_I = 3.94$$

$$\ln A_{max} = I + Er_I = 14.94$$

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A = -6976\ K * \frac{1}{291.15\ K} + 9.44 = -14.52$$

$$\ln k_{min} = \left(-\frac{E_a}{R}\right)_{max}\frac{1}{T} + \ln A_{max} = -8860\ K * \frac{1}{291.15\ K} + 14.94 = -15.50$$

$$\ln k_{max} = \left(-\frac{E_a}{R}\right)_{min}\frac{1}{T} + \ln A_{min} = -5092\ K * \frac{1}{291.15\ K} + 3.94 = -13.55$$

$$k = e^{\ln k} = 4.93 * 10^{-7}\ day^{-1}$$

$$k_{min} = e^{\ln k_{min}} = 1.86 * 10^{-7}\ day^{-1}$$

$$k_{max} = e^{\ln k_{max}} = 1.30 * 10^{-6}\ day^{-1}$$

$$t = \frac{\frac{1}{DP}-\frac{1}{DP_0}}{k*365.25} = \frac{\frac{1}{300}-\frac{1}{560}}{4.93 * 10^{-7}\ day^{-1}*365.25} = 9\ yr$$

$$t_{max} = \frac{\frac{1}{DP}-\frac{1}{DP_0}}{k_{min}*365.25} = \frac{\frac{1}{300}-\frac{1}{560}}{1.86 * 10^{-7}\ day^{-1}*365.25} = 22\ yr$$

$$t_{min} = \frac{\frac{1}{DP}-\frac{1}{DP_0}}{k_{max}*365.25} = \frac{\frac{1}{300}-\frac{1}{560}}{1.30 * 10^{-6}\ day^{-1}*365.25} = 3\ yr$$

Display lifetimes were calculated in a similar way, only the last was different. Instead of the Ekenstam equation used above, the following equation was used:

$$t = \frac{\Delta E_{00}}{k}$$

2. Pollutant effect extrapolation

Sample A1, handling lifetime, NO$_2$

$$k_{control} = 8.06 * 10^{-9}\ day^{-1}$$

$$k_{1000\ ppb\ NO2} = 4.93 * 10^{-7}\ day^{-1}$$

(rounded up degradation rates in Table 7.11)

$$m_{NO2} = \frac{k_{NO2}-k_{cont}}{c_{exp}} = \frac{4.93 * 10^{-7}\ day^{-1} - 8.06 * 10^{-9}\ day^{-1}}{1000\ ppb} =$$

$$= 4.85 * 10^{-10} day^{-1} ppb^{-1}$$

$$k_{100\,ppb\,NO2} = \ k_{cont} + \ m_{NO2} * 100\,ppb =$$

$$= \ 8.06 * \ 10^{-9}\,day^{-1} + \ 4.85 * 10^{-10} day^{-1} ppb^{-1} * 100\,ppb =$$

$$= 5.65 * \ 10^{-8}\,day^{-1}$$

$$k_{10\,ppb\,NO2} = \ k_{cont} + \ m_{NO2} * 10\,ppb =$$

$$= \ 8.06 * \ 10^{-9}\,day^{-1} + \ 4.85 * 10^{-10} day^{-1} ppb^{-1} * 10\,ppb =$$

$$= 1.29 * \ 10^{-8}\,day^{-1}$$

$$t_{100\,ppb\,NO2} = \frac{\frac{1}{DP} - \frac{1}{DP_0}}{k_{100\,ppb\,NO2} * 365.25} = \frac{\frac{1}{300} - \frac{1}{560}}{5.65 * 10^{-8}\,day^{-1} * 365.25} = 74\,yr$$

$$t_{10\,ppb\,NO2} = \frac{\frac{1}{DP} - \frac{1}{DP_0}}{k_{00\,ppb\,NO2} * 365.25} = \frac{\frac{1}{300} - \frac{1}{560}}{1.29 * 10^{-8}\,day^{-1} * 365.25} = 325\,yr$$

3. Different dose approaches

Sample A1, handling lifetime, NO$_2$

a) $c * t = const$

$t_{1000\,ppb\,NO2}\ (18\,^0C) = 8.5\,yr$

(extrapolated to T_{room} as shown in the first calculation example)

$const = c_{exp} * t = 1000\,ppb * 8.5\,yr = 8500\,ppb\,yr$

$$t_{100\,ppb\,NO2} = \frac{const}{100\,ppb} = \frac{8500\,ppb\,yr}{100\,ppb} = 85\,yr$$

$$t_{10\,ppb\,NO2} = \frac{const}{10\,ppb} = \frac{8500\,ppb\,yr}{10\,ppb} = 850\,yr$$

b) calculation carried out at shown in the pollutant extrapolation example above

Appendix C

Degradation rate experiments – effects of pollutants in steady state conditions (Chapter 6, section 6.2.)

Table 1: Chain scission rates for all paper types at four different pollutant conditions, 80 ^{0}C and 60 or 20% RH.

sample	pollutant conditions	T /°C, RH /%	intercept		slope		R^2
			value	st. error	value	st. error	
A	control	80, 60	-1.84E-04	2.70E-04	8.58E-05	1.45E-05	0.87
	AcOH	80, 60	3.00E-04	1.02E-04	3.08E-05	5.55E-06	0.86
	NO_2	80, 60	2.60E-04	6.47E-05	3.61E-05	3.51E-06	0.95
	AcOH + NO_2	80, 60	7.11E-05	1.84E-04	3.93E-05	9.94E-06	0.75
N	control	80, 60	1.71E-04	3.88E-05	3.41E-05	2.09E-06	0.98
	AcOH	80, 60	2.21E-04	4.93E-05	1.85E-05	2.67E-06	0.90
	NO_2	80, 60	1.01E-04	6.10E-05	2.66E-05	3.31E-06	0.93
	AcOH + NO_2	80, 60	1.67E-04	3.97E-05	2.37E-05	2.15E-06	0.96
B	control	80, 60	-1.26E-05	1.33E-05	5.38E-06	7.15E-07	0.92
	AcOH	80, 60	-1.33E-05	6.84E-06	3.30E-06	3.71E-07	0.94
	NO_2	80, 60	-2.92E-05	1.76E-05	4.93E-06	9.57E-07	0.84
	AcOH + NO_2	80, 60	-3.09E-05	1.24E-05	4.37E-06	6.70E-07	0.89
R	control	80, 60	1.41E-04	1.70E-04	3.93E-05	9.31E-06	0.85
	AcOH	80, 60	1.26E-04	1.32E-04	2.93E-05	7.28E-06	0.83
	NO_2	80, 60	1.11E-04	8.97E-05	2.83E-05	4.95E-06	0.91
	AcOH + NO_2	80, 60	1.23E-04	3.64E-05	2.42E-05	2.01E-06	0.98
W	control	80, 60	2.77E-05	5.24E-05	1.50E-05	2.82E-06	0.85
	AcOH	80, 60	1.46E-05	5.72E-05	1.34E-05	3.10E-06	0.78
	NO_2	80, 60	6.11E-05	4.08E-05	7.87E-06	2.21E-06	0.70
	AcOH + NO_2	80, 60	2.22E-06	7.42E-05	1.30E-05	4.02E-06	0.65
A	control	80, 20	1.61E-04	5.79E-05	1.08E-05	2.95E-06	0.71
	AcOH	80, 20	1.11E-04	1.88E-05	8.27E-06	9.46E-07	0.94
	NO_2	80, 20	-5.37E-05	5.41E-05	2.02E-05	2.73E-06	0.91
	AcOH + NO_2	80, 20	-2.54E-05	3.52E-05	1.76E-05	1.77E-06	0.95
N	control	80, 20	2.89E-04	3.20E-05	5.23E-06	7.13E-07	0.91
	AcOH	80, 20	2.06E-04	1.80E-05	7.12E-06	3.99E-07	0.98
	NO_2	80, 20	2.11E-04	3.86E-05	7.30E-06	8.57E-07	0.93
	AcOH + NO_2	80, 20	1.84E-04	5.37E-05	6.86E-06	1.19E-06	0.86
B	control	80, 20	-7.49E-06	6.10E-06	2.94E-06	1.36E-07	0.99
	AcOH	80, 20	8.73E-07	1.22E-05	2.83E-06	2.71E-07	0.96
	NO_2	80, 20	-5.33E-06	6.37E-06	2.67E-06	1.42E-07	0.99
	AcOH + NO_2	80, 20	-6.45E-06	8.14E-06	2.89E-06	1.81E-07	0.98
R	control	80, 20	3.66E-05	7.81E-05	5.53E-06	2.72E-06	0.51
	AcOH	80, 20	-2.06E-06	1.69E-05	4.99E-06	5.87E-07	0.96
	NO_2	80, 20	5.59E-05	7.57E-05	5.04E-06	2.62E-06	0.47
	AcOH + NO_2	80, 20	-9.83E-05	4.41E-05	8.73E-06	1.53E-06	0.91
W	control	80, 20	5.00E-05	3.65E-05	5.37E-06	8.43E-07	0.81
	AcOH	80, 20	1.49E-05	4.46E-05	6.63E-06	1.03E-06	0.82
	NO_2	80, 20	8.43E-06	4.60E-05	6.20E-06	1.06E-06	0.79
	AcOH + NO_2	80, 20	-2.10E-05	4.41E-05	7.12E-06	1.05E-06	0.83

Table2: Colour change rates for all paper types at four different pollutant conditions, 80 ^{0}C and 60 or 20% RH.

			intercept		slope		
sample	pollutant conditions	T /^{o}C, RH /%	value	st. error	value	st. error	R^2
A	control	80, 60	4.47	0.82	0.27	0.04	0.88
	AcOH	80, 60	3.56	0.59	0.21	0.03	0.90
	NO_2	80, 60	3.22	0.40	0.27	0.02	0.97
	AcOH + NO_2	80, 60	3.46	0.52	0.19	0.03	0.89
N	control	80, 60	4.65	1.02	0.18	0.05	0.66
	AcOH	80, 60	4.01	0.71	0.17	0.04	0.79
	NO_2	80, 60	3.57	0.94	0.20	0.05	0.74
	AcOH + NO_2	80, 60	3.92	0.56	0.17	0.03	0.86
B	control	80, 60	5.78	1.05	0.27	0.06	0.82
	AcOH	80, 60	7.26	1.41	0.21	0.08	0.58
	NO_2	80, 60	5.50	1.55	0.24	0.08	0.58
	AcOH + NO_2	80, 60	4.56	0.91	0.26	0.05	0.84
R	control	80, 60	5.03	0.44	0.33	0.02	0.98
	AcOH	80, 60	5.92	0.69	0.23	0.04	0.92
	NO_2	80, 60	4.85	0.17	0.31	0.01	1.00
	AcOH + NO_2	80, 60	4.21	1.42	0.33	0.08	0.85
L	control	80, 60	3.90	0.36	0.19	0.02	0.95
	AcOH	80, 60	3.45	0.63	0.11	0.03	0.65
	NO_2	80, 60	1.52	0.95	0.22	0.05	0.77
	AcOH + NO_2	80, 60	3.16	0.38	0.13	0.02	0.89
W	control	80, 60	2.75	0.37	0.10	0.02	0.83
	AcOH	80, 60	2.51	0.52	0.13	0.03	0.82
	NO_2	80, 60	1.96	0.43	0.16	0.02	0.90
	AcOH + NO_2	80, 60	2.06	0.30	0.16	0.02	0.95
A	control	80, 20	0.82	0.49	0.06	0.03	0.44
	AcOH	80, 20	1.92	0.46	0.00	0.02	-0.25
	NO_2	80, 20	0.41	0.63	0.08	0.03	0.52
	AcOH + NO_2	80, 20	0.88	0.43	0.07	0.02	0.62
N	control	80, 20	1.78	0.29	0.04	0.01	0.90
	AcOH	80, 20	1.70	0.40	0.04	0.01	0.81
	NO_2	80, 20	1.29	0.30	0.05	0.01	0.91
	AcOH + NO_2	80, 20	1.39	0.59	0.05	0.01	0.70
B	control	80, 20	1.78	0.54	0.04	0.01	0.67
	AcOH	80, 20	2.00	0.49	0.03	0.01	0.62
	NO_2	80, 20	1.44	0.41	0.04	0.01	0.76
	AcOH + NO_2	80, 20	1.36	0.40	0.04	0.01	0.81
R	control	80, 20	1.06	0.78	0.02	0.03	-0.10
	AcOH	80, 20	0.03	0.48	0.03	0.02	0.51
	NO_2	80, 20	0.16	0.22	0.05	0.01	0.92
	AcOH + NO_2	80, 20	0.32	0.49	0.04	0.02	0.57
L	control	80, 20	0.80	0.57	0.06	0.01	0.81
	AcOH	80, 20	2.25	0.46	0.03	0.01	0.54
	NO_2	80, 20	1.25	0.60	0.05	0.01	0.71
	AcOH + NO_2	80, 20	1.84	0.41	0.04	0.01	0.77
W	control	80, 20	1.27	0.25	0.04	0.01	0.82
	AcOH	80, 20	1.07	0.24	0.04	0.01	0.83
	NO_2	80, 20	1.07	0.15	0.04	0.00	0.93
	AcOH + NO_2	80, 20	1.05	0.20	0.04	0.00	0.88

Appendix D

Comparison of different dose approaches (Chapter 8, section 8.2.2.)

Handling lifetimes

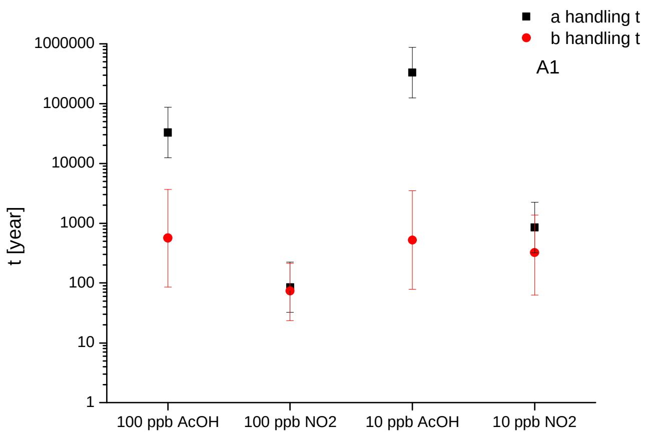

Figure 1: Handling lifetimes of acidic paper 1, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

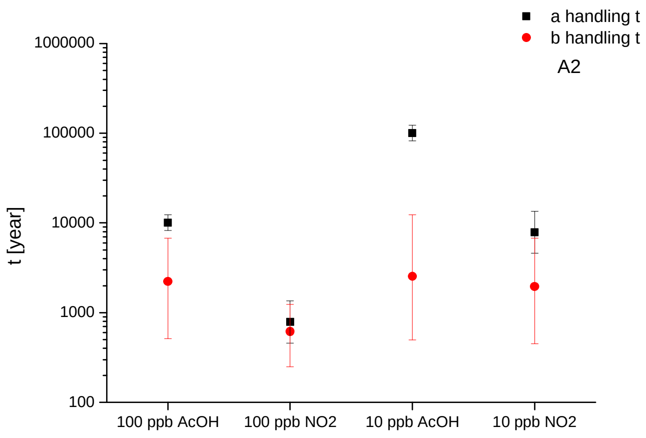

Figure 2: Handling lifetimes of acidic paper 2, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

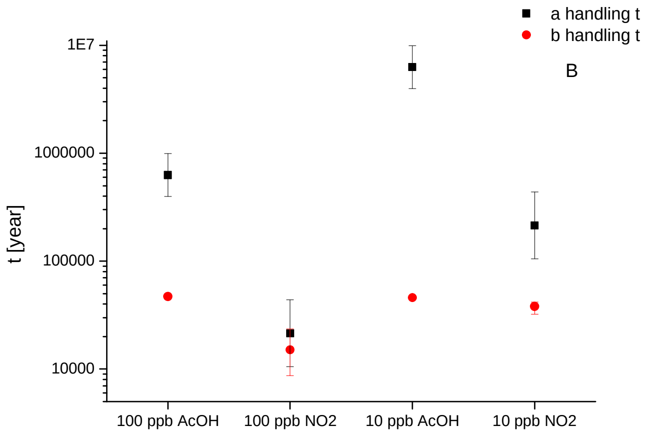

Figure 3: Handling lifetimes of alkaline paper, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

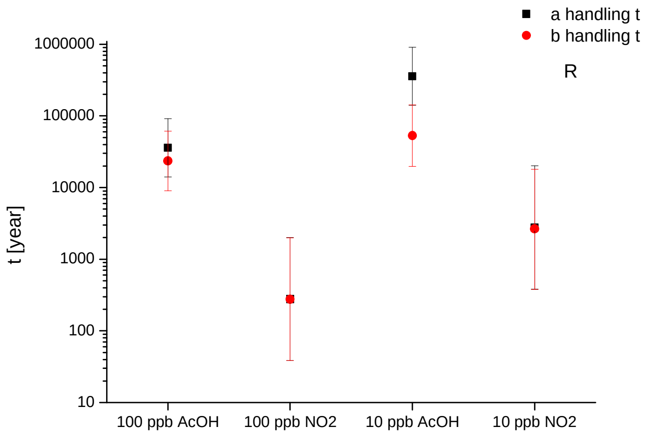

Figure 4: Handling lifetimes of rag paper, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

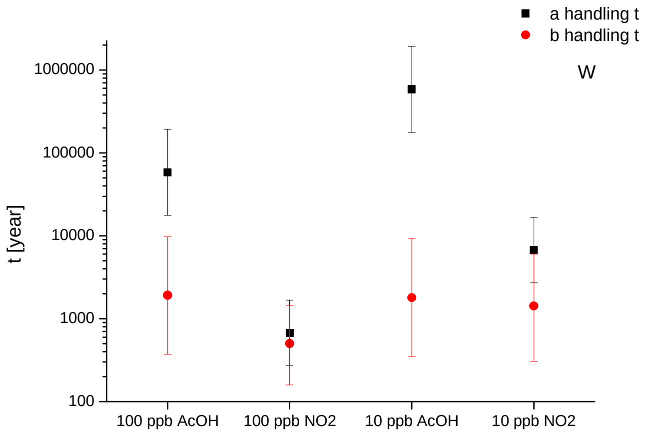

Figure 5: Handling lifetimes of Whatman paper, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

Display lifetimes

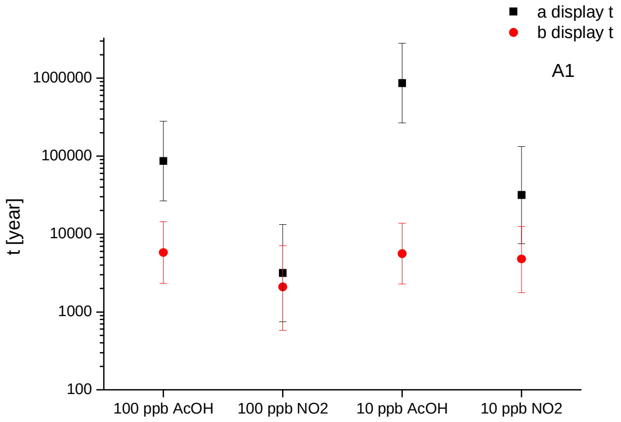

Figure 6: Display lifetimes of acidic paper 1, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

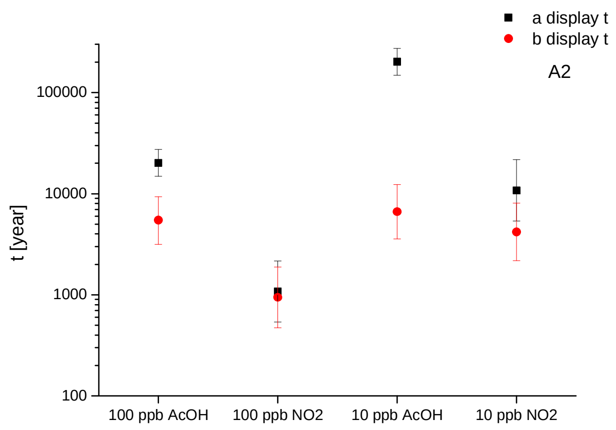

Figure 7: Display lifetimes of acidic paper 2, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

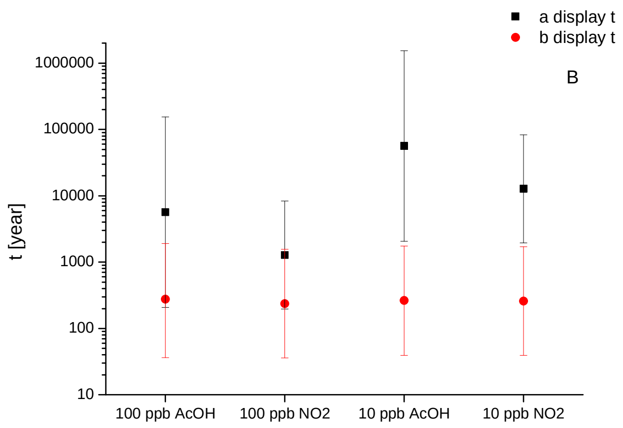

Figure 8: Display lifetimes of alkaline paper, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

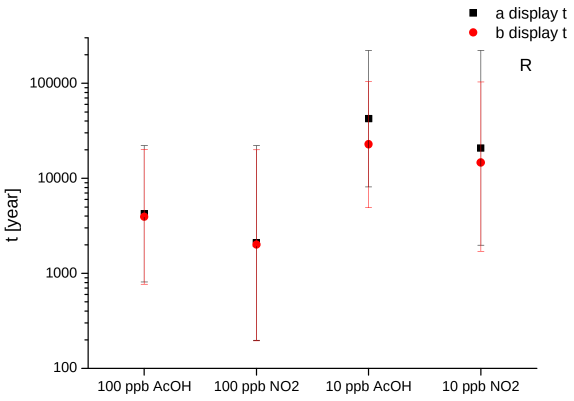

Figure 9: Display lifetimes of rag paper, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

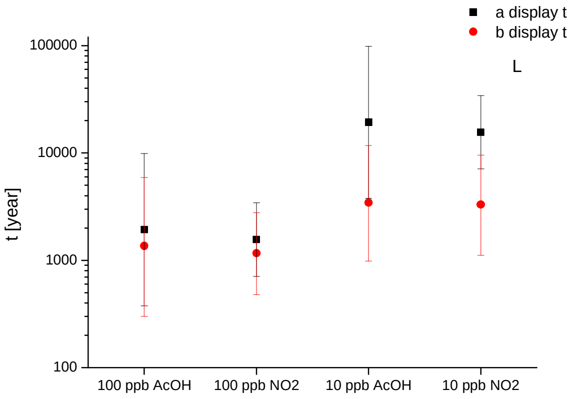

Figure 10: Display lifetimes of lignin-containing paper, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).

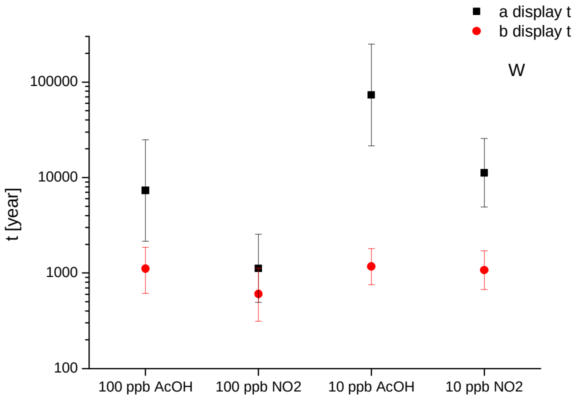

Figure 11: Display lifetimes of Whatman paper, predicted at 18 °C, 43% and 100 & 10 ppb AcOH or NO2, using both approaches (a in black, b in red).