The impact of volatile compounds released by paper on cellulose degradation in ambient hygrothermal conditions

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ABSTRACT

The reactivity towards cellulose of various volatile compounds commonly released by paper was studied. Sheets of Whatman No. 1 (W1) and No. 40 (W40) were exposed to various concentrations of these compounds in vapour phase ranging from 20 to 80 ppm in closed vessels for 52 days in controlled ambient conditions, after which they were hygrothermally aged. The measured properties of the paper were copper number, degree of polymerization, zero-span breaking length, pH and yellowness index. The results showed that hydrogen peroxide was the most aggressive among the volatile compounds tested as it severely degraded W1 cellulose. The exposure of W1 to formic acid led to significant degradation, designating this volatile organic compound (VOC) as the most reactive toward cellulose among the carboxyl and carbonyl functionalized VOCs tested. On the other hand, acetic acid was found comparatively less reactive. Nitrogen oxides, which were produced up to 3 ppm from a side-reaction of the carboxylic acids with the magnesium nitrate used to control the relative humidity in the closed vessels, appeared to contribute significantly to the degradation despite their low concentration. Antagonistic effects were evidenced in binary vapour mixtures where the presence of aldehydes (formaldehyde and acetaldehyde) counteracted substantially the degradation induced by the most reactive compounds. It was also shown that acetaldehyde, hexanal and furfural in individual exposures had little to no reactivity. Upon exposure to formaldehyde, the rate of glycosidic bond cleavage of cellulose induced by the ageing of W1 was significantly reduced.

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1. Introduction

Notwithstanding recent developments, the research field of indoor air quality in heritage buildings is still in its infancy. Martin and Blades were among the first to report on the measurement of levels of volatile organic compounds (VOCs) inside museums in 1994 [1]. In 2003, an extensive review of the pollutants found in heritage institutions was conducted by Tétreault [2]. The bulk of this emerging research has largely been geared towards identifying and quantifying the pollutants in indoor air. The past decade, in particular, has seen a growing interest on the issue of indoor generated pollutants in libraries and archives. Recent studies have been devoted mostly to the measurement of VOCs in storage rooms housing paper-based collections, with a focus on carboxylic acids and aldehydes [3–6]. Research has also been dedicated to analysing

emissions from papers and books [7–18], as the main sources of VOCs in archival storage rooms are the paper-based items themselves. In view of the adverse contribution of off-gassing from paper collections to the indoor air quality, Ramalho et al. measured the emission rates of a selection of VOCs identified in various types of unaged and aged model papers and in naturally aged books [19].

To date, little is known on the potential damaging effect of the VOCs on cultural objects. Upon measuring the emission levels of acetic acid from typical archival cardboard storage boxes, Dupont and Tétreault [20] evaluated the deterioration of paper exposed to ppm levels of acid vapour, in terms of decrease in degree of polymerization of the cellulose. More recently, high temperature exposures to formic acid, 2-pentyl furan and NO_x at ppm levels were shown to unfavourably affect the degree of polymerization of cellulose in papers, while the effects of acetic acid were found to be more modest, and those of hexanal, furfural and formaldehyde were negligible on most papers [21,22]. Organic compounds with a high oxidative power such as hydroperoxides, the initial products in free radical autocatalytic oxidation, have been identified in pure

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cellulose paper [23–25]. Their presence was identified as free hydroperoxides cleaved from the cellulose chain as well as hydroperoxide functionalized cellulose, and their adverse impacts on cellulose degradation were quantified [24,25]. Hydroperoxides are also known to cause discolouration of black and white photographic prints [26,27]. Using Russell-effect images, Strlič et al. [28] were able to demonstrate that high levels of hydrogen peroxide (H_2O_2) were produced in aged papers containing iron-gall ink. Despite this new knowledge, there are still gaps concerning the effects of VOCs on paper and cellulose-based materials in typical indoor environmental conditions.

The present research aims to identify the volatile compounds that can induce or initiate deterioration in cellulose, and to simulate their long-term effects on the stability of paper using artificial ageing. Unlike other investigations, the exposures were carried out in ambient conditions in order to observe possible damage in real time, as well as to avoid initiating chemical processes that can take place at elevated temperatures. Hygrothermal ageing was performed after a desorption period of 10 days following the exposures.

Two pure cotton cellulose papers were used: Whatman No. 1 (W1), with a high molar mass, neutral pH and negligible initial oxidation level, and Whatman No. 40 (W40), a lower molar mass, pre-oxidized and more acidic paper. In 'Phase I' of the research, the papers were exposed to individual volatile compounds commonly released by paper. These were acetaldehyde, acetic acid, formaldehyde, formic acid, furfural, hexanal and hydrogen peroxide. However, real situations are complex as they bring simultaneously into play a number of volatile compounds, which are both released and absorbed by paper, depending on environmental and intrinsic parameters. For instance, during hygrothermal ageing, cross-contamination from paper or cellulose-based storage materials to neighbouring paper has been observed [29]. Air chemistry can also take place, and new volatile compounds can arise from reactions between different volatile compounds. Since it is not possible to test all conceivable combinations of volatile compounds, in 'Phase II' of the research, the synergistic and/or antagonistic effects of exposures to binary mixtures of volatile compounds were assessed in an attempt to model real exposure situations. These combinations included two compounds, which had been identified in Phase I as highly reactive and less reactive at ambient temperature, respectively. The impact of exposures where adventitious nitrogen oxides (NO_x) were additionally present was also investigated.

Previous studies have evaluated the migration of VOCs internally generated in stacks of paper [30,31] and the migration of outdoor pollutants such as sulphur dioxide through papers [32] and cardboard [33]. To simulate paper sheets in a closed book this research also examined the migration of volatile compounds through stacks of paper from the edges inward at ambient conditions.

2. Experimental

2.1. Chemicals

Acetaldehyde (99%), formaldehyde (37%), furfural (99%) and hexanal (98%) were purchased from Sigma–Aldrich. Acetic acid glacial, formic acid (88%), magnesium nitrate hexahydrate and sodium chloride were from Fisher Scientific. Hydrogen peroxide (30%) was obtained from J.T. Baker.

2.2. Generation and measurement of specific vapour phase environments

A three component system of volatile compound–water–salt was used. This system is based on the equilibrium of water vapour with a saturated salt mixture and the equilibrium of a volatile compound between its vapour and liquid phases. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) and sodium chloride (NaCl) were used to generate a relative humidity (RH) of 54% and 75% at ambient temperature, respectively [34]. Aqueous solutions (40 ml) of the volatile compounds at different concentrations were mixed with 100 g of salt and placed in airtight 9 L Pyrex desiccators (200 mm i.d.). The presence of volatile compounds does not modify the RH in the desiccators, as shown in previous research [35]. Since hexanal is not water soluble, pure hexanal (0.1 ml) was deposited inside the desiccator, adjacent to the water/salt solution. For the binary compounds exposures, the solutions were poured into separate beakers and placed in the desiccator (20 ml and 50 g of salt each). Control samples were produced by exposing paper to the water/salt mixture only. The volatile compounds used and the environmental conditions are listed in Tables 1 and 2.

Measurements of the volatile compounds in the headspace of the desiccators were carried out with Dräger and Gastec detector tubes. According to the suppliers, the relative standard deviations (RSD) on the quantitation are 5%, except for formic acid (RSD 15–10%) and formaldehyde (RSD 20–15%). The measurement of hexanal had to be done with the tubes designed for acetaldehyde measurement as commercial hexanal-dedicated tubes were not available. The conversion for the concentration calculation was done as follows. At saturation, hexanal generates 2000 ppm in the headspace, which yielded a measurement of 26 ppm (equivalent) acetaldehyde. The level of hexanal was then calculated as 77 (~2000/26) times the level of acetaldehyde measured assuming a linear relationship.

Three air sampling measurements were made in each desiccator containing the paper samples: once the equilibrium was reached, a few days after the beginning of the exposure, and again at the end

Table 1
Exposure conditions of W1 in the temperature range 20.6–21.6 °C.

Volatile compounds	Solution's concentration (vol/vol %)	RH during exposure (%)	Average concentration in air with papers (ppm)
Water (control)	100	54	
Water (control)	100	75	
Acetaldehyde (Ac)	0.017	54	60 ± 4
Acetic acid (AA)	2.17	54	AA: 41 ± 4, NO_x: 0.5
Acetic acid	2.17	54	AA: 37 ± 4, NO_x < 0.5
Acetic acid	2.17	75	67 ± 9
Acetic acid	1.00	75	28 ± 4
Formaldehyde (F)	1.98	54	30 ± 5
Formaldehyde	1.98	75	19 ± 5
Formic acid (FA)	3.04	75	38 ± 9
Furfural	1.14	54	82 ± 8
Hexanal	0.10 ml[a]	54	810 ± 280[b]
Hydrogen peroxide (H_2O_2)[c]	30	75	H_2O_2: 30, F < 1, FA: 3[d]
Acetaldehyde + acetic acid	0.012, 4.30	54	Ac: 91 ± 8, AA: 40 ± 4, NO_x: 3 ± 1
Formaldehyde + formic acid	3.90, 3.77	75	57 ± 6, 28 ± 5
H_2O_2 + formaldehyde[c]	30, 4.00	75	H_2O_2 < 1, F: 16, FA: 41[d]
H_2O_2 + formaldehyde without papers[c]	30, 4.00	100	H_2O_2 < 1, F: 31, FA: 20

[a] 0.1 ml of hexanal 98% in separate beaker (not mixed with water-salt solution).
[b] Measured with acetaldehyde detection tube.
[c] Average vapour concentration based on integration of polynomial fit curve.
[d] Detection made with formic acid tubes.

Table 2
Exposure conditions of W40 at $21.3 \pm 0.3\ °C$ and 75% RH.

	Solution's concentration (vol/vol %)	Average concentration in air with papers (ppm)
Water (control)	100	
Acetic acid	1.00	34 ± 5
Formaldehyde	1.98	24 ± 5
Formic acid	1.52	28 ± 5
Furfural	1.14	131 ± 28
Formaldehyde + formic acid	4.00, 3.04	$64 \pm 5, 24 \pm 5$

of the exposure period. The vapour concentrations were in the range 20–80 ppm depending on the volatile compound (Tables 1 and 2), and were found to be relatively constant over the whole exposure period, except for hydrogen peroxide as detailed in section 3.1. For simplicity in the presentation of the results, the average concentrations of hydrogen peroxide and of its reaction products over the exposure period were obtained using a curve fit program (Table Curve 2D, Systat Software Inc.), and subsequently used in the graphs as well as for designating the corresponding exposed samples.
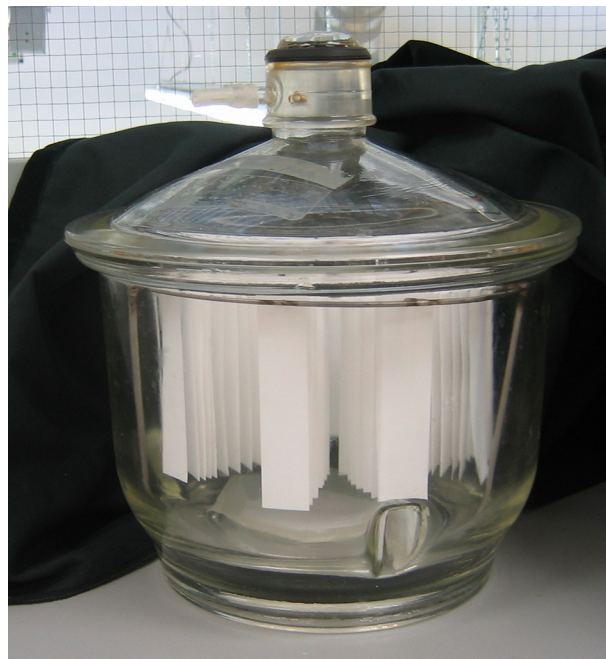
2.3. Paper samples

The two papers used as models were pure cotton cellulose filter papers, Whatman No. 1 (W1) and Whatman No. 40 (W40). W1 is neutral (cold extract pH = 6.51 ± 0.02), has an ash content of 0.06% and a basis weight of 88 g m^{-2}. W40 is more acidic (cold extract pH = 5.68 ± 0.06), with an ash content of 0.007% and a basis weight of 92 g m^{-2}. While the cellulose of W1 is unoxidized, that of W40 was found to have a sizeable degree of oxidation, evidenced by a copper number of 1.61 ± 0.09. Considering the value of DP_n (number average degree of polymerization), this corresponds approximately to a content in total carbonyl groups of 26 μmol g^{-1} (henceforth abbreviated CO_{tot}), which, excluding the cellulose's reducing end-groups, yields 15 μmol g^{-1} in carbonyl groups on cellulose (henceforth abbreviated CO) (see section 2.5). These papers were chosen as models because of their simple composition. W1 has been widely used for this very reason in studies of cellulose degradation, including work by the authors, while W40 was deemed to better represent more oxidized and acidic paper.

Sets of 100 paper strips (2.5 × 12 cm^2) were hung vertically on stainless steel holders and placed in the desiccators with their lower edges about 5 cm above the surface of the salt solution as shown in Fig. 1. The exposures lasted 52 days during which the desiccators were kept in the dark. After exposure, the samples were left to off-gas for 10 days prior to any further action. Despite this ventilation period it was not possible to rule out the residual presence of volatile compounds still absorbed in the paper samples, thus more emphasis will be given in the discussion on the data obtained upon real time exposure and less on the data obtained upon ageing.

2.4. Hygrothermal ageing

After the exposure and the desorption period, the samples were hygrothermally aged at 100 °C for 5 and 10 days, in hermetically closed Lab-Line hybridization tubes (35 mm internal diameter (ID) × 147 mm, 144 ml) according to ASTM standard D6819 – 02(2007). During the ageing, the humidity in the tube is supplied and buffered by the paper, and stabilizes between 50 and 60% RH

Fig. 1. Paper samples exposed to a volatile compound.

[36]. W40 samples were aged for 5 days only as degradation was deemed too pronounced after 10 days ageing.

2.5. Physicochemical measurements

Two methods were used for the determination of the degree of polymerization of cellulose (DP): viscometry (V) and size-exclusion chromatography with multiangle light scattering and differential refractive index detection (SEC/MALS-DRI). Measurements were carried out in duplicate or triplicate.

SEC/MALS-DRI allows the experimental determination of the average molar masses of cellulose (M_n, M_w, M_z), and thus the corresponding DP values (DP_n, DP_w, DP_z). The dissolution of the paper samples prior to analysis was carried out in N,N-dimethylacetamide (DMAc) with 8% lithium chloride according to a procedure detailed in a previous publication [37]. A 515 isocratic HPLC pump (Waters), ACC-3000T autosampler (Dionex), Dawn EOS MALS detector (Wyatt Technologies), and 2414 (Waters) differential refractive index (DRI) detector were part of the chromatographic set-up. The separation was carried out on a set of three Phenogel Linear(2) polystyrene divinyl benzene (PSDVB) columns (5-μm particle-diameter mixed bed pores columns, Phenomenex) preceded by a Phenogel guard column (5-μm, Phenomenex). The columns compartment and the MALS detector were thermostated at 60 °C, the DRI was set to 55 °C. The mobile phase was DMAc with 0.5% lithium chloride (wt/vol). The system was operated at a flow rate of 0.4 mL min^{-1} with an injection volume of 100 μL. The repeatability of the method was previously determined to be RSD% = 2.5 on M_w for 3 separate cellulose samples analysed two to three times nonconsecutively.

The average viscometric degree of polymerization of cellulose (DP_v) was determined by measuring the intrinsic viscosity ($[\eta]$) of a dilute cellulose solution in the solvent cupriethylenediamine (CED), according to the standard method ISO 5351. To minimize the alkaline degradation of oxidized cellulose in CED [38,39], all W40 samples underwent reduction in 0.01 M ethanolic solution of sodium borohydride for 17 h before measuring the viscosity. The

sample size varied from 15 to 50 mg. The repeatability of the measurement (within the laboratory) as indicated in TAPPI (Technical Association of the Pulp and Paper Industry) Test Method T 230 om-99 is 4%.

For polymers in dilute solutions, the relation between $[\eta]$ and the molar mass is described by the empirical Mark–Houwink–Sakurada equation:

$$[\eta] = K' M_v^a$$

Where K' and a are constants for a given polymer-solvent system, temperature and molar mass range. For cellulose in CED the relationship has been formulated as [40]:

$$[\eta] = 0.91 \, [DP_v]^{0.85}$$

M_n always falls between M_n and M_w [41]. For pure cellulose paper, a is often found close to unity, and M_v is usually reported in the literature to be closer to M_w than to M_n. Based on the fairly good correlation obtained in the experimental values of DP_w and DP_v (less than 10% difference in 90% of the cases, and less than 5% difference in 60% of the cases), both values were used indiscriminately and henceforth named 'DP' for convenience.

The rate of glycosidic bond cleavage (k) as a function of time (t) was estimated using the model based on first order kinetics proposed by Ekamstam [42], which uses the value of DP_n at any given time (DP_{nt}) as expressed in the following relationship with respect to its initial value DP_{nt_0}:

$$(1/DP_{nt} - 1/DP_{nt_0}) = k \, t$$

The following expression was used to convert DP_v into DP_n when needed:

$$[DP_v] = [DP_n] \times [(1 + a)\Gamma(1 + a)]^{1/a}$$

Where a is the Mark–Houwink coefficient for the cellulose/CED system, and $\Gamma(1 + a)$ is the gamma function of a evaluated by reference to tabulated values [43].

The copper number (NCu) (g Cu$_2$O) was determined according to TAPPI Test Method T 430 cm-99, where the mass of paper was reduced from 1 g to 300 mg. Two to three repeat measurements were performed for each sample type. The repeatability of the measurement was 10%. NCu represents an index for functions on cellulose and other compounds in paper which possess reducing properties [44]. These are mostly carbonyl functions, and in pure cellulose they arise from the C1 end-groups and from carbonyl groups along the macromolecule on C2, C3 and C6. While the former are informative of cellulose chain cleavage, the latter indicate cellulose oxidation. It is thus necessary to distinguish between them in order to assess cellulose oxidation. This can be done by subtracting from the total carbonyl groups content (CO$_{tot}$) the portion that relates to reducing end-groups, which can be roughly calculated based on the DP_n values, to yield the content in carbonyl functions on the cellulose (CO). In this study, in order to better estimate the oxidation of cellulose, the linear relationship between CO and NCu determined by Röhrling et al. [44] as CO = (NCu−0.07)/0.06 (µmol g^{-1}) was used .

The machine direction zero-span tensile strength of paper was measured according to TAPPI Test Method T231 cm-96 using a Troubleshooter Pulmac Instrument. Zero-span breaking length (BL) was calculated using the moisture-free basis weight of the paper samples. Twenty repeat measurements were carried out per sample type. The repeatability of the measurement was 5%. Breaking Length was calculated as follows:

$$BL = 102000 \, (T/R)$$

where BL = breaking length (m), T = tensile strength (kN m^{-1}) (1kgf/15 mm = 0.654 kN m^{-1}) and R = basis weight (dry) (g m^{-2}).

The cold extraction pH and the yellowness index measurement methodologies are described in section 1 in the supplementary material. Graphs in the supplementary material file are labelled S1 to S3.

2.6. Migration of volatile compounds through paper stacks

Three stacks of 13 W1 strips (2.5 × 12 cm^2) tightly wrapped in vapour barrier laminated aluminium foil (Marvelseal 360) with only one transversal side open were built as book mock ups. The paper strip stacks were exposed to different vapour concentrations of formic acid and acetic acid at 75% RH for various periods in a 9 L desiccator. In this configuration, the migration of the volatile compounds into the stacks can occur only through the open section. One stack was removed weekly, and a strip from the middle was sampled for pH measurement. Tiny drops of universal pH indicator solution (pH range 4–10) were applied every 0.5 cm along the strip starting from the edge of the open side. The pH variation along the paper strip indicated the progressive migration of the acids. Further details of the experimental conditions can be found in Table 3. One 20-strip stack of W1 was exposed to H$_2$O$_2$ in a 9 L desiccator. The H$_2$O$_2$ migration was measured using a peroxide test strip test (Em Quant 10011-1, EMD Chemicals Inc.). The limit of quantitation (LOQ) reported by the manufacturer is 0.5 mg L^{-1}.

3. Results and discussion

3.1. Specific vapour phase environments

The concentrations of volatile compounds in the desiccators are listed in Tables 1 and 2. The vapour phase equilibrium with individual volatile compounds was reached in two days and was stable over the 52 days. With binary mixtures 5 days were necessary for full equilibration. No acid was detected after 52 days with the solutions of individual aldehydes, whether paper samples were present or absent in the desiccators. The oxidation of aldehydes to the corresponding acid did not seem to occur to any detectable level, which was attributed to the absence of an oxidant in the system. This confirms previous research where the oxidation of formaldehyde in the presence of lead and copper materials was not observed [45].

A side-reaction was found to occur between the carboxylic VOCs and magnesium nitrate used to regulate the RH to 54%, producing nitrogen oxides. With formic acid, about 10 ppm of NO$_x$ were

Table 3
Exposure conditions for the migration of volatile compounds through W1 stacked papers at 21.3 ± 0.3 °C and 75% RH. The dimensions of the open edges were 0.2 × 1.5 mm^2 for the 13 strips stack and 0.3 × 2.5 mm^2 for the 20 strips stack.

	Solution's concentration (vol/vol %)	Average concentration in air with papers (ppm)	Exposure period (week)
Acetic acid	0.10	4	1, 2, 3
	0.05	1	2, 3
	0.01	0.4[a]	2, 3
Formic acid	0.15	2	1, 2, 3
	0.05	0.5	2, 3
	0.015	0.2[a]	2, 3
H$_2$O$_2$	30	20	0.43

[a] Estimated; not measured with detection tubes.

generated. It was thus decided to carry out new formic acid exposures of the samples using sodium chloride (75% RH) instead of magnesium nitrate. With acetic acid, the release of NO_x was smaller, clearly measurable in one case (3 ppm), and suspected in trace amounts in two cases (<0.5 and 0.5 (= LOQ)). The samples were still considered worth studying further even though the exposures were also repeated using NaCl salt as RH adjuster.

The monitoring of the concentrations of volatile compounds present in vapour phase in the desiccators containing hydrogen peroxide showed that chemical reactions took place during the exposure period. As shown in Fig. 2a, in the desiccator containing W1 in which a solution of H_2O_2 (30%) was placed, the concentration of the latter rapidly increased reaching 36 ppm in 15 days, but was followed by a slow decay over the remaining exposure period. Concomitantly, up to 7 ppm of organic acids (measured with a detector tube calibrated for formic acid) were progressively formed. This was attributed to the gradual degradation and off-gassing of acids from the paper upon reaction with H_2O_2 (see section 3.2.1.1). When both H_2O_2 (30%) and formaldehyde (4%) were introduced in a desiccator with W1, the concentration of H_2O_2 never raised above LOQ (<1 ppm) during the whole exposure period, while a rapid production of organic acids occurred, most likely predominantly formic acid given the two chemical compounds present (Fig. 2b). The level of formaldehyde reached about 30 ppm in 7 days, but then declined quickly while the formic acid was gradually generated, reaching a plateau at about 47 ppm. To better understand the chemistry taking place and to characterize the reactivity of H_2O_2 with formaldehyde, an experiment was set up without the paper samples and at a relative humidity of 100%, thus avoiding any possible interference of the NaCl salt solution. Fig. 2c shows that formic acid was produced, reaching a plateau around 35 ppm at 35 days, while formaldehyde initially at 40 ppm during a few days was steadily consumed after that. H_2O_2 did not attain a measurable concentration during the experiment period. This shows that the oxidation of formaldehyde to formic acid by H_2O_2 had occurred in the air. It also proves that the presence of W1 contributed to a faster and higher conversion yield of formaldehyde (Fig. 2b and c), indicating that paper surface chemistry and/or degradation chemistry play a role.

The conversion of formaldehyde to formic acid in alkaline solutions was already known in the 19th century [46], and more recently, this conversion was speculated to occur in the presence of H_2O_2 at 100% RH [47]. While it is known that this reaction can happen in an aqueous solution, it was not clear from the literature whether it occurred in high yield in the vapour phase or in porous materials such as cellulose.

3.2. Exposure of paper strips to volatile compounds

By exposing papers to various volatile compounds at ambient conditions of temperature and RH, and by studying the various effects on papers and in real time, not only of individual volatile compounds, but also of their mixtures, the present research expands beyond past and recent studies based on individual VOCs exposures at high temperature [21,22]. Figs. 3–5 and S1–S3 (in the supplementary material) show the changes in the physicochemical properties of the papers exposed to volatile compounds and hygrothermally aged.

3.2.1. Individual volatile compounds
3.2.1.1. Exposure to formic acid and to hydrogen peroxide. Hydrogen peroxide in average concentration of 30 ppm (mixed, as explained above, with an average of 3 ppm of organic acids) ('H_2O_2 30 + OA 3') and formic acid (38 ppm) ('FA 38') were found to be the most reactive volatile compounds toward cellulose, with considerable damage observed after the 52 day exposure, and resulting in a decrease in DP for W1 of 91% and 39%, respectively (Fig. 4b). This corresponds to rates of glycosidic bond cleavage $k_{exp52d,\ 21\ °C}$ (W1/H_2O_2) of 1.15×10^{-4} and $k_{exp52d,\ 21\ °C}$ (W1/FA) of 6.39×10^{-6} days^{-1}, respectively ($k_{exp52d,\ 21\ °C}$ (W1/Ctrl) is of course too slow to be measured), and indicates also that cellulose degrades about 18 times faster when exposed to H_2O_2 than to formic acid at similar concentrations. The spectacular decrease in DP of W1 exposed to H_2O_2 (3163–293) was actually the largest possible as cellulose has reached the levelling-off degree of polymerization (LODP). As a result further change in DP upon ageing could hardly be measured [48]. Such a large degradation could explain the release by the paper of 3 ppm organic acids as measured [15,19].

The exposure to H_2O_2 also modified greatly the other measured properties of W1, with the exception of the yellowness index (YI), which decreased slightly initially (Fig. S3b), most likely due to the bleaching effect of H_2O_2. The oxidation of cellulose rose very significantly, with NCu = 5.0 (Fig. S1b), which amounts to approximately 83 μmol g^{-1} CO$_{tot}$, *i.e.* 42 μmol g^{-1} CO (Fig. 3b). This high CO value lies in the upper limit of the oxidation range measured for a set of historic European rag papers from the 16th to the 19th century (5–45 μmol g^{-1} CO) [49] and compares to the
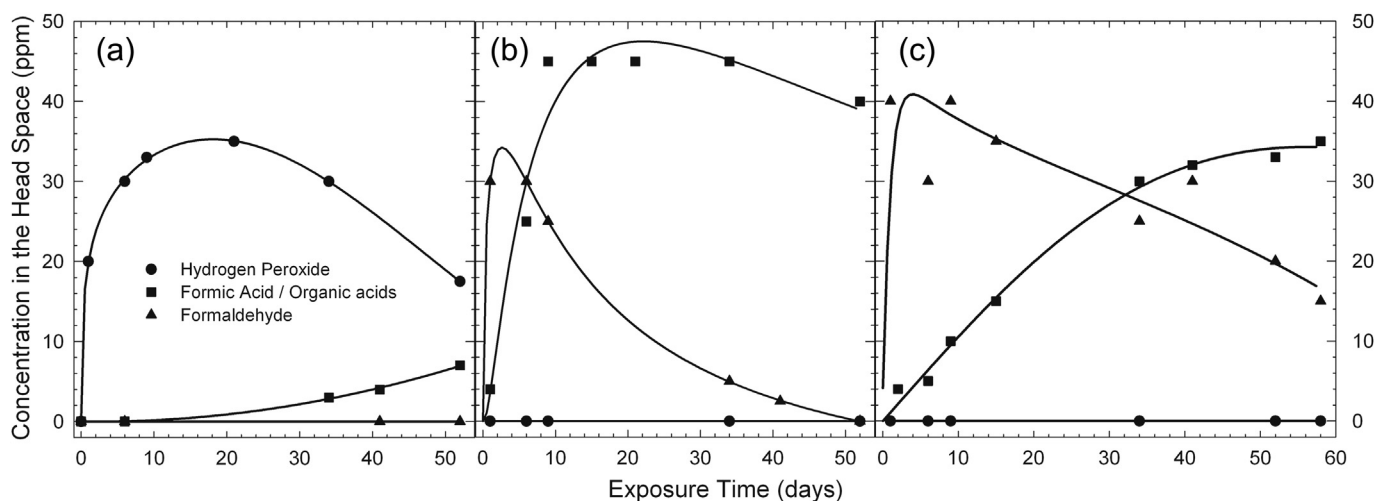
Fig. 2. Evolution of the concentration of volatile compounds in desiccators containing (a) NaCl salt solution (RH 75%) + 30% H_2O_2, with W1; (b) NaCl salt solution (RH 75%) + 30% H_2O_2 + 4% formaldehyde, with W1; (c) 30% H_2O_2 + 4% formaldehyde (RH 100%) without W1.
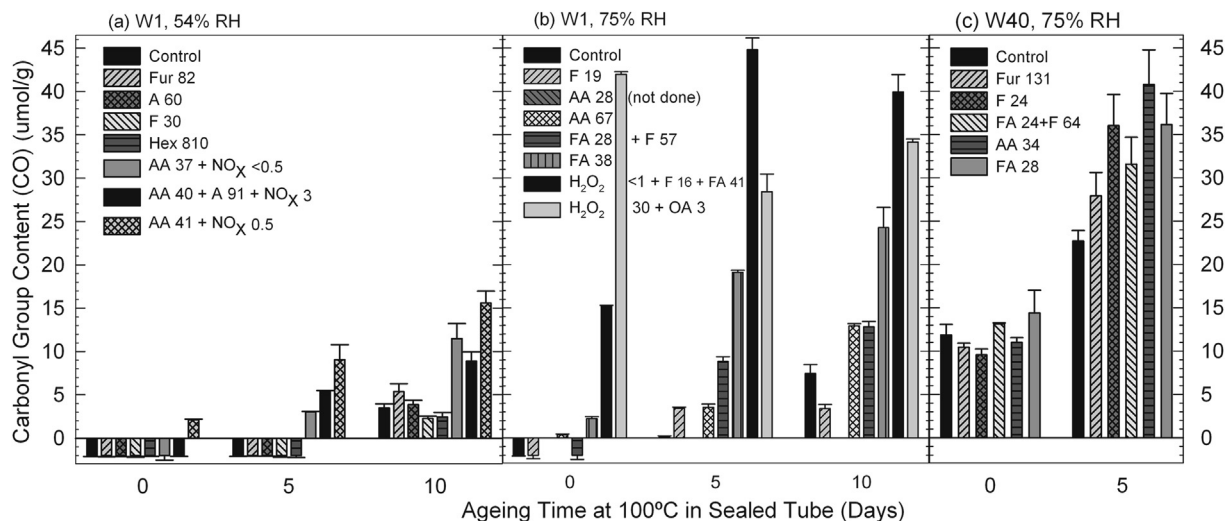
Fig. 3. Carbonyl groups content (CO) (µmol g^{-1}) of cellulose of W1 and W40 exposed for 52 days to volatile compounds, with: A: acetaldehyde, AA: acetic acid, F: formaldehyde, FA: formic acid, Fur: furfural, Hex: hexanal, OA: organic acids. Numbers adjacent to the compounds are in ppm units. (a) W1 at 54% RH, (b) W1 at 75% RH, (c) W40 at 75% RH. Detailed data can be found in Tables 1 and 2. Zero values have been offset at −2 for better visualisation.

oxidation state of iron-gall ink corroded papers [50]. Thus, besides hydrolysis, significant oxidation of the cellulose hydroxyl groups took place (a rough back-calculation shows that to account exclusively for the reducing end-groups, NCu should be approximately of 2.5 in that case). The BL results were consistent with the other measurements, with a decrease of 63% upon exposure to H$_2$O$_2$. Hydrogen peroxide is known to be a non-selective oxidant to cellulose and induce oxidation of the 2-OH, 3-OH or 6-OH to carbonyl or carboxyl groups in acidic conditions, as well as oxidative depolymerization, leading to loss of fibre strength [51]. The present results, in gas phase, are consistent with this action of H$_2$O$_2$. After 5 days of ageing, BL was as low as 1.0 (Fig. 5b) and after 10 days, the samples were too fragile to undergo the measurement. The yellowing increased significantly upon ageing as well. It is known that oxidative bleaches used for pulp and paper oxidize cellulose [52–54] and lead to colour reversion of paper (browning) [55,56].

Conversely, the impact of the exposure to formic acid on the oxidation of W1 was more modest, with NCu = 0.55 (Fig. S1b),

which corresponds to 8 µmol g^{-1} CO$_{tot}$, i.e. 2 µmol g^{-1} CO (Fig. 3b). Indeed, an acid is expected to produce primarily acid catalyzed hydrolysis of cellulose. BL decreased slightly and the pH varied from 6.5 (W1 control) to 5.8 (Fig. S2b). Degradation increased considerably upon ageing. After 5 days, the drop in DP was 73% larger than for the aged W1 control, and after 10 days the LODP was reached (Fig. 4b). The rate of glycosidic bond cleavage upon ageing was about five times higher than for W1 control, with $kt_{ageing, 100 °C}$ (W1/FA) = 5.51 × 10^{-4} days^{-1} ($kt_{ageing, 100 °C}$ (W1/Ctrl) = 1.05 × 10^{-4} days^{-1}). Oxidation also increased considerably with ageing, with NCu of 2.6 after 5 days, and 3.9 after 10 days, which correspond to 43 and 64 µmol g^{-1} CO$_{tot}$, respectively, i.e. 19 and 24 µmol g^{-1} CO, a 20-fold increase. This shows that the hygro-thermal ageing enhanced both hydrolysis and oxidation reactions initiated in cellulose during the VOC exposure. This degradation upon ageing was again corroborated by a decrease in BL, pH and by a small increase of YI (Fig. 5b, S2b and S3b). Traces of formic acid still absorbed in the fibres after the sample desorption period could
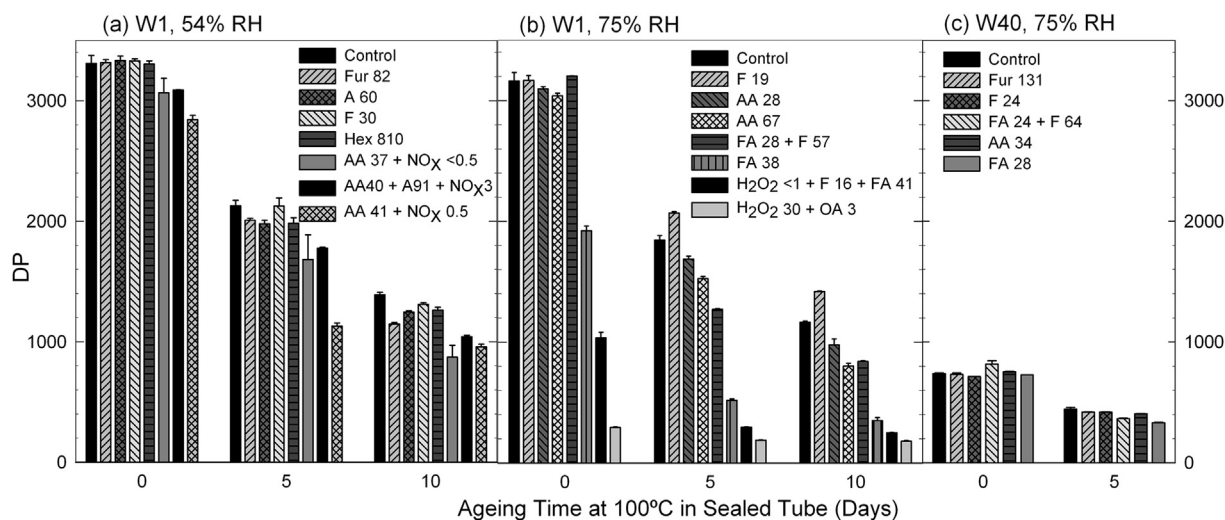
Fig. 4. Degree of polymerisation of W1 and W40 exposed for 52 days to volatile compounds (same abbreviations and numbers as in Fig. 3). (a) W1 at 54% RH, (b) W1 at 75% RH, (c) W40 at 75% RH. Detailed data can be found in Tables 1 and 2.
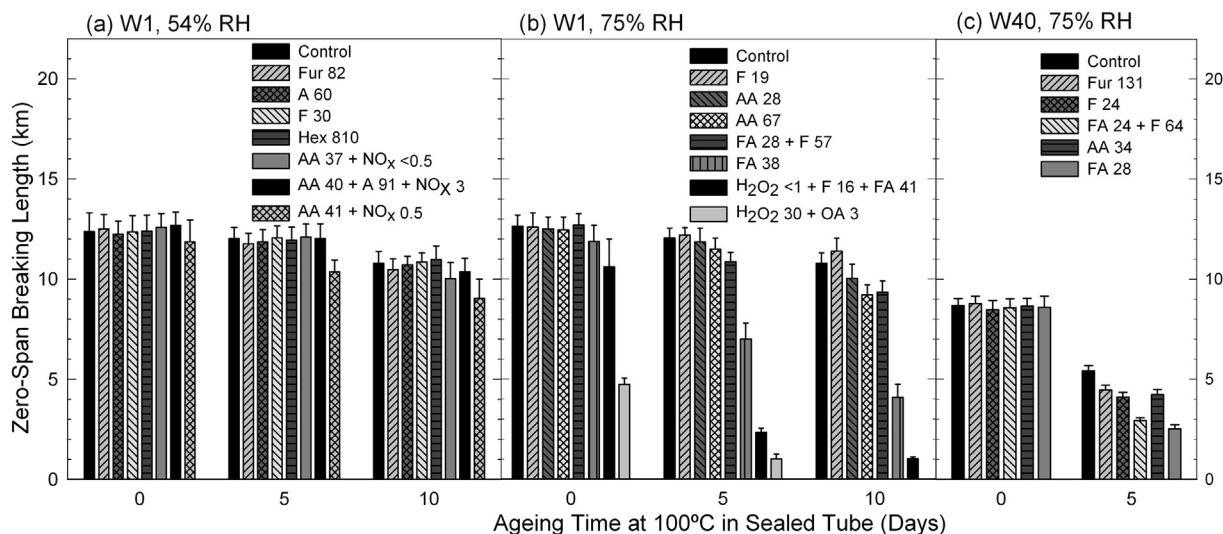
Fig. 5. Zero-span breaking length of W1 and W40 exposed for 52 days to volatile compounds (same abbreviations and numbers as in Fig. 3). (a) W1 at 54% RH, (b) W1 at 75% RH, (c) W40 at 75% RH. Detailed data can be found in Tables 1 and 2.

be responsible for this fast ageing behaviour, but this could not be verified.

Upon the extensive deterioration observed for W1, exposures of W40 to H_2O_2 were not carried out. At the end of the exposure period to formic acid (28 ppm), only small changes in the physicochemical properties of W40 were measured (Figs. 3c–5c and S1c–S3c), indicating no immediate reaction of cellulose with formic acid. Nevertheless, upon ageing the oxidation increased more than for W1, with NCu = 4.4 after 5 days ageing (Fig. S1c), corresponding to 72 µmol g^{-1} CO_{tot}, *i.e.* 36 µmol g^{-1} CO (Fig. 3c), and pointing to the higher sensitivity of W40 to oxidation upon ageing compared to W1. A difference of 25% in DP was observed compared to the aged W40 control sample (Fig. 4c). The rate of glycosidic bond cleavage $kt_{ageing, 100 °C}$ (W40/FA) was 6.33 × 10^{-4} days^{-1}, which is only slightly higher than $kt_{ageing, 100 °C}$ (W1/FA).

3.2.1.2. Exposure to acetic acid. Acetic acid exposures (28 ppm and 67 ppm) at 75% RH caused little damage to W1 cellulose as shown by marginal drops of 2% and of 4% in DP, respectively (Fig. 4b). As observed with formic acid, the level of oxidation upon exposure to the highest acetic acid concentration (67 ppm) was negligible, with NCu = 0.33 (Fig. S1b), corresponding to 4 µmol g^{-1} CO_{tot}, *i.e.* a CO content of 0.4 µmol g^{-1} (Fig. 3b). After hygrothermal ageing, some additional measurable adverse impact was found compared to the aged W1 control sample, especially at the highest concentration, with further reduction in DP of 17% after 5 days (28 ppm exposure induced 8% DP drop). Oxidation slightly increased, with NCu = 0.75 and 1.74 upon 5 and 10 days, respectively, which corresponds to 11 and 28 µmol g^{-1} CO_{tot}, *i.e.* 4 and 13 µmol g^{-1} CO. No significant immediate changes in BL and pH were observed, and after ageing their decrease was still moderate (Fig. 5b and S2b). The correlation between the evolution of DP and zero-span tensile strength of pure cellulose paper upon hygrothermal ageing has been shown to be non-linear [57] in conditions where acid catalyzed hydrolysis degradation is predominant. Whereas a small DP drop can easily be measured for cellulose with relatively high DP, mechanical properties are much less sensitive. Conversely, when the DP has substantially decreased and further DP change is hardly measurable, the variations in tensile strength allow evaluating further degradation.

In the experiments carried out at 54% RH W1 samples exposed to acetic acid (37 ppm) underwent more degradation than during the exposures at 75% RH, with a 7% DP loss, and a pH drop from 6.6 to 6.3 (Fig. 4a and S2a). Here again, no oxidation occurred, with NCu = 0.2 (Fig. S1a), *i.e.* 2 µmol g^{-1} CO_{tot} attributed to the reducing end-groups alone (Fig. 3a). After 5 and 10 days ageing, oxidation increased slightly more than for the respective aged control samples, with NCu = 0.68, (10 µmol g^{-1} CO_{tot}, *i.e.* 3 µmol g^{-1} CO) and 1.58 (25 µmol g^{-1} CO_{tot}, *i.e.* 11 µmol g^{-1} CO), a level comparable to that obtained after ageing upon the exposures at 75% RH. The changes in DP and YI (Fig. S3a) were also somewhat more pronounced than for the respective aged control samples. As explained in section 3.1, it is likely that during this exposure, trace levels of NO_x, below the LOQ of 0.5 ppm, were formed (faint colour of the detection tube). Taking into account the results of the exposures to acetic acid at 75% RH, which had indicated a fairly low reactivity of the acid, it was assumed that this possible trace presence of NO_x had contributed to some extent to the moderate changes observed upon the exposure at 54% RH. This is discussed further on (section 3.2.2.2).

Similarly, acetic acid exposure (34 ppm) did not cause immediate deterioration on W40 nor did it affect significantly its ageing behaviour, in terms of DP, NCu, CO and YI (Figs. 3c and 4c, S1c and S3c). Upon 5 days ageing the DP decreased slightly (by 9%), similarly as for W1, whereas oxidation augmented more significantly to NCu = 4.3, corresponding to 70 µmol g^{-1} CO_{tot}, *i.e.* 41 µmol g^{-1} CO, a four-fold increase. The cellulose degradation was also reflected by a decrease in pH (5.2) and by a decrease in BL (22%) (Fig. 5c and S2c).

Further investigation is needed to understand fully the considerably lower reactivity towards cellulose of acetic acid compared to that of formic acid. However, it can be observed that in the papers, which have a pH in the range 5.5–6.5, acetic acid (pKa = 4.75) is most likely in partially dissociated form. Formic acid being a stronger acid (pKa = 3.75) is more dissociated, therefore resulting in a higher concentration of hydronium ions in the paper, which could explain its higher hydrolytic activity towards cellulose. These considerations are based on solution chemistry, but are to some extent also relevant to paper due to the residual water present in the fibres, which in W1 and W40 was measured in the range 5.4–5.8% (wt/wt).

3.2.1.3. Exposures to aldehydes. Individual aldehydes (formaldehyde, acetaldehyde, hexanal and furfural) did not cause physicochemical degradation in any of the two papers immediately after

exposure whether at 54% RH or 75% RH. Moreover, it was observed that the exposures to formaldehyde even seemed beneficial. W1 exposed to formaldehyde (30 ppm) at 54% RH showed slightly less yellowing than the control samples (Fig. S3a), and at 75% RH (19 ppm) smaller decreases in DP, pH, BL and YI were recorded after ageing (Figs. 4b and 5b, S2b and S3b). After 10 days of ageing W1 exposed to formaldehyde at 75% RH (19 ppm) maintained a higher DP (by 22%) and a lower oxidation level than the control samples, with NCu = 0.78 (Fig. S1b), corresponding to 12 μmol g^{-1} CO$_{tot}$, *i.e.* about 3 μmol g^{-1} CO (for W1 control CO = 7 μmol g^{-1}) (Fig. 3b). The rate of glycosidic bond cleavage upon ageing was about 30% lower than for W1 control ($kt_{ageing, 100\,°C}$ (W1/F) = 7.51 × 10^{-5} and $kt_{ageing, 100\,°C}$ (W1/Ctrl) = 1.05 × 10^{-4} days^{-1}). This retention of the properties measured upon ageing was not observed with the samples exposed to acetaldehyde (Figs. 3a–5a and S1a–S3a).

After 5 days of ageing, the NCu of W40 exposed to furfural (131 ppm) and to formaldehyde (24 ppm) at 75% RH increased slightly, from 3.1 (aged W40 control) to 3.45 and 3.94 (Fig. S1c), respectively, indicating that from 51 μmol g^{-1}, CO$_{tot}$ rose marginally to 56 and 65 μmol g^{-1}, *i.e.* CO from 24 μmol g^{-1} (W40 control) to 28 and 36 μmol g^{-1} (Fig. 3c). The BL of W40 was also moderately affected upon ageing (Fig. 5c). The pH of W40 exposed to formaldehyde decreased slightly less (of 0.2 pH units) upon ageing than for the control samples (Fig. S2c). It appears that carboxylic acids formed somewhat more slowly during the ageing for W40 exposed to formaldehyde. It is known that during the oxidation of cellulose by unspecific oxidants, aldehyde groups are first formed, and further oxidation results in the formation of carboxylic groups on cellulose and small carboxylic acids [51]. These results suggest that the formaldehyde slightly slowed down the course of cellulose oxidation of W40 as well, and corroborate the results obtained with W1.

One hypothesis for the counter-degradation effect of formaldehyde could be a preferential weak affinity bonding. Formaldehyde may be weakly bonded near reactive sites on the cellulose macromolecule (glycosidic bonds and hydroxyl groups), thereby limiting the access for acids, oxidants and/or water molecules, and lowering the rates of acid hydrolysis and oxidation. In the textile industry, formaldehyde is used as a cross-linking agent for cellulose, indicating its reactivity. The reaction occurs under specific conditions of water swelling of the fibres, acid catalyst, reactant concentration and temperature [58,59]. It has been shown to evolve through methylene ether cross-linking, where each methylene bridge blocks two hydroxyl groups from adjacent cellulose macromolecules (Cell-O–CH$_2$–O-Cell) [60]. Whether such cross-linking can also occur in the present experimental conditions, and to what extent, is not known. The lack of degradation from formaldehyde exposure has been observed recently on other materials too, such as aged colour photographic prints [61] and soda silicate glass [62].

3.2.2. Binary mixtures of volatile compounds

3.2.2.1. Exposure to formaldehyde/formic acid.

Corroborating the results obtained upon individual exposure to formaldehyde, less damage was found in both W1 and W40 when exposed to a mixture of formic acid (FA) and formaldehyde (F) than when exposed to formic acid alone (Figs. 3b and c–5b and c and S1b and c–S3b and c). The greatest reduction in damage was observed for W1 ('FA 28 + F 57'). While formic acid (38 ppm) had caused a DP loss of 39%, no change in DP was measured upon exposure to the mixture of formic acid (28 ppm) and formaldehyde (57 ppm) (Fig. 4b). After 5 days of ageing, the DP loss was inferior by 59% compared to the sample exposed to formic acid alone, and the rate of glycosidic bond cleavage was over three times slower, with $kt_{ageing,100\,°C}$ (W1/FA + F) = 1.70 × 10^{-4} days^{-1}. It has to be kept in mind that this is still about three times faster than for W1 Control.

Oxidation occurred on W1 but was also much reduced (by 50%) compared to the oxidation incurred by the formic acid exposure: NCu increased slightly from 0.2 after the exposure to 1.2 and 1.7 upon 5 and 10 days ageing (Fig. S1b), corresponding to 2, 18 and 27 μmol g^{-1} CO$_{tot}$, respectively, *i.e.* 0, 9 and 13 μmol g^{-1} CO (Fig. 3b).

Similarly, W40 samples exposed to the binary mixture of formic acid (24 ppm) and formaldehyde (64 ppm) ('FA 24 + F 64') showed 12% retention in DP and a significantly better BL compared to the samples exposed to formic acid alone (28 ppm) ('FA 28') (Figs. 4c and 5c). Less oxidation was also measured (13 *vs* 36 μmol g^{-1} CO) (Fig. 3c). After 5 days ageing, as observed earlier with W40, oxidation increased with NCu = 3.9, corresponding to 64 μmol g^{-1} CO$_{tot}$, *i.e.* 32 μmol g^{-1} CO, a similar degree of ageing-induced oxidation than that incurred when the paper was exposed to formaldehyde alone and somewhat less than upon exposure to formic acid alone.

More research is needed to fully understand these inhibiting effects but a competition of unreactive and more reactive molecules near the reactive cellulose functions can be proposed.

3.2.2.2. Exposure to acetic acid/NO$_x$ and to acetaldehyde/acetic acid/NO$_x$.

As previously described, in one instance acetic acid (AA) (41 ppm) and magnesium nitrate were suspected of generating small amounts of NO$_x$ (0.5 ppm) (Table 1). What was intended as an individual volatile compound exposure most likely became a binary exposure. In that case, the deterioration observed in W1 was a 14% drop in DP compared to the W1 control sample (Fig. 4a), and some marginal oxidation (NCu = 0,38, *i.e.* 5 μmol g^{-1} CO$_{tot}$ and 2 μmol g^{-1} CO) (Fig. 3a and S1a). After 5 days of ageing, the DP difference was of 47% compared to the aged control sample, with $kt_{ageing, 100\,°C}$ (W1/AA + NO$_x$ 0.5) = 1.74 × 10^{-4} days^{-1}, the degradation rate of W1 control $kt_{ageing, 100\,°C}$ (W1/Ctrl) being 1.05 × 10^{-4} days^{-1}. As reported earlier in section 3.2.1.2, since acetic acid alone (28 and 67 ppm at 75% RH) had been found to cause minor damage, it was concluded that NO$_x$ contributed sizeably to this degradation. This is also consistent with the hypothesis of the presence of trace NO$_x$ (sub-LOQ) in one case of exposure to acetic acid at 54% RH that was assumed to accelerate the degradation. Chain cleavage of cellulose due to acetic acid vapours was reported earlier by the authors [20], and could possibly have been partially due to the production of NO$_x$ in low concentration, which, being an unexpected side-reaction, was not measured at the time. Indeed, the harmful effects of NO$_x$ on papers have been previously reported by various authors [21,63–65].

Likewise, upon the same side-reaction with the magnesium nitrate salt, up to 3 ppm of NO$_x$ were produced in the mixture of acetaldehyde (A) (91 ppm) with acetic acid (AA) (40 ppm) (Table 1). Here, the intended binary volatile compound exposure had become a tertiary exposure ('AA + A + NO$_x$ 3'). Remarkably, even though NO$_x$ was in higher concentration in this tertiary exposure, the DP of W1 decreased less than for the exposure where acetaldehyde was absent but where the occurrence of NO$_x$ was smaller ('AA + NO$_x$ 0.5') (Fig. 4a). With NCu = 0.05, *i.e.* CO = 0 μmol g^{-1} (Fig. 3a and S1a), the oxidation was also much lower for the exposure 'AA + A + NO$_x$ 3' than for the exposure without acetaldehyde. Other properties including BL, pH, and YI followed the same tendency (Fig. 5a, S2a and S3a). Similar to the observations with the mixture of formic acid with formaldehyde, the presence of acetaldehyde led to a considerable inhibition of the reactivity of acetic acid and acetic acid/NO$_x$ on W1. This trend was maintained after ageing. In terms of the degradation rate, $kt_{ageing, 100\,°C}$ (W1/AA + A + NO$_x$ 3) was 1.23 × 10^{-4} days^{-1}, *i.e.* slightly slower than $kt_{ageing, 100\,°C}$ (W1/AA + NO$_x$ 0.5).

3.2.2.3. Exposure to formaldehyde/formic acid/hydrogen peroxide.

Fig. 4b shows that despite a larger degradation compared to the W1

control (DP 67% lower), the DP of W1 exposed to the mixture initially intended, prepared with formaldehyde (4%) and H_2O_2 (30%), was still 3.5 times higher than that of the samples exposed to H_2O_2 alone (30%). From 83 μmol g^{-1} CO_{tot} due to the exposure to H_2O_2 (i.e. 42 μmol g^{-1} CO), in the presence of formaldehyde, the value of NCu dropped to 1.7 (Fig. S1b), with CO_{tot} of 27 μmol g^{-1}, i.e. 15 μmol g^{-1} CO, indicating 64% less oxidation (Fig. 3b). This shows that when formaldehyde was present, considerably less cellulose chain cleavage and oxidation occurred. As explained in section 3.1, it has to be reminded here that H_2O_2 was found to be highly reactive in the gas phase, leading to the production of formic acid when formaldehyde was present, and leaving less than 1 ppm H_2O_2 in the air (Fig. 2b). The actual volatile compounds to which the samples were exposed in the two cases thus were H_2O_2 (<1 ppm)/formaldehyde (16 ppm)/formic acid (41 ppm) ('H_2O_2 < 1 + F 16 + FA 41') and H_2O_2 (30 ppm)/organic acids (3 ppm) ('H_2O_2 30 + OA 3'), respectively. Under similar formic acid concentrations, W1 exposed to the mixture hydrogen peroxide/formaldehyde/formic acid suffered 46% less DP loss than W1 exposed to formic acid alone. Despite its very low concentration, H_2O_2 appears therefore extremely aggressive towards cellulose, as already observed (section 3.2.1.1). The lower degradation when formaldehyde was mixed with H_2O_2 compared to the dramatic effect of H_2O_2 alone was also observed consistently in the values of BL of W1 (Fig. 5b). This damage dampening result was however completely annulled after ageing, as shown by the oxidation taking place after 5 and 10 days, respectively, indicating 85 and 88 μmol g^{-1} CO_{tot}, i.e. 45 and 40 μmol g^{-1} CO, for the sample exposed to 'H_2O_2 <1 + F 16 + FA 41' (NCu of 5.2 and 5.3). Surprisingly, it was even higher than for the sample exposed to 'H_2O_2 30 + OA 3' (NCu of 5.6 and 6.1 after 5 and 10 days, i.e. 92 and 100 μmol g^{-1} CO_{tot}, respectively, and 28 and 35 μmol g^{-1} CO). It has to be noted though, that at the near-LODP values such as those obtained for 'H_2O_2 30 + OA 3', the measurements bear a higher imprecision.

Antagonistic effects upon mixing gases of different reactivity toward cellulose have been observed by other researchers. For instance, nitrogen dioxide (NO_2) is more reactive on paper than sulphur dioxide (SO_2). Adelstein reported that the damage observed on papers exposed to a mixture of NO_2 and SO_2 was smaller than when exposed to NO_2 alone [66]. The mechanism of this is unclear. This aspect of the antagonism on the impact of VOCs needs further investigation.

3.3. Migration of volatile compounds through paper stacks

It is known that damage in books often starts at the edges, and deeper migration occurs with time [67–73]. Literature data is available on the migration of SO_2 through stacks of papers or books [74]. The effect of paper additives such as rosin [75], metals and pigments [76,77] and calcium carbonate [77] on the migration or sorption of SO_2 has also been studied. However, the migration rate of carboxylic acids, peroxides and nitrogen oxides remains unknown.

The migration of formic and acetic acids through a tight stack of W1 sheets at 75% RH as a function of the dose of acid (ppb year) is presented in Fig. 6. It was expected that the most reactive compounds would be mainly adsorbed or retained at the edges of the paper stack while the non-reactive compounds would migrate deeper into the stack. However, the opposite situation was observed. Formic acid was found to migrate deeper into the paper stack than acetic acid and H_2O_2. The results show that, at a dose of 200 ppb year, formic acid would migrate deeper (about 4 cm) than acetic acid by almost of factor of two.

The migration rate in W1 of pollutants in low concentration such as the levels found in archive repositories and archival boxes
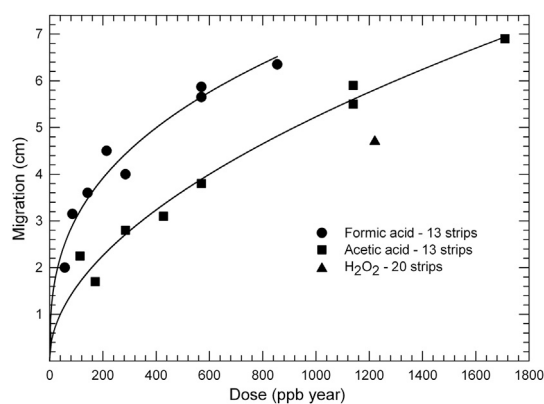

Fig. 6. Migration distance of volatile compounds through W1 stacks kept at 75% RH.

can be extrapolated using a dose-effect approach. Assuming that a concentration as high as 100 ppb formic acid can be present in an enclosure [78], our data indicates that the time required to observe 4 cm-deep migration would be about 2 years (200 ppb year/100 ppb) (Fig. 6). At a few ppb levels, formic acid would migrate less deep inside the paper, consequently leading to a larger degradation of cellulose at the edges than inside the stack, which is the situation often observed in old books. On the other hand, on-going natural acid hydrolysis and oxidation of cellulose inside the stacks also would generate formic acid, acetic acid and other low molar mass organic acids [15], which in turn would slowly migrate their way through the stack, towards the centre or the edges. Several factors could account for these observations, one being, as observed earlier, that at the pH of the paper, the equilibrium of formic acid should be more favourable to dissociation than that of acetic acid, leading to a higher concentration of hydronium ions. This larger amount of H_3O^+ may explain the deeper migration of formic acid in the stack. Other factors that could possibly influence the migration are the size of the molecules and their physicochemical affinity with cellulose functional groups. Further investigation is thus needed to fully understand the kinetics and the equilibria at play in a stack of paper exposed to volatile compounds. Moreover, the results cannot be easily compared with previous research since data on the migration of pollutants in stacks in a specific environment is scarce. One exception is the work by Smith on old books dated from 1899 to 1964 [70]. A small increase in acidity was observed in the centre of the pages of the books which, based on our calculations, corresponded to an exposure to a dose of NO_2 of about 1700 ppb year with an average concentration of 18 ppb of SO_2. This brings the migration rate of NO_2 and SO_2 to the same order of magnitude as that observed with acetic and formic acids in the stacks.

4. Conclusions

The results of this research provided a better understanding of the relative reactivity of volatile compounds on paper at ambient temperature and RH. Formic acid was by far the most destructive carboxyl functionalized VOC toward cellulose. Acetic acid was found to be mildly aggressive, although the results have to be put into perspective as a 52 days-exposure period is certainly short compared to real situations in archives which can sometimes approach several centuries. Additionally, when present in low concentrations, nitrogen oxides seemed to contribute sizeably to the degradation induced by the carboxylic VOCs, and the adverse effect of hydrogen peroxide was found to outreach largely the impact of formic acid. Furthermore, as shown by the exposures of the mock up books to volatile compounds, formic acid penetrates

deeper inside stacks of papers than acetic acid and even H_2O_2, which shows its degradation potential in archives and libraries.

The aldehydes in individual exposures (acetaldehyde, hexanal, formaldehyde and furfural) did not affect non-oxidized cellulose but slightly affected pre-oxidized cellulose. It is noteworthy that the exposure to formaldehyde was actually found to lower the degradation rate of W1 upon ageing. However, since residual volatile compounds in the paper fibres after the post-exposure desorption period of the samples may have contributed to some extent to the effects observed, the results of the hygrothermally aged samples can be taken as indicative.

These degradation effects were found to be largely dampened during the multiple exposures, where the presence of the aldehydes - formaldehyde and acetaldehyde - resulted in a significant reduction of the degradation incurred by the reactive compounds cited above. In the case of the mix of formaldehyde with hydrogen peroxide, formic acid was produced thereby inducing a damage caused by the latter instead of the even larger damage that would be incurred by hydrogen peroxide.

Apart from NO_x, which is an exogenous pollutant, most of these compounds are endogenous as they are commonly released by papers upon natural ageing. The same effects as observed in this study are thus expected to occur through cross-contamination between neighbouring papers, such as in archival boxes. The results clearly show that ambient air quality mostly adversely affects the long-term preservation of historic papers. However, as real situations are extremely complex, more research is needed to better understand the degradation inhibitory effects observed in volatile compounds mixtures, especially those involving an acid or a strong oxidant with an aldehyde, chiefly formaldehyde, as well as the influence of other components than the cellulose in the paper, such as lignin, hemicelluloses, fillers and sizing material.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymdegradstab.2013.05.017.

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