Anal Bioanal Chem (2016) 408:8133–8147
DOI 10.1007/s00216-016-9916-y

RESEARCH PAPER

Understanding paper degradation: identification of products of cellulosic paper decomposition at the wet-dry "tideline" interface using GC-MS

Sergey Sladkevich[1] · **Anne-Laurence Dupont**[2] · **Michel Sablier**[2] · **Dalila Seghouane**[1] · **Richard B. Cole**[1]

Received: 26 May 2016 / Revised: 13 July 2016 / Accepted: 29 August 2016 / Published online: 14 September 2016

Abstract Cellulose paper degradation products forming in the "tideline" area at the wet-dry interface of pure cellulose paper were analyzed using gas chromatography-electron ionization-mass spectrometry (GC-EI-MS) and high-resolution electrospray ionization-mass spectrometry (ESI-MS, LTQ Orbitrap) techniques. Different extraction protocols were employed in order to solubilize the products of oxidative cellulose decomposition, i.e., a direct solvent extraction or a more laborious *chromophore release and identification* (CRI) technique aiming to reveal products responsible for paper discoloration in the tideline area. Several groups of low molecular weight compounds were identified, suggesting a complex pathway of cellulose decomposition in the tidelines formed at the cellulose-water-oxygen interface. Our findings, namely the appearance of a wide range of linear saturated carboxylic acids (from formic to nonanoic), support the oxidative autocatalytic mechanism of decomposition. In addition, the identification of several furanic compounds (which can be, in part, responsible for paper discoloration) plus anhydro carbohydrate derivatives sheds more light on the pathways of cellulose decomposition. Most notably, the mechanisms of tideline formation in the presence of molecular oxygen appear surprisingly similar to pathways of pyrolytic cellulose degradation. More complex chromophore compounds were not detected in this study, thereby revealing a difference between this short-term tideline experiment and longer-term cellulose aging.

Keywords Cellulose degradation · Tideline · Chromophores · Paper conservation

Introduction

Cellulose paper degradation and discoloration caused by the exposure to different environmental conditions remains a main concern for paper-based artwork conservation professionals. A well-documented phenomenon is the appearance of readily visible brown lines during the submerging of cellulose materials into water [1–9]. These narrow "tidelines" appear exclusively on the wet-dry interface—the boundary where the capillary force bringing water up cellulose fibers is compensated by the water evaporation process. A deeper understanding of the cellulose degradation mechanisms is essential to elaborating strategies for preservation and remediation of valuable paper specimens. Water is widely used for the cleaning of degraded graphic documents in conservation workplaces. During a cleaning treatment of a localized area, such wet-dry interfaces can be created in the paper. In addition, dramatic events such as natural floods, water pipe leaks, and water sprinkler inundations caused by fire alarms can unfortunately occur in archival repositories, putting paper documents at risk of water damage. The elucidation of the nature of compounds responsible for the visible paper

Electronic supplementary material The online version of this article (doi:10.1007/s00216-016-9916-y) contains supplementary material, which is available to authorized users.

✉ Anne-Laurence Dupont
aldupont@mnhn.fr

✉ Richard B. Cole
richard.cole@upmc.fr

[1] UPMC Univ Paris 06, CNRS, Institut Parisien de Chimie Moléculaire (IPCM), Sorbonne Universités, 4 Place Jussieu, 75252 Paris Cedex 05, France

[2] Centre de Recherche sur la Conservation des Collections (CRC, USR 3224), Muséum National d'Histoire Naturelle, Ministère de la culture et de la communication, CNRS, Sorbonne Universités, CP 21, 36 rue Geoffroy Saint-Hilaire, 75005 Paris, France

discoloration at the tideline can provide a better comprehension of the specific chemical reactions involved in their formation, which will enable the use of appropriate measures to limit or stop the degradation involved.

Documentation of the appearance of brown-colored tidelines in cellulose-containing materials was described in the 1930s [1], and early research aiming to find an explanation for this phenomenon dates from the early 1950s [2–4]. Nonetheless, the mechanism of brown line formation during cellulose degradation at the wet-dry boundary has not been completely clarified, including the identification and cataloging of low molecular weight products forming at the interface.

Bone and Turner [2], Bogaty et al. [3], and Madaras and Turner [4] reported the observation of increased UV fluorescence and cellulose depolymerization and thus established via the use of different experimental setups and conditions that the tideline formed at the cellulose-water interface in the presence of atmospheric oxygen involves oxidative degradation of cellulose. More recent research concerning tidelines [5–8] has largely confirmed these observations. Early infrared (IR) spectroscopy experiments of brown line extracts [6] showed the absorbance bands of long-chain alkanes, and likely those of aliphatic ethers, as well as the bands corresponding to carboxylic acid salts. The FTIR study of the dry residues of brown line extracts [8] also established the presence of aliphatic ether groups and carboxylate salt bands (though no evidence of acidic O–H bands was found). This same FTIR experiment also revealed the vibrational bands characteristic of alcohol O–H, carbonyl (probably from ketone or lactone), and ethylene groups.

Further evidence of the oxidative nature of acid-catalyzed cellulose degradation in the tideline area was shown by analyzing the low molecular weight products forming in the tideline using capillary zone electrophoresis, and by quantification of acetic and formic acids, as well as various hydroperoxo species, which accumulate in the tideline over time [10]. Exposure to atmospheric oxygen at the wet-dry interface is proposed to promote the formation of hydroperoxide species which, in the presence of trace amounts of metal ion catalyzers such as Fe, Mn, or Cu, can decompose to free radicals. The latter species can contribute to amplified cellulose degradation and the appearance of chromophore containing products responsible for discoloration in the tideline area [9–12].

Though several groups of low molecular weight compounds forming in the wet-dry interface on cellulose paper were identified, isolation and identification of compounds responsible for the characteristic discoloration at the tideline remain a challenge. In this regard, some similarities can be drawn between cellulose degradation occurring in the narrow tideline area and that taking place in artificially aged cellulose samples. Application of accelerated aging techniques, whose protocols can vary considerably, is often used to evince mechanisms of cellulose oxidation and hydrolysis as well as demonstrate physical deterioration of cellulose (degree of polymerization, mechanical properties, etc.) [9, 13]. The work by Lewin and colleagues [14–16] on oxidized cellulose showed that yellowing of the material is due to the formation of free aldehyde groups at the C1 carbon of terminal glucose moieties of the cellulose chain. This leads to “peeling” of glucose units, their decomposition and isomerization, and finally, condensation to furan derivatives. This conclusion was further confirmed by other researchers [8] who identified the glucose C1 oxidation products—gluconic acid and its lactone. Moreover, the oxidation at C6 was also evidenced by the formation of glucuronic acid; however, furan derivatives were not detected in this later work.

In a series of articles published by Lojewska et al. [17–19], the artificial aging of cellulose paper was investigated using FTIR, UV-vis, and Raman spectroscopy in order to trace hydrolytic cellulose degradation and pertinent oxidation processes. Production of oxidized species containing carbonyls, diketones, aldehydes, and carboxyls was shown in these studies, and the model of chromophore formation through the appearance of conjugated ketones on cellulose chains was proposed.

The employment of nondestructive ambient desorption electrospray ionization-mass spectrometry (DESI-MS and paper spray-MS) techniques was recently shown to be useful for the detection of individual chromophore compounds in both artificially aged cellulose specimens and historical paper [20]. Although present in the paper at only very low concentrations, key chromophores (2,5-dihydroxyacetophenone, 2,5-dihydroxybenzoquinone, 5,8-dihydroxynaphthoquinone) were successfully detected by these techniques.

Corsaro et al. [21] used the ^{1}H magic-angle spinning (MAS) NMR technique to investigate cellulose degradation products in ancient and artificially aged paper. NMR spectral interpretation allowed the authors to conclude that the main products of cellulose degradation are low-mass carboxylic acids. Hexanoic acids (six carbon atoms) should be the main acid product due to the ring opening of glucopyranose. Other common degradation products for all types of paper are formic and acetic acids. Among other compounds identified by MAS NMR were dicarboxylic acids and hydroxycarboxylic acids.

Ab initio density functional theory calculations were also carried out in order to estimate the probability of formation of different chromophore groups responsible for paper discoloration appearing during cellulose aging [22, 23]. By comparing the calculation results to the UV-visible reflectance spectra, it was shown that the main chromophore moieties responsible for paper discoloration are aldehyde groups and conjugated diketones [22].

The aim of the present study is to further investigate the low molecular weight compounds forming in the wet-dry interface in cellulose paper and to put an effort into

identification of key products responsible for visible tideline discoloration using hyphenated gas chromatography-mass spectrometry (GC-MS) analysis. Several extraction protocols and analysis configurations were employed in order to broaden the ability to detect a wide range of products forming in the tidelines. Brown line extracts were prepared either by direct solvent extraction (in water or methanol) or by utilizing a more laborious chromophore release and identification (CRI) protocol, proposed originally by Rosenau et al. [24–26] to liberate chromophore compounds covalently bound to cellulose chains.

Materials and methods

Materials and chemicals

Whatman No. 1 paper sheets (Fisher Scientific, Illkirch, France) composed of pure cotton cellulose were used to prepare tidelines. Water (HPLC-grade), dichloromethane (99.5 %), boron trifluoride acetic acid complex (36 % BF_3), acetic acid (glacial), ethereal hydrogen chloride solution (2 mol L^{-1}), α-tocopherol, sodium sulfite (98 %), and sodium hydrogen carbonate (99 %) were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France). Methanol (HPLC-grade) was purchased from Fisher Scientific (Illkirch, France). Ethyl acetate (SupraSolv® MS) and sodium sulfate (p.a.) were purchased from VWR International (Fontenay-sous-Bois, France). All reagents were used without further purification.

Tideline preparation

Tideline preparation was carried out in different environments. First, direct extractions were performed for the tidelines prepared in a climate-controlled room at fixed temperature and relative humidity. Twenty-two sheets of Whatman No. 1 paper (15 cm × 28 cm) were suspended vertically; the lower part was immersed 2 cm deep in deionized water (Millipore, Molsheim, France) with a few centimeters of space between adjacent sheets. The experiment was carried out in a climate-controlled room in the dark at 23 °C, with 50 % relative humidity, for 16 h. The sheets were then left to dry. Formed brown lines were cut out from paper sheets as close as possible to the boundary. The lines were further cut into smaller pieces of ca. 2–3 mm. Subsequently, the whole tideline preparation was carried out in an analogous manner under "clean" ambient conditions using HPLC-grade water in a laboratory where no paper-related experiments were previously conducted. The environment can thus be considered to be free of any reagents used in paper treatment experiments. This second approach was used for the preparation of tidelines extracted further by direct aqueous and modified CRI protocols (see Table 1).

Preparation of aqueous tideline extract

Soluble products formed in the tidelines were extracted in triplicate by wetting the sample with deionized water. Deionized water (2.5–3.0 mL) was sufficient to cover the tideline sample cuts in the extraction vial (generally 0.33–0.39 g of tidelines produced by the procedure described above). After 6 h, the liquid above the tidelines was collected by pressing the paper cuts through a 0.45-μm-pore sized polytetrafluoroethylene (PTFE) syringe filter. The obtained filtrate of pale yellow color was stored at −18 °C before analysis.

Preparation of methanol tideline extract

Tideline extract in methanol was prepared by the same protocol described above, using an HPLC-grade solvent instead of water.

Preparation of aqueous and methanol extracts of untreated Whatman paper

Aqueous and methanol extracts were also prepared in triplicate using the untreated Whatman No. 1 paper as another

Table 1 Tideline and untreated Whatman No. 1 paper samples, tideline preparation conditions, and different extraction protocols employed to release low molecular weight compounds from the samples

Sample type	Tideline preparation conditions	Method of extraction	Solvent	Extract color
Tidelines formed on Whatman No. 1 paper	Climate-controlled room	Direct extraction	Water	Pale yellow
			Methanol	Almost colorless
Pure Whatman No. 1 paper		Direct extraction	Water	Colorless
			Methanol	Colorless
Tidelines formed on Whatman No. 1 paper	Ambient, using HPLC-grade water	Direct extraction	Water	Pale yellow
Tidelines formed on Whatman No. 1 paper	Ambient, using HPLC-grade water	Modified CRI method	Dichloromethane	Brown-green
Pure Whatman No. 1 paper		Modified CRI method	Dichloromethane	Almost colorless

"blank," according to the procedure described above. Small pieces of Whatman paper were exposed to solvent in a closed vial and filtered after 6 h using a PTFE syringe filter. The collected filtrate was analyzed in the same way as the tideline extracts in order to distinguish the products present in the untreated paper.

Preparation of tideline extract using a modified CRI method

A modified version of the CRI protocol, proposed originally by Rosenau et al. [24], was utilized in this work in an attempt to solubilize and identify compounds containing chromophore moieties covalently bound to cellulose chains. The tideline extraction using the CRI protocol was performed in triplicate as follows:

To a vial containing tideline cuts (0.33 g), 10 mg of sodium sulfite, 2.1 mL of dichloromethane, and 0.9 mL of boron trifluoride acetic acid complex were added. The closed vial was slightly shaken to let the sample be covered completely with solution and was left for 48 h. The extract was separated from the tideline cuts by filtering through a 0.45-μm-pore sized PTFE filter connected to a 10-mL glass syringe equipped with a Luer Lock connector. The sample was put into the syringe, pressed out, and washed three times with glacial acetic acid. The solids were discarded, and the filtrate was transferred to a separatory funnel. The solution of 10 mg of α-tocopherol in 1 mL dichloromethane was added, followed by 10 mL of Milli-Q water; then, the solution was shaken, and after phase separation, the organic part was decanted to a separate flask. The water phase was then extracted three times with 2 mL of dichloromethane. The organic phases were combined and washed with 0.5 mol L^{-1} sodium hydrogen carbonate until acid-free and then dried over sodium sulfate. The volume of the obtained extract was reduced to half by solvent evaporation at 45 °C. Methanol (0.3 mL) and 2 mol L^{-1} ethereal hydrogen chloride solution (0.1 mL) were then added to the extract, the mixture was heated again at 45 °C for 15 min, and the final extract volume was adjusted to 2 mL by solvent evaporation. The product was filtered again through a 0.45-μm-pore sized PTFE syringe filter and stored in a refrigerator before analysis.

In the extraction method used in the current work, several modifications of the original CRI procedure were introduced. First, the experimental setup was scaled down to perform the extraction of a small amount of the tideline sample. In addition, the resulting extract was not evaporated to dryness, and a step of chromatographic separation of different fractions of products on a silica column was omitted, as the resulting extract was a clear solution with low chromophore concentration.

Preparation of Whatman No. 1 paper extract using a modified CRI method

A reagent blank was prepared in triplicate by the same protocol without tidelines. The blank was analyzed in the same way as the tideline extracts in order to identify contaminants which do not originate from the tideline sample. The untreated Whatman No. 1 paper was used to prepare the extract by the modified CRI protocol. Similarly, the small cuts of paper were extracted instead of tidelines following the same steps described above. The obtained extract was analyzed in the same way as the tideline extracts in order to reveal contaminants which are present in the untreated paper or form during the extraction.

GC-MS experiments

GC-MS experiments were conducted on an Agilent 7890B GC system coupled to a 5977A MSD mass spectrometer equipped with an extractor electron ionization source and a single quadrupole analyzer (Agilent Technologies, Les Ulis, France). Sample injection was performed in triplicate in the splitless mode using an automatic sampler. The chromatographic separation was performed on two different capillary columns: nonpolar highly inert VF-5ms with 5 % phenylmethylpolysiloxane phase (30 m, 0.25 mm, 0.25 μm, Agilent Technologies) and a polar DB-FFAP with nitroterephthalic acid-modified polyethylene glycol stationary phase (60 m, 0.32 mm, 1.00 μm, Agilent Technologies). Helium was used as a carrier gas with a flow of 1 mL min^{-1} for the nonpolar column and 1.8 mL min^{-1} for the polar column. The injector temperature was set to 250 °C for all runs; the interface temperature was 280 °C in the case of the nonpolar column and 250 °C for the polar one. Temperature programming was employed for both the nonpolar column (50–80 °C in 1.5 min and then 80–280 °C in 40 min with a hold time of 1 and 5 min at starting and end temperatures, respectively) and the polar column (30–240 °C in 10.5 min with a hold time of 1 and 20 min at starting and end temperatures, respectively). All mass spectra were acquired in scan mode over the range m/z 29–420. The ion source and the quadrupole detector temperatures were held at 230 and 150 °C, respectively, and the ionization energy was 70 eV. Qualitative analysis of the obtained data was carried out using MassHunter Workstation software (Agilent Technologies). Attribution of the mass spectra to chemical compounds was performed with assistance from the NIST mass spectral library.

Tideline sample analyses by GC-MS

Triplicate aliquots of aqueous tideline and Whatman No. 1 paper extracts were dried at room temperature in vacuo and

dissolved in an equal amount of methanol prior to GC-MS analyses using the polar column. For the analyses with the nonpolar column, the samples were further diluted tenfold with ethyl acetate. The tideline and untreated Whatman No. 1 paper samples prepared by direct methanol extraction protocols were analyzed by GC-MS, equipped with a polar column without dilution or pretreatment. For analyses with the nonpolar column, the samples were diluted tenfold with ethyl acetate prior to GC-MS injection. No dilution or pretreatment was employed prior to polar column GC-MS analyses of the reagent blank, the untreated Whatman No. 1 paper samples, or the tideline extracts prepared by the modified CRI protocol. For analyses with the nonpolar column, the samples were diluted tenfold with methanol prior to GC-MS injection.

Electrospray ionization using an Orbitrap mass analyzer (Orbitrap ESI-MS)

High-resolution mass spectra were recorded on an LTQ Orbitrap XL mass spectrometer equipped with an ESI source (Thermo Instruments). The experiments were performed in positive and negative ion modes; spray voltage was set to ±3.5 kV. In the positive ion mode, the capillary voltage and the tube lens offset were set to 8 and 46 V, respectively, and in the negative ion mode, they were set to −2 and −23 V, respectively. The mass spectra were acquired in the range *m*/*z* 50–1000 at a resolution of 100,000 at *m*/*z* 400. The maximum injection time was 200 ms, and each mass spectrum represents the average of three scans. All samples were diluted tenfold with methanol and introduced into the ESI source at a flow rate of 5 μL min^{-1} using a syringe pump. Elemental composition was calculated using Xcalibur software (Thermo).

Results and discussion

Tideline samples and extracts

To begin our investigation of the low molecular weight compounds formed in so-called "tidelines" at the wet-dry interface of cellulose paper, pure cotton paper (Whatman No. 1) was used to prepare tideline samples following the procedure outlined in the "Materials and methods" section (Fig. 1a). The variety of samples prepared and analyzed in the current work, along with their preparation conditions and methods of extraction, are summarized in Table 1. Two different protocols were employed to extract low molecular weight soluble products of cellulose oxidative decomposition from the tidelines. First, a direct extraction was performed using either water or methanol as the solvent. Filtered water extracts typically exhibited a light yellow coloration (Fig. 1b), whereas methanol extracts were almost colorless. This observation further confirms previous reports claiming that the most effective

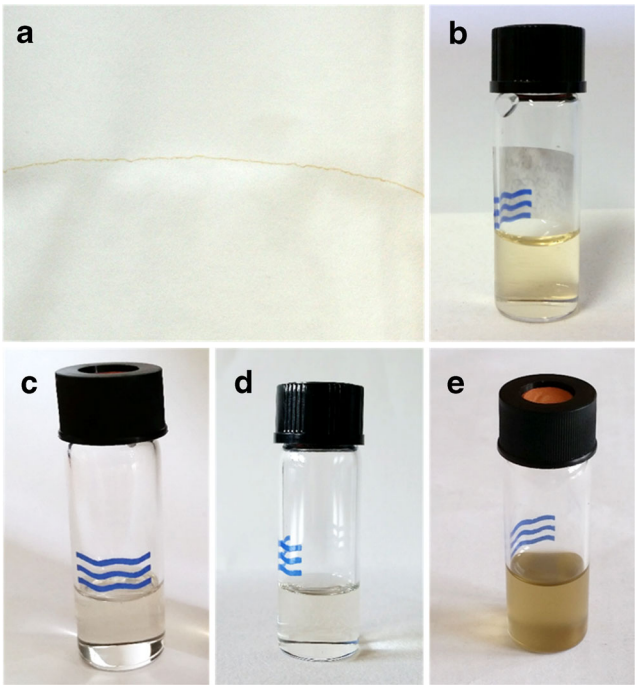

Fig. 1 **a** Tideline formed on the wet-dry boundary in pure cellulose paper by partial immersion in water. **b** Direct aqueous extract of tidelines. **c** Extracts prepared by the modified CRI protocol for chromophore release: reagent blank, **d** Whatman No. 1 paper blank, and **e** tideline extract

extraction of colored materials from brown lines can be reached when the solvent used for tideline preparation and extraction is the same [7]. A second extraction protocol, chromophore release and identification (CRI) developed by Rosenau et al. [24–26], employs a method for chromophore release from cellulose materials. In this case, the obtained extract had a deeper brown color (Fig. 1e), which signals a more efficient release of colored compounds from paper to solvent. In addition to the tideline samples analyzed, both protocols were used to prepare extracts from pure, *untreated* Whatman No. 1 paper (Fig. 1d). The analysis of these blank samples served to distinguish between the compounds formed in cellulose exclusively at the wet-dry interface of tidelines, and those present in paper or adsorbed during storage, which can be brought to this interface with the waterfront.

Direct aqueous extraction of tidelines

Figure 2 presents the total ion current (TIC) chromatograms obtained by GC-MS using a nonpolar column for the direct aqueous extracts of: (a) untreated Whatman paper, (b) tidelines prepared in the climate-controlled room, and (c) tidelines prepared under ambient conditions in the contamination-free laboratory using HPLC-grade water. The GC-MS data obtained using the polar column is shown in Fig. 3, which presents the TIC chromatograms of the aqueous extract of: (a) the untreated Whatman paper and (b) tidelines prepared under ambient

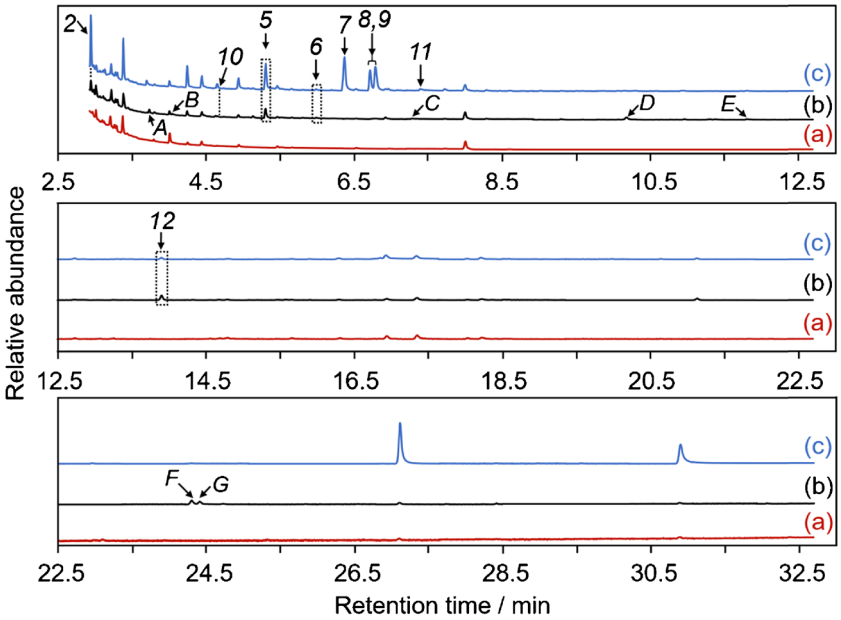

Fig. 2 TIC chromatograms obtained from GC-MS experiments with a nonpolar column for aqueous extracts of untreated Whatman No. 1 paper (**a**), tidelines prepared in climate-controlled room (**b**), and tidelines prepared in the contamination-free laboratory using HPLC-grade water (**c**). *Peak labels* correspond to the assignments indicated in Table 2 and Fig. 4. Pollutants originating from a fused silica column or solvents used in the process are not labeled

conditions in the contamination-free laboratory using HPLC-grade water. Several chromatographic peaks observed in the aqueous tideline extracts are absent from the untreated Whatman paper chromatogram and can be thus attributed to the compounds formed exclusively in the brown line during paper immersion into water. These peaks are denoted by numbers, and they are listed in Table 2 next to the column type (polar or nonpolar) used for their separation. Identification of several compounds isolated by GC-MS was additionally confirmed by high-resolution mass spectrometry (HR-MS) experiments performed on an LTQ Orbitrap mass spectrometer. The exact masses of molecular ion adducts with sodium (formed in positive mode) or deprotonated species (in negative mode) are shown in Table 2 with the corresponding mass error.

The compounds identified during GC-MS analyses are reported in Table 2, and the structures of some of these compounds appear in Fig. 4. The compounds can be divided into several groups: first, a series of linear carboxylic acids, from acetic to octanoic acids (compounds **13** to **19** in Fig. 3 and Table 2), were observed when using the polar GC column. This data confirms previous observations showing the formation of carboxylic acids among the major products of cellulose oxidation both in tidelines and in aged (both naturally and artificially) cellulose paper [10, 17, 21, 27–30]. Formation of carboxylic acids during the oxidation of cellulose portions can increase the overall acidity of paper and further accelerate/amplify the breakup of cellulose chains, in accordance with an autocatalytic nature of oxidative paper degradation [31]. Second, ethylene glycol and propylene glycol (compounds **1** and **2**, respectively) were identified. These diols were not reported previously as main products of cellulose degradation, though the presence of hydroxyl groups from alcohols in the

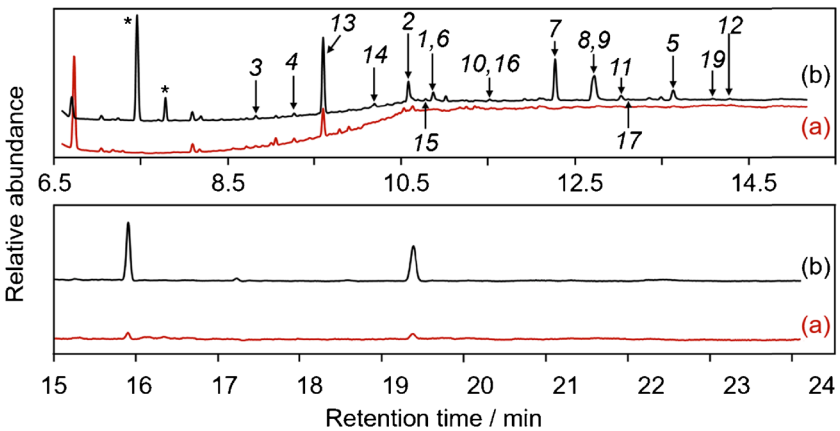

Fig. 3 TIC chromatograms obtained from GC-MS experiments with a polar column for aqueous extracts of untreated Whatman No. 1 paper (**a**) and tidelines prepared in the contamination-free laboratory using HPLC-grade water (**b**). *Peak labels* correspond to the assignments indicated in Table 2 and Fig. 4. Peaks of contaminants appearing due to the sample preparation are marked with *asterisks*. Pollutants originating from a fused silica column or solvents used in the process are not labeled

Table 2 Low molecular weight compounds identified in the tideline extract prepared by direct aqueous or methanol extraction protocols using GC-MS and Orbitrap ESI-MS

Peak label	Compounds identified by GC-MS using the NIST library	Formula	Molecular weight	Column type[a]	Exact mass confirmation by Orbitrap ESI-MS[b], exact mass (formula) [error, ppm]
1	Ethylene glycol	$C_2H_6O_2$	62	P	
2	Propylene glycol	$C_3H_8O_2$	76	N, P	99.0412 ($C_3H_8O_2Na$) [−3.4]
3	1-Hydroxyacetone (acetol)	$C_3H_6O_2$	74	P	73.0292 ($C_3H_5O_2$) [−3.5]
4	Methyl glycolate	$C_3H_6O_3$	90	P	89.0240 ($C_3H_5O_3$) [−4.5]
5	2,2′-Oxydiethanol (diethylene glycol)	$C_4H_{10}O_3$	106	N, P	129.0520 ($C_4H_{10}O_3Na$) [−1.2]
6	2-(2-Ethoxyethoxy)ethanol	$C_6H_{14}O_3$	134	N, P	157.0833 ($C_6H_{14}O_3Na$) [−0.1]
7	1,1′-Oxydi-2-propanol	$C_6H_{14}O_3$	134	N, P	
8	2-(2-Hydroxypropoxy)-1-propanol	$C_6H_{14}O_3$	134	N, P	
9	2,2′-Oxydi-1-propanol	$C_6H_{14}O_3$	134	N, P	
10	γ-Butyrolactone	$C_4H_6O_2$	86	N, P	85.0291 ($C_4H_5O_2$) [−4.8]
11	3,3′-Oxydi-2-butanol	$C_8H_{18}O_3$	162	N, P	185.1147 ($C_8H_{18}O_3Na$) [0.6]
12	1,2,3-Propanetriol triacetate (triacetin)	$C_9H_{14}O_6$	218	N, P	241.0681 ($C_9H_{14}O_6Na$) [−0.7]
13	Acetic acid	$C_2H_4O_2$	60	P	
14	Propanoic acid	$C_3H_6O_2$	74	P	73.0292 ($C_3H_5O_2$) [−3.5]
15	Butanoic acid	$C_4H_8O_2$	88	P	87.0449 ($C_4H_7O_2$) [−4.3]
16	Pentanoic acid	$C_5H_{10}O_2$	102	P	101.0603 ($C_5H_9O_2$) [−5.0]
17	Hexanoic acid	$C_6H_{12}O_2$	116	P	115.0758 ($C_6H_{11}O_2$) [−5.4]
18	Heptanoic acid	$C_7H_{14}O_2$	130	P	129.0914 ($C_7H_{13}O_2$) [−5.4]
19	Octanoic acid	$C_8H_{16}O_2$	144	P	143.1071 ($C_8H_{15}O_2$) [−4.8]
20	Nonanoic acid	$C_9H_{18}O_2$	158	P	157.1227 ($C_9H_{17}O_2$) [−4.4]

[a] Column type used for compound separation: N = nonpolar column VF-5ms and P = polar column DB-FFAP

[b] The presented exact masses are for sodium adduct species $[M+Na]^+$ in positive ESI mode and for deprotonated species $[M-H]^-$ in negative mode

tideline extracts was shown using IR spectroscopy [8]. Ethylene and propylene glycols, as well as 1-hydroxyacetone (**3**), were reported as products of catalytic cellulose decomposition [32, 33], with 1-hydroxyacetone also being one of the products of cellulose pyrolysis [34]. Identification of methyl glycolate (**4**) is in line with previous studies of aged cellulose samples and tidelines that mention the formation of glycolic acid [13, 30]. Ethylene glycol (**1**) and propylene glycol (**2**) likely serve as precursors for the formation of a third group of compounds identified in the tideline extracts (i.e., **5** to **9** in Figs. 2, 3, and 4 and Table 2). Diethylene glycol (**5**) and 2-(2-ethoxyethoxy)ethanol (**6**) can be regarded as condensation products of ethylene glycol, whereas 1,1′-oxydi-2-propanol (**7**) and its structural isomers (**8** and **9**) are the condensation products of propylene glycol. These condensation products can form during tideline

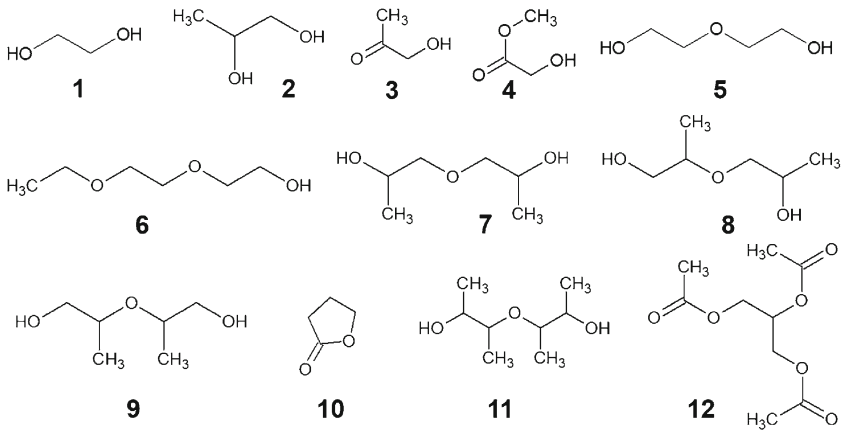

Fig. 4 Several low molecular weight compounds identified by GC-MS in the tideline extract prepared by direct aqueous and methanol extraction protocol

formation, and their appearance and relative abundance in GC-MS spectra depend upon the conditions of tideline preparation. In comparing the chromatograms in Fig. 2(b, c), which present correspondingly the data obtained for the tidelines prepared under controlled conditions in the climate-controlled room versus under ambient conditions with temperature and relative humidity differences during the overnight experiment, one can observe the lower abundances of condensation products **5** and **6** and the absence of the products **7**, **8**, and **9** in the spectrum of tidelines prepared in the climate-controlled room. Higher ambient temperature during the preparation of the tidelines out of the climate-controlled room is likely responsible for the more pronounced signals of condensation products **7**–**9**. Compound **11** (Table 2, Fig. 4) also can be regarded as a condensation product of two lower mass monomer compounds; the latter were not detected by GC-MS.

γ-Butyrolactone (**10**) was detected in low abundance in GC-MS spectra of tideline samples obtained for both polar and nonpolar columns. This compound was previously found among the volatile products of aged cellulose paper [29]. In general, the formation of lactones (e.g., D-gluconic acid δ-lactone) is highly probable during acidic cellulose oxidation, if carboxyl groups form in positions suitable for intramolecular esterification [8, 35, 36]. Compound **12**, identified as triacetin, was found in the GC-MS spectra of tidelines obtained with both polar (Fig. 3, trace (b)) and nonpolar (Fig. 2, traces (b) and (c)) columns, and its peak is absent in the spectra of pure Whatman paper (trace (a) in Figs. 2 and 3). Triacetin is a widely used plasticizer in the cellulose acetate industry, and its presence in the tidelines can be reasonably explained by sample contamination, which stems from cellulose acetate film samples stored in the same climate-controlled room during the course of the experiment. Adsorbed onto paper in a polluted environment, it can be brought to the wet-dry interface by the capillary effect and accumulate in this area.

Direct methanol extract of tidelines

The GC-MS TIC chromatographic peaks for the methanol extracts are presented in Figs. S1 and S2 of Electronic Supplementary Material (ESM) for nonpolar and polar capillary columns, respectively (trace (a) shows the data for pure Whatman No. 1 paper and trace (b) for the tidelines prepared in the climate-controlled room). The chromatographic peaks (denoted by numbers in ESM Figs. S1 and S2) and their assignments to compounds are reported in Table 2 and Fig. 4. Similar to the aqueous extracts results, the juxtaposition of the spectra obtained for the tidelines and the untreated Whatman paper allows the visualization of the peaks corresponding to compounds formed in the tideline. The comparison of the results obtained for the same type of column but with different extraction solvents (water or methanol) reveals little difference. Fewer chromatographic peaks can be discerned in the spectrum obtained for the methanolic tideline extract with the nonpolar column (ESM Fig. S1, trace (b)), and all products identified in the methanolic extract were found in the aqueous extract (Fig. 2, trace (b)). In the case of GC-MS analysis with the polar column, most of the identified compounds were also found in aqueous extracts, except heptanoic acid (**18**) and nonanoic acid (**20**), which were found only in the methanolic extract.

Thus, the change of solvent from water to polar organic (methanol) did not reveal additional groups of compounds originating from cellulose decomposition, compared to those already found in the aqueous extracts. This observation, and also the fact that more intense coloration was achieved for the aqueous extract of the tidelines, further strengthens the findings of preceding researchers, who concluded that the most efficient solvent for extraction is the same one that was used for tideline formation in paper [7]. Despite the successful identification of several low molecular weight compounds which form exclusively in the tideline area, and which can be described as cellulose oxidation products, paper discoloration cannot be explained by any of the, at best, weakly absorbing compounds detected in the direct aqueous and methanol extracts of tidelines.

Several contaminants identified in the tideline extracts

One can expect that only compounds containing C, H, and O are produced from pure cellulose during its oxidative degradation. However, several compounds containing nitrogen, phosphorus, or sulfur were identified (in low abundances) by GC-MS analysis of aqueous and methanol extracts of tidelines (Fig. 2, trace (b); ESM Figs. S1 and S2). The appearance of these compounds, denoted by letters (A–H), in the TIC of tideline extracts, and their absence in the spectra of the pure Whatman paper extracts (trace (a) in Fig. 2, ESM Figs. S1 and S2) can be explained from our point of view by the presence of contaminants in the experimental environment (air and/or water), and these contaminants should not be confused with the products originating from cellulose degradation.

Several of the identified pollutant compounds, i.e., those with the most intense chromatographic peaks, are presented in Table 3. *N*,*N*-Dimethylacetamide (B) is commonly used as a solvent for cellulose, and it may have originated from a working zone adjacent to the climate-controlled room, where cellulose-related experiments are routinely carried out. Formation of compounds A (2-methylpyrrole) and C (2-pyrrolidinone) can be reasonably explained by the reaction between carbohydrate fragments and amino compounds (amino acids), resembling the Maillard reaction, which can be present as contaminants in the working zone. The probability of the formation of pyrrols and pyrrolidones from carbohydrates was shown,

Table 3 Several pollutant compounds identified using GC-MS with a nonpolar column in the tideline extracts prepared by direct aqueous or methanol extraction protocols. Tidelines were prepared in a climate-controlled room using Milli-Q deionized water

Peak label in TIC	Compounds identified by GC-MS using the NIST library	Formula	Molecular weight	Probable source of sample contamination	Exact mass confirmation by Orbitrap ESI-MS[a], exact mass (formula) [error, ppm]
A	2-Methyl-1*H*-pyrrole	C_5H_7N	81	Unknown	
B	*N*,*N*-Dimethylacetamide	C_4H_9NO	87	Common cellulose solvent	110.0574 (C_4H_9NONa) [−2.4]
C	2-Pyrrolidinone	C_4H_7NO	85	Unknown	108.0415 (C_4H_7NONa) [−2.9]
D	Glutarimide	$C_5H_7NO_2$	113	Unknown	
E	Caprolactam	$C_6H_{11}NO$	113	Unknown	
F	*N*-Butyl-benzenesulfonamide	$C_{10}H_{15}NO_2S$	213	Common plasticizer	214.0898 ($C_{10}H_{16}NO_2S$) [0.7]
G	Tris(1-chloro-2-propyl) phosphate	$C_9H_{18}Cl_3O_4P$	326	Flame retardant in polyurethane foams used for construction	

[a] The presented exact masses are for protonated species $[M+H]^+$ or for sodium adduct species $[M+Na]^+$ in positive ESI mode

for example, by Tressl and Kersten [37], though the reaction tests were conducted under much harsher conditions of temperature and pressure than in the current study. The origins of the cyclic amides D (glutarimide) and E (caprolactam), or the pathway of their formation under the described experimental conditions, remain unknown. Compound F (*N*-butyl-benzenesulfonamide) is a commercially used plasticizer for polyamide compounds; its presence in the tidelines prepared with Milli-Q water in the climate-controlled room cannot be easily explained. Compound G (tris(1-chloro-2-propyl) phosphate) is a common fire retardant for polyurethane widely used for construction applications, for example, in insulation. Its use in construction materials may explain its accumulation in the confined atmosphere of a climate-controlled room. Moreover, other samples made of polyurethane foams were stored in the climate-controlled room during tideline preparation.

In order to prove the assumption that the presence of these products in the extracts is due either to the contamination of air in a working zone of the climate-controlled room, or to contaminants in water used in tideline preparation, it was decided to repeat the entire process of tideline preparation and extraction in a laboratory where no paper material is stored and no paper-related experiments are carried out. In addition, HPLC-grade reagent water was used in tideline preparation instead of the deionized Milli-Q water that was used in the standard experiment. The GC-MS analysis obtained for the aqueous extract of the tidelines prepared under these conditions is shown in Fig. 2 (trace (c)). The obtained GC-MS data supports our assumption about the pollutant nature of discovered N, P, and S compounds, as chromatographic peaks of the contaminant products described above do not appear in the TIC spectrum, or their abundance decreased significantly (i.e., caprolactam) under conditions where risks of pollution due to routine paper chemical analysis have been precluded.

Analysis of cellulose degradation products in the tidelines using a modified CRI method

The absence of chromophore compounds among those discovered in the brown-hued samples prepared by the direct extractions described above can be explained by covalent bonding or strong adsorption of chromophore compounds to oligomeric chains of cellulose. Moreover, chromophores can provide a strong coloration even at very low concentrations (as low as ppb), but the use of direct solvent extractions may not provide sufficient quantities of chromophore compounds to detect them using GC-MS. Rosenau et al. proposed in a series of papers investigating aged cellulose samples an original technique for CRI [24–26]. This technique is based on the treatment of cellulose paper with a Lewis acid (boron trifluoride acetic acid complex) containing a reducing agent (sodium sulfite), followed by chromatographic separation of the released compounds in the presence of an antioxidant (tocopherol). The CRI protocol, elaborated by Rosenau for aged cellulosic materials, was applied with several experimental modifications (see the "Materials and methods" section) to the tidelines prepared in our laboratory from pure Whatman No. 1 paper. These extracts were analyzed by GC-MS using either the nonpolar or polar column in procedures analogous to those described for analyses of the direct extracts. LTQ Orbitrap ESI-MS analysis of these same extracts was used to confirm GC-MS compound identifications.

Figure 5 (trace (c)) presents the chromatographic data for the tideline extract prepared using the modified CRI protocol obtained using the nonpolar capillary column. A reagent blank, prepared by the same protocol using the same solvents and reagents without paper, was analyzed by GC-MS (trace (a) in Fig. 5) under the same conditions. The TIC obtained for the pure untreated Whatman No. 1 paper extract is shown in Fig. 5, trace (b). This data was compared to the tideline extract in order to distinguish compounds initially present in the untreated paper or formed during the extraction procedure from

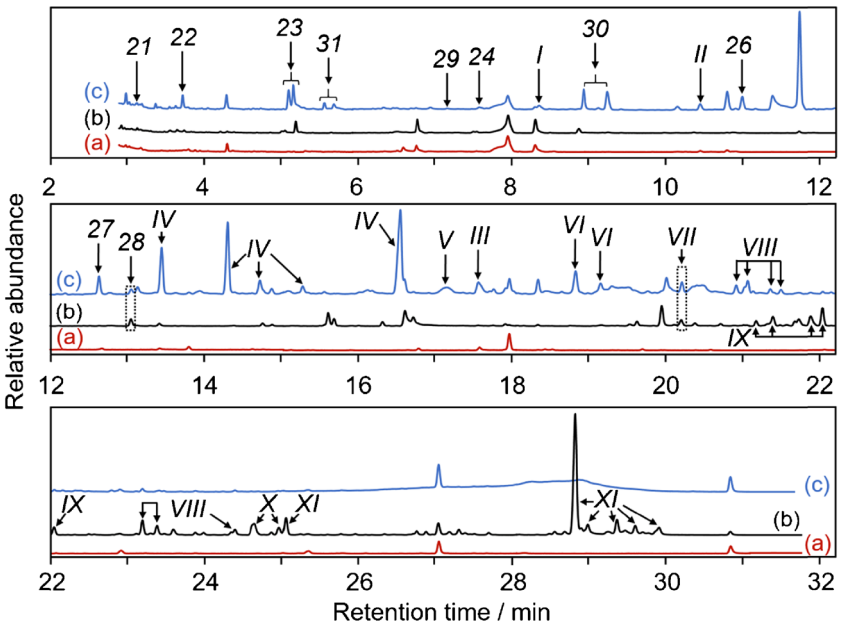

Fig. 5 TIC chromatograms obtained from GC-MS experiments with a nonpolar column for the extracts prepared by the modified CRI protocol for the reagent blank (**a**), untreated Whatman No. 1 paper (**b**), and tidelines prepared in the contamination-free laboratory using HPLC-grade water (**c**). *Peak labels* correspond to the assignments indicated in Tables 4 and 5 and Fig. 7. Pollutants originating from a fused silica column or solvents used in the process are not labeled

the products of cellulose oxidative degradation originating form the tidelines. Figure 6 shows the ensemble of GC-MS data obtained using the polar capillary column.

Numerous chromatographic peaks corresponding to the compounds formed exclusively in the tideline can be observed in the TIC spectrum (trace (c) in Figs. 5 and 6). Low molecular weight compounds corresponding to these peaks were identified using the NIST spectral library. The identified compounds can be divided into two main groups: (i) low molecular weight products of cellulose acid hydrolysis or oxidative degradation and (ii) carbohydrate derivatives formed as a result of cellulose chain hydrolysis and dehydration. The compounds from the first group (denoted in the TIC by numbers **7**–**32**) have retention times in the range 3–13 min for the nonpolar column (Fig. 5) and 9–18 min for the polar one (Fig. 6). Saccharide derivatives from the second group have higher retention times; they are denoted by numbers **I**–**XI** in the TIC.

The peak assignments, identification results, and the GC column (polar or nonpolar) that was employed in compound separation are presented in Tables 4 and 5. The identities of several compounds revealed by GC-MS were further confirmed using LTQ Orbitrap ESI-MS. The exact masses of protonated species are also shown in Table 4 with the corresponding mass error. The chemical structures of several

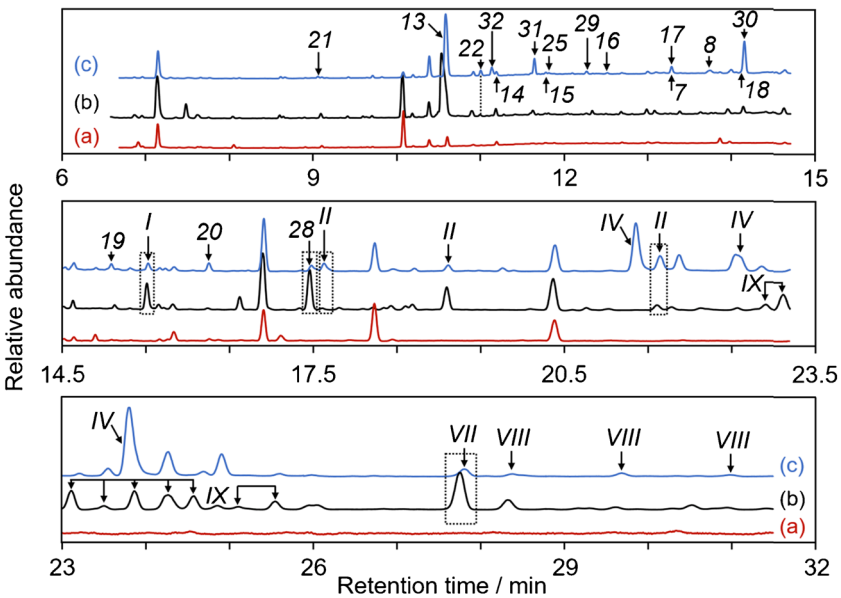

Fig. 6 TIC chromatograms obtained from GC-MS experiments with a polar column for the extracts prepared by the modified CRI protocol for the reagent blank (**a**), untreated Whatman No. 1 paper (**b**), and tidelines prepared in the contamination-free laboratory using HPLC-grade water (**c**). *Peak labels* correspond to the assignment indicated in Tables 4 and 5 and Fig. 7. Pollutants originating from a fused silica column or solvents used in the process are not labeled

Table 4 The first group of low molecular weight compounds identified in the tideline extract prepared by the modified CRI protocol using GC-MS and Orbitrap ESI-MS

Peak label	Compounds identified by GC-MS using the NIST library	Formula	Molecular weight	Column type[a]	Exact mass confirmation by Orbitrap ESI-MS[b], exact mass (formula) [error, ppm]
21	2-Methylfuran	C_5H_6O	82	N, P	
22	Furfural (2-furaldehyde)	$C_5H_4O_2$	96	N, P	97.0279 ($C_5H_5O_2$) [−5.6]
23	β-Methoxy-2-furanethanol	$C_7H_{10}O_3$	142	N	
24	2,5-Furandicarboxaldehyde	$C_6H_4O_3$	124	N	
25	5-Methyl-2-furaldehyde	$C_6H_6O_2$	110	P	
26	5-(Hydroxymethyl)-2-furaldehyde	$C_6H_6O_3$	126	N	127.0386 ($C_6H_7O_3$) [−3.1]
27	5-(Dimethoxymethyl)-2-furylmethanol	$C_8H_{12}O_4$	172	N	173.0808 ($C_8H_{13}O_4$) [0.03]
28	5-Acetoxymethyl-2-furaldehyde	$C_8H_8O_4$	168	N, P	169.0495 ($C_8H_9O_4$) [−0.4]
29	3-Methyl-2-cyclohexen-1-one	$C_7H_{10}O$	110	N, P	
30	5-Methoxy-1,3-benzenediol	$C_7H_8O_3$	140	N, P	141.0544 ($C_7H_9O_3$) [−1.7]
7	1,1′-Oxydi-2-propanol[c]	$C_6H_{14}O_3$	134	P	
8	2-(2-Hydroxypropoxy)-1-propanol[c]	$C_6H_{14}O_3$	134	P	
31	Methyl levulinate (methyl 4-oxopentanoate)	$C_6H_{10}O_3$	130	N, P	
32	Formic acid	CH_2O_2	46	P	
13	Acetic acid	$C_2H_4O_2$	60	P	
14	Propanoic acid	$C_3H_6O_2$	74	P	
15	Butanoic acid	$C_4H_8O_2$	88	P	
16	Pentanoic acid	$C_5H_{10}O_2$	102	P	
17	Hexanoic acid	$C_6H_{12}O_2$	116	P	
18	Heptanoic acid	$C_7H_{14}O_2$	130	P	
19	Octanoic acid	$C_8H_{16}O_2$	144	P	
20	Nonanoic acid	$C_9H_{18}O_2$	158	P	

[a] Column type used for compound separation: N = nonpolar column VF-5ms and P = polar column DB-FFAP

[b] The presented exact masses are for protonated species $[M+H]^+$ in positive ESI mode

[c] The chromatographic peak can be also attributed to the structural isomer 2,2′-oxydi-1-propanol (compounds **8** and **9** in Table 2 and Fig. 4)

identified compounds, presented in Table 4 and Figs. 5 and 6, are shown in Fig. 7. The compounds listed in Table 4 can be further divided into several groups:

(1) Various furan derivatives (**21**–**28**) were identified in the tideline extract. Furfural (**22**), hydroxymethyl furaldehyde (**26**), and other furanic derivatives are often reported as products of acidic cellulose hydrolysis and oxidation in aged paper, formed as a result of dehydration of glucose and pentose units [19, 24, 27–29, 38]. Furfural (**22**) and 5-acetoxymethyl-2-furaldehyde (**28**) were also detected in the extract of pure Whatman paper; product **8** is even more abundant in the Whatman paper extract than in the tidelines. This fact indicates that some furan compounds can form as a result of natural aging and accumulate in the cellulose paper during its storage under ambient conditions.

Notably, furanic derivatives have been previously detected among the products of pyrolytic cellulose decomposition [39–41]. For example, 2-methylfuran (**21**), furfural (**22**), 5-(hydroxymethyl)-2-furaldehyde (**26**), and 5-methyl-2-furaldehyde (**25**) are reported as being among the major products of cellulose pyrolysis formed at temperatures above 400 °C.

Compound **29** (3-methyl-2-cyclohexen-1-one) was reported as a product of catalytic biomass pyrolysis [42]. In addition, the structurally similar cyclopentenone derivative (2,3-dihydroxy-2-cyclopenten-1-one) was identified by Popoff and Theander [38] in a study of low molecular weight compounds formed during acidic decompositions of carbohydrates. The aromatic compound **30** (5-methoxy-1,3-benzenediol) is probably the product of sugar dehydration and cyclization. Its isomer, 3-methoxy-1,2-benzenediol, was reported among the products of biomass pyrolysis [42]. To the best of our knowledge, compounds **29** and **30** were not previously

Table 5 The second group of low molecular weight compounds (carbohydrates derivatives) identified in the tideline extract prepared by the modified CRI protocol using GC-MS and Orbitrap ESI-MS

Peak label	Molecular formula	Molecular weight	Possible peak attribution by the NIST library	Sample type[a]	Column type[b]	Exact mass confirmation by Orbitrap ESI-MS[c], exact mass (formula) [error, ppm]
I	$C_6H_6O_3$	126	Levoglucosenone	T, W	N, P	127.0386 ($C_6H_7O_3$) [−0.4]
II	$C_6H_8O_4$	144	1,4:3,6-Dianhydro-α-D-glucopyranose	T, W	N, P	145.0493 ($C_6H_9O_4$) [−1.4]
III	$C_6H_{10}O_5$	162	Levoglucosan (1,6-anhydro-β-D-glucopyranose)	T	N	163.0560 ($C_6H_{11}O_5$) [−0.9]
IV	$C_7H_{14}O_6$	194	Methyl glucoside (or other aldohexose derivatives)	T	N, P	195.0865 ($C_7H_{15}O_6$) [1.0]
V	$C_6H_{12}O_6$	180	D-Glucose (or other aldohexose derivatives)	T	N	
VI	$C_6H_{10}O_5$	162	1,6-Anhydro-galactofuranose (or other aldohexose derivatives)	T	N	163.0560 ($C_6H_{11}O_5$) [−0.9]
VII	$C_{15}H_{22}O_{10}$	362	Methyl glucoside tetraacetate (or other aldohexose derivatives)	T, W	N, P	
VIII	$C_{12}H_{16}O_8$	288	1,6-Anhydro-glucopyranose triacetate (or other aldohexose derivatives)	T, W	N, P	289.0919 ($C_{12}H_{17}O_8$) [0.5]
IX	$C_{12}H_{18}O_8$	290	Methyl ribofuranoside triacetate (or other aldopentose derivatives)	W	N, P	
X	$C_{13}H_{18}O_9$	318	Ribose tetraacetate (or other aldopentose derivatives)	W	N	
XI	$C_{16}H_{22}O_{11}$	390	Glucose pentaacetate (or other aldohexose derivatives)	W	N	

[a] Type of sample extract (W = pure Whatman paper and T = tidelines), where the product was detected

[b] Column type resulted in compound separation: N = nonpolar column VF-5ms and P = polar column DB-FFAP

[c] The presented exact masses are for protonated species $[M+H]^+$ in positive ESI mode

reported as cellulose degradation products formed during paper aging. Compounds assembled in this group, which possess conjugated double-bond systems, may be responsible, at least in part, for the visible paper discoloration. Formation of more condensed chromophoric structures, detected using the CRI extraction method for aged cellulose [24–26, 38], is not probable during the tideline experiment, as the tideline formation is carried out under mild ambient conditions for a relatively short time.

(2) Ethers **7** and **8** identified in the extracts prepared by the modified CRI method were also detected in the tideline samples prepared by direct extraction (Table 2, Fig. 4). As noted above, both products can be regarded as condensation products of propylene glycol, which is one of the major products found in the tideline extracts prepared by the direct solvent extraction protocol. The chromatographic peak corresponding to compound **8** can be assigned to either of two structural isomers that are virtually indistinguishable in the GC-MS spectral library (compounds **8** and **9** as reported in Table 2 and Fig. 4 for the direct tideline extracts).

(3) Similar to direct aqueous and methanol extraction results, a series of carboxylic acids, from formic to nonanoic (compounds **32**, **13**–**20**), were identified by GC-MS analysis using the polar capillary column (Fig. 6, Table 4), confirming previously reported results for tidelines and aged paper [10, 17, 21, 27–29].

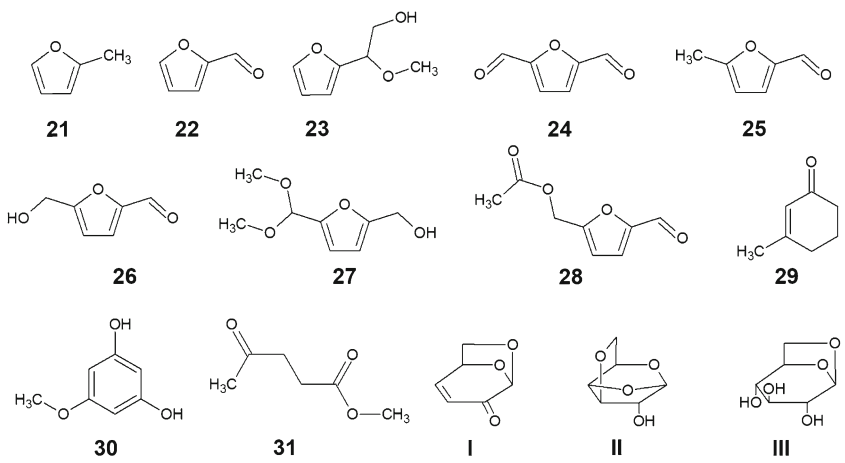

Fig. 7 Several low molecular weight compounds identified by GC-MS in the tideline extract prepared by the modified CRI extraction protocol

Detection of the methyl ester of levulinic acid (**31**) is also in line with previous observations showing the formation of levulinic acid during cellulose acid degradation (in the presence or absence of catalysts) via the intermediate hydroxymethyl-2-furaldehyde (**26**) [43, 44].

Carbohydrate derivatives formed during scission and oxidation of cellulose chains were separated into a second group of low molecular compounds identified in the tidelines and pure Whatman No. 1 paper extracts prepared by the modified CRI protocol. Chromatographic peaks corresponding to these products are denoted by numbers **I**–**XI** in Figs. 5 and 6 and in Table 5. Several peaks with different retention times offer similar mass spectral patterns and thus are not distinguished from one another using the MS spectral library. Closely related structural isomers (five- or six-membered ring structures) likely contribute to this multiplicity of chromatographic peaks. The similarity of MS spectra for certain isomeric compounds together with an incompleteness of the reference mass spectral library hinders the unambiguous assignment of the obtained GC-MS data to unique compounds. The proposed assignments for this group of compounds, alongside the column type used in their separation, are presented in Table 5. The identification of several compounds isolated by GC-MS was also confirmed using LTQ Orbitrap MS. The exact masses of protonated species are shown as well in Table 5.

Several anhydro derivatives of carbohydrates were detected in the tideline extract prepared by the modified CRI method. Levoglucosenone (**I**), 1,4:3,6-dianhydro-α-D-glucopyranose (**II**), and levoglucosan (1,6-anhydro-β-D-glucopyranose) (**III**) are well-known products of cellulose dehydration, and these compounds are reported as the major products of carbohydrate pyrolysis [39–41, 45]. In addition, in the current work, two other 1,6-anhydro derivatives of aldohexose carbohydrates (**VI** and **VIII**) were separated using GC-MS. The exact assignment of structures for these anhydro sugars was not possible using only the NIST spectral library. Although GC-MS is perhaps not the best method for analyses of nonderivatized carbohydrates, a low and broad chromatographic peak of glucose (or another hexose sugar, **V**) was also detected in the tideline extract.

Levoglucosenone (**I**) and anhydro-glucose derivatives **II** and **VIII**, found in the tideline extract, were also detected in the Whatman paper extract (Table 5, graph (b) in Figs. 5 and 6). The appearance of cellulose dehydration products in the pure untreated cellulose paper may indicate the existence of a pyrolytic-like degradation pathway for cellulose decomposition during paper storage under ambient conditions. Furthermore, we cannot exclude the possibility of the formation of these compounds under the harsh conditions of the modified CRI extraction protocol, although interestingly, their formation was not reported previously [24–26].

Additionally, several carbohydrate derivatives were detected exclusively in the untreated Whatman paper extract, prepared by the modified CRI extraction protocol (**IX**–**XI**). Two acetyl derivatives of aldopentose carbohydrates (**IX** and **X**) and glucose pentaacetate (**XI**) are likely products formed and accumulated in the "pure" paper during storage under ambient conditions or during the CRI extraction procedure. They may serve as precursors for dehydrated carbohydrates and oxidation products formed at the tideline interface.

Conclusions

The formation of low molecular weight compounds in tidelines at the wet-dry interface of pure cellulose paper was thoroughly investigated using GC-EI-MS and high-resolution LTQ Orbitrap MS. The specific products detected vary depending upon the sample extraction technique employed. The use of direct solvent extraction of the tidelines employing water or methanol served to reveal several cellulose oxidation products, but the brownish color of the extract and of the tideline itself could not be associated with any of these compounds. The application of the more complex chromophore release and identification (CRI) technique led to the formation of more intensely colored extracts indicating improved efficiency in chromophore extraction.

Several groups of compounds were detected and identified as cellulose degradation products, thus indicating a very complex mechanism of tideline formation. On the one hand, a clear indication is given for the oxidative pathway of cellulose decomposition as evidenced by the formation of different low molecular weight oxidation products, i.e., linear unsaturated carboxylic acids, diols (and their condensation products), esters, and ketones. On the other hand, the appearance of several furanic compounds, which form through successive carbohydrate dehydration steps, points to another cellulose decomposition pathway that is not necessarily oxidative in nature. Interestingly, furans and furanic compounds are also found among products of pyrolytic cellulose degradation. The similarity between the "wet" tideline formation process and the pyrolytic cellulose decomposition does not stop there because various anhydro carbohydrate derivatives that were detected in the tidelines have also been reported as major products of cellulose pyrolysis. The formation of these anhydro carbohydrate derivatives might indicate another cellulose decomposition pathway competitive to that of furanic compound production [40, 41].

Furan derivatives and carboxylic acids have been previously reported as degradation products in artificially aged cellulose specimens [10, 17, 19, 21, 24, 38]. Although one can draw certain parallels between tideline formation and cellulose aging, the former is a relatively short-term process,

indicating that the conditions at the tideline are correct for promoting the complex process of cellulose degradation.

Acknowledgments SS thanks the Chateaubriand Fellowship Program for the financial support for this research. SS also thanks the Office of Scientific and Academic Cooperation at the French Embassy in Israel for the support. We thank Agilent Technologies (Les Ulis, France) for providing the GC-MS equipment necessary to complete the project.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Bone WH. Evaporation of water from cellulose. J Soc Dyer Colour. 1934;50:307–9.
2. Bone WA, Turner HA. Some effects of the evaporation of water from cotton cellulose. J Soc Dyer Colour. 1950;66:315–27.
3. Bogaty H, Campbell KS, Appel WD. Some observations on the evaporation of water from cellulose. Text Res J. 1952;22:75–81.
4. Madaras GW, Turner HA. Further observations on the effects of evaporating water from cotton cellulose. J Soc Dyer Colour. 1953;69:371–7.
5. Schaffer R, Appel WD, Forziati FH. Reactions at wet-dry interfaces on fibrous materials. J Res Natl Bur Stand. 1955;54:103–6.
6. Fox MR. Wet and dry boundaries on cellulosic textiles and their influence on dyes and dyeing. I. J Soc Dyer Colour. 1965;81:7–11.
7. Dupont AL. Degradation of cellulose at the wet/dry interface. I. The effect of some conservation treatments on brown lines. Restaurator. 1996;17:1–21.
8. Dupont AL. Degradation of cellulose at the wet/dry interface. II. An approach to the identification of the oxidation compounds. Restaurator. 1996;17:145–64.
9. Area MC, Cheradame H. Paper aging and degradation: recent findings and research methods. BioResources. 2011;6:5307–37.
10. Souguir Z, Dupont AL. Formation of brown lines in paper: characterization of cellulose degradation at the wet-dry interface. Biomacromolecules. 2008;9:2546–52.
11. Jeong MJ, Dupont AL, René de la Rie E. Degradation of cellulose at the wet-dry interface. I. Study of the depolymerization. Cellulose. 2012;19:1135–47.
12. Jeong MJ, Dupont AL, René de la Rie E. Degradation of cellulose at the wet-dry interface. II. Study of oxidation reactions and effect of antioxidants. Carbohydr Polym. 2014;101:671–83.
13. Zervos S. Natural and accelerated ageing of cellulose and paper: a literature review. In: Lejeune A, Deprez T, editors. Cellulose: structure and properties, derivatives and industrial uses. New York: Nova Science Publishers Inc.; 2010. p. 155–203.
14. Albeck M, Ben-Bassat A, Epstein JA, Lewin M. The yellowing of cotton cellulose. Part I. A new method for the determination of yellowing. Text Res J. 1965;35:836–43.
15. Albeck M, Ben-Bassat A, Lewin M. The yellowing of cotton cellulose. Part II. The influence of functional groups and the nature of the yellowing. Text Res J. 1965;35:935–42.
16. Lewin M. The yellowing of cotton cellulose. Part III. On the mechanism of yellowing upon aging and alkaline extraction. Text Res J. 1965;35:979–86.
17. Łojewska J, Miśkowiec P, Łojewski T, Proniewicz LM. Cellulose oxidative and hydrolytic degradation: in situ FTIR approach. Polym Degrad Stab. 2005;88:512–20.
18. Łojewska J, Missori M, Lubańska A, Grimaldi P, Zięba K, Proniewicz LM, et al. Carbonyl groups development on degraded cellulose. Correlation between spectroscopic and chemical results. Appl Phys A. 2007;89:883–7.
19. Łojewski T, Zięba K, Knapik A, Bagniuk J, Lubańska A, Łojewska J. Evaluating paper degradation progress. Cross-linking between chromatographic, spectroscopic and chemical results. Appl Phys A. 2010;100:809–21.
20. Schedl A, Korntner P, Zweckmair T, Henniges U, Rosenau T, Potthast A. Detection of cellulose-derived chromophores by ambient ionization-MS. Anal Chem. 2016;88:1253–8.
21. Corsaro C, Mallamace D, Łojewska J, Mallamace F, Pietronero L, Missori M. Molecular degradation of ancient documents revealed by ^{1}H HR-MAS NMR spectroscopy. Sci Rep. 2013;3:2896.
22. Mosca Conte A, Pulci O, Knapik A, Bagniuk J, Del Sole R, Lojewska J, et al. Role of cellulose oxidation in the yellowing of ancient paper. Phys Rev Lett. 2012;108:158301.
23. Violante C, Teodonio L, Mosca Conte A, Pulci O, Kupchak I, Missori M. An ab-initio approach to cultural heritage: the case of ancient paper degradation. Phys Status Solidi B. 2015;252:112–7.
24. Rosenau T, Potthast A, Milacher W, Hofinger A, Kosma P. Isolation and identification of residual chromophores in cellulosic materials. Polymer. 2004;45:6437–43.
25. Rosenau T, Potthast A, Krainz K, Yoneda Y, Dietz T, Shields ZPI, et al. Chromophores in cellulosics. VI. First isolation and identification of residual chromophores from aged cotton linters. Cellulose. 2011;18:1623–33.
26. Rosenau T, Potthast A, Krainz K, Hettegger H, Henniges U, Yoneda Y, et al. Chromophores in cellulosics. XI. Isolation and identification of residual chromophores from bacterial cellulose. Cellulose. 2014;21:2271–83.
27. Strlič M, Kralj Cigić I, Kolar J, de Bruin G, Pihlar B. Non-destructive evaluation of historical paper based on pH estimation from VOC emissions. Sensors. 2007;7:3136–45.
28. Lattuati-Derieux A, Bonnassies-Termes S, Lavédrine B. Characterisation of compounds emitted during natural and artificial ageing of a book. Use of headspace-solid-phase microextraction/gas chromatography/mass spectrometry. J Cult Herit. 2006;7:123–33.
29. Ramalho O, Dupont AL, Egasse C, Lattuati-Derieux A. Emission rates of volatile organic compounds from paper. e-Preserv Sci. 2009;6:53–9.
30. Dupont AL, Egasse C, Mori A, Vasseur F. Comprehensive characterisation of cellulose- and lignocellulose-degradation products in aged papers: capillary zone electrophoresis of low-molar mass organic acids, carbohydrates, and aromatic lignin derivatives. Carbohydr Polym. 2007;68:1–16.
31. Shahani CJ, Harrison G. Spontaneous formation of acids in the natural aging of paper. In: Daniels V, Donithorne A, Smith P, editors. Works of art on paper, books, documents and photographs. Techniques and conservation, Congress of the International Institute for Conservation. London: International Institute for Conservation; 2002. p. 189–92.
32. Deng T, Liu H. Direct conversion of cellulose into acetol on bimetallic Ni-SnO_x/Al_2O_3 catalysts. J Mol Catal A Chem. 2014;388–389:66–73.
33. Ji N, Zhang T, Zheng MY, Wang AQ, Wang H, Wang XD, et al. Direct catalytic conversion of cellulose into ethylene glycol using nickel-promoted tungsten carbide catalysts. Angew Chem Int Ed. 2008;47:8510–3.
34. Lin YC, Cho J, Tompsett GA, Westmoreland PR, Huber GW. Kinetics and mechanism of cellulose pyrolysis. J Phys Chem C. 2009;113:20097–107.
35. Shenai VA, Sudan RK. Studies in chemically modified celluloses. IV. Lactones in chemically modified celluloses. J Appl Polym Sci. 1972;16:545–50.

36. Potthast A, Rosenau T, Kosma P. Analysis of oxidized functionalities in cellulose. Adv Polym Sci. 2006;205:1–48.
37. Tressl R, Kersten E. Formation of pyrroles, 2-pyrrolidones, and pyridones by heating of 4-aminobutyric acid and reducing sugars. J Agric Food Chem. 1993;41:2125–30.
38. Popoff T, Theander O. Formation of aromatic compounds from carbohydrates. Part I. Reaction of D-glucuronic acid, D-galacturonic acid, D-xylose, and L-arabinose in slightly acidic, aqueous solution. Carbohydr Res. 1972;22:135–49.
39. Lu Q, Yang XC, Dong CQ, Zhang ZF, Zhan XM, Zhu XF. Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: analytical Py-GC/MS study. J Anal Appl Pyrolysis. 2011;92:430–8.
40. Paine III JB, Pithawalla YB, Naworal JD. Carbohydrate pyrolysis mechanisms from isotopic labeling. Part 4. The pyrolysis of D-glucose: the formation of furans. J Anal Appl Pyrolysis. 2008;83:37–63.
41. Patwardhan PR, Satrio JA, Brown RC, Shanks BH. Product distribution from fast pyrolysis of glucose-based carbohydrates. J Anal Appl Pyrolysis. 2009;86:323–30.
42. Lu Q, Zhang ZF, Dong CQ, Zhu XF. Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: an analytical Py-GC/MS study. Energies. 2010;3:1805–20.
43. Pierson Y, Bobbink F, Yan N. Alcohol mediated liquefaction of lignocellulosic materials: a mini review. Chem Eng Process Technol. 2013;1:1014.
44. Alonso DM, Gallo JMR, Mellmer MA, Wettstein SG, Dumesic JA. Direct conversion of cellulose to levulinic acid and gamma-valerolactone using solid acid catalysts. Catal Sci Technol. 2013;3:927–31.
45. Halpern Y, Riffer R, Broido A. Levoglucosenone (1,6-anhydro-3,4-dideoxy-Δ^3-β-D-pyranosen-2-one). A major product of the acid-catalyzed pyrolysis of cellulose and related carbohydrates. J Org Chem. 1973;38:204–9.