

## Changes in the Chemical and Physical Properties of Paper Documents due to Natural Ageing

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The aim of this study was to assess the changes in chemical and physical properties of selected paper documents, dating from the 18<sup>th</sup> century to the present date. Paper documents from the 18<sup>th</sup>, 19<sup>th</sup>, and 21<sup>st</sup> centuries had a pH ranging from slightly acidic to alkaline values, whereas paper documents from the 20<sup>th</sup> century were more acidic. The contents of mannose, glucose, holocellulose, and lignin were significantly correlated with the pH of the paper. High contents of both carboxylic acids (acetic and formic) and the most durable monosaccharide (glucose) were found in the oldest examined paper documents originating from the 18<sup>th</sup> and 19<sup>th</sup> centuries. The lowest percentage of brightness was found in paper documents originating from 1920 and 1923. The lowest breaking length was associated with papers originating from 1920.

*Keywords:* Paper documents; Natural ageing; pH; Formic acid; Acetic acid; Fibre length; Holocellulose

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### INTRODUCTION

The deterioration of paper is caused by several factors such as acid hydrolysis, oxidative agents, light, air pollution, or the presence of microorganisms (Zou *et al.* 1996a,b; Zotti *et al.* 2008; Zervos 2010; Area and Cheradame 2011; Kraková *et al.* 2012). During natural ageing, loss of paper strength is a result of the degradation of cellulose, its main structural component. Cellulose degradation in paper reaches various modes depending on a variety of chemical processes (acid and enzymatic hydrolysis, alkaline and oxidative degradation), thermal impact (influence of different temperatures), and radiation (ultraviolet and high energy), considering the acid hydrolysis to be most prevailing (Whitmore and Bogaard 1994).

Lignin content is of major interest in the preservation of paper-based materials. It is a complex and partly unstable natural organic polymer, and its limited photostability is important for exhibited objects. The influence of lignin on the stability of cellulose in paper is not well understood, but it may provide a limited antioxidant effect. However, its oxidation may also contribute to an accumulation of acids, which destabilize the material (Zou *et al.* 1993; Schmidt *et al.* 1995; Begin *et al.* 1998; Trafela *et al.* 2007). A major source of acidity development within paper documents during aging is known to be the hydrolysis of acetate ester groups in the hemicellulose (Polovka *et al.* 2006; Zervos 2007; Jablonský *et al.* 2012a).

Paper before *ca.* 1850 was produced with the traditional sizing process using gelatine (Dupont 2003), which resulted in an approximately neutral or slightly acidic material. Generally, gelatin within old books remains in good condition if it has been kept in a favourable environment in the absence of corrosive inks or biodeteriogens. Gelatine is beneficial to paper and increases its longevity (Strlič *et al.* 2004; Lichtblau *et al.* 2008). For paper produced between 1850 and 1990, the pH values of aqueous extracts are frequently lower than 6 due to the application of the alum-rosin size system. This decreases the lifetime expectancy of paper. From 1990 to the present, the production of paper has changed to alkaline sizing, and contemporary paper is once again more stable (Trafela *et al.* 2007). The reason was to reduce costs. The modern “PCC” calcium carbonate filler, which is required for alkaline pH during paper forming, made it less expensive to make bright paper (Hubbe 2005). The strength of paper is determined by the strength of the individual fibres and the strength of the bonding of these fibres into a network (Page and Seth 1979; Ververis *et al.* 2004).

According to Paavilainen (1993a,b), there is a decrease in tensile strength corresponding to an increase in fiber coarseness, suggesting that the most important factors for high tensile strength of paper are a good bonding ability and a high intrinsic fibre strength. Tensile strength is determined by the bonded area, both external and internal fibrillations, the amount of fines, and especially by wet fibre flexibility. Gandini and Pasquini (2012) noted that the mechanical properties of paper are directly linked to the capacity of its fibres to establish inter- and intra-fibre bonds. Maximizing the bonded area and fibre length can increase the activation process, while deformations such as kink and curl can decrease activation.

Deformed fibres also lead to a non-uniform load distribution, thereby decreasing the networks ability to carry load because they cause local stress points (Vainio 2007). Mohlin *et al.* (1996) studied the impact of fibre deformation on sheet strength. The authors reported a decrease in tensile strength and tensile stiffness with an increase in the number of fibre deformations and a decrease in the shape factor.

Analysis of fibre traits such as fibre length, fibre diameter, lumen width, cell wall thickness, and their derived morphological characteristics has become important in estimating the pulp quality of fibre (Dinwoodie 1965; Amidon 1981). Fibre length and strength are particularly important for tearing resistance (Tamolang *et al.* 1968; Wangaard and Williams 1970; Seth and Page 1988). In addition, Seth (1990) showed that tensile strength is affected by fibre length.

The objectives of this study were to assess the changes in pH values, contents of carboxylic acids, holocellulose and lignin, fibre dimensions, breaking length, and the brightness of paper documents at various ages. The study also serves to clarify significant relationships between the examined traits.

## EXPERIMENTAL

### Materials

Paper samples were taken from a book printed in each of the years 1719, 1762, 1784, 1807, 1839, 1853, 1859, 1920, 1923, 1956, and 2007. All the researched books were stored in one single place, in an old church in the central part of Slovakia, which means these were undergoing a natural aging process. The publication year was considered to be the production year of the paper document.

## Methods

### *Determination of the pH values*

Determination of the pH values of paper surfaces (pH<sub>s</sub>) was performed according to the Slovak Technical Standard (STN) 500374 (1996) (with a drop of distilled water and subsequently by placing the pH electrode on the paper surface, with sampling at five locations), whereas determination of the pH values of cold aqueous paper extracts (pH<sub>E</sub>) was conducted according to the standard STN ISO 6588 (50 0381) (1993) (cold extraction, 2 g of paper sample per 100 mL of water, 1 h). The precision in pH determinations was estimated to be less than  $\pm 0.2$  units. Measurements were performed on five replicates per sample.

### *Contents of carboxylic acids*

Approximately 2 g of paper were accurately weighed and added to 15 mL of pure water. The suspension was mixed for 2 h and subsequently filtered through a 0.45  $\mu\text{m}$  filter (Jablonsky *et al.* 2012b). The carboxylic acid (formic, acetic) contents were analysed using high-performance liquid chromatography (HPLC) and a method slightly modified from Sluiter *et al.* (2008a), as follows: chromatograph, HPLC 1200 (Agilent, Santa Clara, CA, USA); column, Polymer IEX H form (Watrex, Praha, Czech Republic); mobile phase, 9 mM H<sub>2</sub>SO<sub>4</sub>; flow rate, 0.5 mL min<sup>-1</sup>; detector, RI (refractive index); injected volume, 100  $\mu\text{l}$ ; and temperature, 35 °C. Results are presented as formic and acetic acids for both free acids and their water soluble salts. Measurements were performed on four replicates per sample.

### *Contents of saccharides and lignin*

Paper samples were hydrolysed using 72% (w/w) sulfuric acid, and both lignin and neutral saccharides were determined according to the NREL method (Sluiter *et al.* 2010). Quantitative analyses of saccharides were carried out by HPLC under the following conditions: chromatograph, HPLC 1200 (Agilent, Santa Clara, CA, USA); column, Aminex HPX - 87P (Bio-Rad, Hercules, CA, USA); mobile phase, deionized water; flow rate, 0.6 mL min<sup>-1</sup>; detector, RI; injected volume, 50  $\mu\text{L}$ ; and temperature, 80 °C. Measurements were performed on four replicates per sample.

### *Ash content*

Oven-dry paper samples ranging from 0.5 to 2.0 g were placed in the muffle furnace at  $575 \pm 25$  °C for at least 4 h and dried to a constant weight. The ash content was determined according to Sluiter *et al.* (2008b) in a single replicate per sample.

### *Fibre length determination*

Paper samples (approximately 0.1 g) were placed into polyethylene vials and allowed to swell with a small amount of water. Subsequently, they were pulped in a shaker. After complete shredding, the suspension was diluted several times so that in about 100 mL of suspension, there were at least one thousand fibres. The proportion of fibre length classes (< 0.5 mm, 0.5 to 1 mm, 1 to 2 mm, 2 to 3 mm, 3 to 7 mm) was determined using a fibre analyzer FS-100 (Kajaani Oy Electronics, Kajaani, Finland). Measurements were performed on a single replicate per sample, and the number of fibres within each population of replicate ranged from 16,138 to 20,112 cells.

### *Light microscopy of fibres*

Fibre composition was analysed using a Nikon ECLIPSE 80i light microscope equipped with a Nikon DS-Fi1 digital camera (Nikon Instruments Europe, Amsterdam, Netherlands) on a small amount of stained fibres representing the tested sample, according to the standard ISO 9184 (1990). The fibres were stained by adding 2 to 3 drops of various colouring agents (Herzberg, Graff, and Loffton-Merritt).

### *Breaking length*

Breaking length of paper samples was measured in accordance with STN 500340 (1998). For the calculation of breaking length, it was necessary to measure the basic weight of the paper samples according to the STN EN ISO 536 (50 0310) (1999). Measurements were performed on twenty replicates per sample (150 × 15 mm).

### *Brightness*

Brightness of paper samples was assessed according to the STN ISO 3688 (50 0240) (1994) using a Fibre Leucometer PL 11 6565 ZP (Carl Zeiss, Jena, Germany). Measurements were performed on 20 replicates per sample.

### *Statistical analysis*

Data were analysed using one-way analysis of variance, and Duncan's multiple range tests were used for comparisons of means. The Pearson correlation coefficients were calculated for the examined trait-trait linkages. The relationships were considered significant if  $P < 0.05$ . Multivariate associations among 15 paper traits were analysed using a principal component analysis (PCA) in order to describe patterns of covariation among the examined traits.

## RESULTS AND DISCUSSION

### *Changes in the pH values*

The pH value of paper is a significant factor in determining its ageing stability. The measurements presented in Table 1 show that paper documents from the 18<sup>th</sup> and 19<sup>th</sup> centuries had values ranging from slightly acidic to neutral pH. Paper documents from the 20<sup>th</sup> century were characterized by acidic pH values, whereas paper documents from the 21<sup>st</sup> century possessed slightly alkaline pH values. Acidity promotes acid hydrolysis, which accelerates cellulose degradation in paper (Wilson and Parks 1983). Lignocellulosic materials with low pH values and high lignin content generally exhibit faster degradation than alkaline or neutral materials. Along with the use of raw materials possessing high lignin contents, the acidic sulphite process of pulp production and/or the process of acidic sizing also contribute to paper degradation. A low pH value is the most significant factor in the degradation of most endangered paper documents (Vizárová *et al.* 2012). Alkaline or neutral papers are more stable due to the suppression of acid hydrolysis with regards to the degree of degradation and the rate of ageing (Zappala 1991; Area and Cheradame 2011). Maršala *et al.* (2009) published pH values of papers from the 20<sup>th</sup> century and the early years of the 21<sup>st</sup> century. The most acidic documents (pH 3.9) originated between the years 1920 and 1960. The authors also discovered that the number of documents with neutral pH values (pH 7) gradually increased from the 1990s to the present.

**Table 1.** Principal Paper Characteristics for the Examined Paper Documents

Trait/Year	1719	1762	1784	1807	1839	1853
pH <sub>s</sub>	6.69 ± 0.07 <sup>d</sup>	6.58 ± 0.08 <sup>e</sup>	7.70 ± 0.07 <sup>b</sup>	6.94 ± 0.06 <sup>c</sup>	6.51 ± 0.03 <sup>ef</sup>	6.47 ± 0.02 <sup>f</sup>
pH <sub>E</sub>	6.46 ± 0.06 <sup>f</sup>	7.66 ± 0.04 <sup>c</sup>	7.23 ± 0.05 <sup>d</sup>	7.82 ± 0.03 <sup>b</sup>	7.24 ± 0.03 <sup>d</sup>	7.18 ± 0.04 <sup>e</sup>
FA (mg/g)	1.42 ± 0.02 <sup>g</sup>	3.75 ± 0.02 <sup>a</sup>	2.12 ± 0.04 <sup>c</sup>	2.22 ± 0.02 <sup>b</sup>	1.03 ± 0.03 <sup>h</sup>	0.43 ± 0.02 <sup>k</sup>
AA (mg/g)	2.41 ± 0.02 <sup>e</sup>	5.80 ± 0.07 <sup>a</sup>	4.68 ± 0.04 <sup>b</sup>	3.70 ± 0.03 <sup>d</sup>	3.84 ± 0.02 <sup>c</sup>	0.76 ± 0.01 <sup>j</sup>
XYL (%)	0.00 ± 0.00 <sup>e</sup>	0.00 ± 0.00 <sup>e</sup>	0.00 ± 0.00 <sup>e</sup>	0.00 ± 0.00 <sup>e</sup>	0.00 ± 0.00 <sup>e</sup>	0.00 ± 0.00 <sup>e</sup>
GAL (%)	1.14 ± 0.02 <sup>d</sup>	0.87 ± 0.01 <sup>h</sup>	1.16 ± 0.01 <sup>c</sup>	1.23 ± 0.01 <sup>b</sup>	1.24 ± 0.02 <sup>b</sup>	1.00 ± 0.01 <sup>f</sup>
ARA (%)	2.30 ± 0.01 <sup>a</sup>	1.93 ± 0.01 <sup>c</sup>	1.05 ± 0.01 <sup>i</sup>	1.11 ± 0.01 <sup>h</sup>	1.04 ± 0.02 <sup>i</sup>	1.57 ± 0.01 <sup>f</sup>
MAN (%)	2.61 ± 0.02 <sup>e</sup>	1.80 ± 0.01 <sup>i</sup>	2.23 ± 0.01 <sup>f</sup>	1.95 ± 0.01 <sup>h</sup>	2.20 ± 0.01 <sup>fg</sup>	2.19 ± 0.02 <sup>g</sup>
GLC (%)	88.83 ± 0.09 <sup>c</sup>	89.44 ± 0.07 <sup>b</sup>	88.61 ± 0.04 <sup>c</sup>	89.33 ± 0.27 <sup>b</sup>	88.22 ± 0.21 <sup>d</sup>	91.04 ± 0.15 <sup>a</sup>
HOL (%)	94.88 ± 0.06 <sup>b</sup>	94.04 ± 0.06 <sup>c</sup>	93.06 ± 0.04 <sup>e</sup>	93.63 ± 0.24 <sup>d</sup>	92.70 ± 0.18 <sup>f</sup>	95.79 ± 0.14 <sup>a</sup>
LIG (%)	1.30 ± 0.02 <sup>g</sup>	1.20 ± 0.02 <sup>h</sup>	1.00 ± 0.01 <sup>i</sup>	1.20 ± 0.02 <sup>h</sup>	2.68 ± 0.01 <sup>f</sup>	1.20 ± 0.01 <sup>h</sup>
BW (g m <sup>-2</sup> )	96.20 ± 0.39 <sup>a</sup>	56.80 ± 0.43 <sup>k</sup>	81.71 ± 0.24 <sup>f</sup>	69.64 ± 0.22 <sup>i</sup>	87.93 ± 0.24 <sup>b</sup>	86.67 ± 0.20 <sup>d</sup>
BL (km)	2.03 ± 0.40 <sup>ef</sup>	2.48 ± 0.38 <sup>d</sup>	1.90 ± 0.23 <sup>f</sup>	2.13 ± 0.20 <sup>ef</sup>	2.22 ± 0.23 <sup>e</sup>	2.96 ± 0.18 <sup>c</sup>
B (% MgO)	37.53 ± 4.02 <sup>g</sup>	52.70 ± 2.20 <sup>bc</sup>	46.60 ± 1.91 <sup>f</sup>	45.07 ± 2.51 <sup>f</sup>	50.61 ± 2.71 <sup>cd</sup>	47.63 ± 1.35 <sup>ef</sup>
ASH (%)	4.51	2.98	3.51	2.99	2.78	2.08

Data represent the means ± SD. Mean values followed by the same letters, a–i, within the same row across examined paper documents, are not significantly different at  $p < 0.05$ .

pH<sub>s</sub>, pH of paper surface; pH<sub>E</sub>, pH of aqueous paper extract; FA, formic acid; AA, acetic acid; XYL, D-xylose; GAL, D-galactose; ARA, L-arabinose; MAN, D-mannose; GLC, D-glucose; HOL, holocellulose; LIG, lignin; BW, basis weight; BL, breaking length; B, brightness; ASH, ash content

**Table 1- continued.** Principal Paper Characteristics for the Examined Paper Documents

Trait/Year	1859	1920	1923	1950	1956	2007
pH <sub>s</sub>	6.27 ± 0.01 <sup>g</sup>	4.31 ± 0.06 <sup>j</sup>	4.35 ± 0.03 <sup>j</sup>	4.58 ± 0.07 <sup>i</sup>	4.79 ± 0.04 <sup>h</sup>	7.79 ± 0.07 <sup>a</sup>
pH <sub>E</sub>	7.63 ± 0.02 <sup>c</sup>	5.55 ± 0.03 <sup>i</sup>	5.62 ± 0.04 <sup>h</sup>	5.76 ± 0.02 <sup>g</sup>	5.41 ± 0.01 <sup>j</sup>	7.96 ± 0.02 <sup>a</sup>
FA (mg/g)	0.69 ± 0.03 <sup>j</sup>	1.59 ± 0.03 <sup>f</sup>	1.38 ± 0.04 <sup>g</sup>	1.83 ± 0.03 <sup>d</sup>	1.65 ± 0.03 <sup>e</sup>	0.80 ± 0.02 <sup>i</sup>
AA (mg/g)	1.97 ± 0.02 <sup>f</sup>	1.98 ± 0.04 <sup>f</sup>	1.21 ± 0.04 <sup>i</sup>	1.82 ± 0.01 <sup>g</sup>	1.66 ± 0.02 <sup>h</sup>	1.81 ± 0.02 <sup>g</sup>
XYL (%)	0.00 ± 0.00 <sup>e</sup>	3.26 ± 0.01 <sup>c</sup>	4.18 ± 0.01 <sup>b</sup>	3.16 ± 0.02 <sup>d</sup>	3.24 ± 0.04 <sup>c</sup>	11.18 ± 0.02 <sup>a</sup>
GAL (%)	0.96 ± 0.01 <sup>g</sup>	1.10 ± 0.01 <sup>e</sup>	1.47 ± 0.02 <sup>a</sup>	0.00 ± 0.00 <sup>j</sup>	0.00 ± 0.00 <sup>i</sup>	1.00 ± 0.01 <sup>f</sup>
ARA (%)	1.58 ± 0.02 <sup>f</sup>	1.98 ± 0.01 <sup>b</sup>	1.92 ± 0.01 <sup>c</sup>	1.64 ± 0.01 <sup>e</sup>	1.70 ± 0.01 <sup>d</sup>	1.54 ± 0.02 <sup>g</sup>
MAN (%)	1.59 ± 0.02 <sup>j</sup>	5.50 ± 0.03 <sup>b</sup>	7.02 ± 0.02 <sup>a</sup>	2.85 ± 0.03 <sup>c</sup>	2.64 ± 0.03 <sup>d</sup>	1.79 ± 0.02 <sup>i</sup>
GLC (%)	87.27 ± 0.15 <sup>e</sup>	35.38 ± 0.20 <sup>j</sup>	41.24 ± 0.23 <sup>i</sup>	72.85 ± 0.09 <sup>g</sup>	75.16 ± 0.08 <sup>f</sup>	71.15 ± 0.35 <sup>h</sup>
HOL (%)	91.39 ± 0.16 <sup>g</sup>	47.22 ± 0.13 <sup>l</sup>	55.83 ± 0.22 <sup>k</sup>	80.51 ± 0.05 <sup>j</sup>	82.74 ± 0.12 <sup>i</sup>	86.65 ± 0.30 <sup>h</sup>
LIG (%)	5.17 ± 0.01 <sup>e</sup>	31.70 ± 0.05 <sup>b</sup>	32.64 ± 0.04 <sup>a</sup>	10.50 ± 0.02 <sup>c</sup>	5.30 ± 0.02 <sup>d</sup>	0.40 ± 0.02 <sup>j</sup>
BW (g m <sup>-2</sup> )	50.97 ± 0.17 <sup>l</sup>	87.40 ± 0.12 <sup>c</sup>	64.10 ± 0.13 <sup>j</sup>	83.80 ± 0.10 <sup>e</sup>	78.30 ± 0.10 <sup>h</sup>	79.89 ± 0.07 <sup>g</sup>
BL (km)	4.87 ± 0.18 <sup>b</sup>	1.17 ± 0.10 <sup>g</sup>	2.15 ± 0.12 <sup>ef</sup>	2.82 ± 0.08 <sup>c</sup>	2.77 ± 0.08 <sup>c</sup>	5.94 ± 0.08 <sup>a</sup>
B (% MgO)	54.03 ± 1.28 <sup>b</sup>	34.40 ± 2.88 <sup>h</sup>	35.34 ± 2.69 <sup>gh</sup>	47.86 ± 0.92 <sup>ef</sup>	49.58 ± 1.14 <sup>de</sup>	82.73 ± 0.16 <sup>a</sup>
ASH (%)	2.11	21.92	12.26	10.02	12.95	12.04

Data represent the means ± SD. Mean values followed by the same letters, a–i, within the same row across examined paper documents, are not significantly different at  $p < 0.05$ .

pH<sub>s</sub>, pH of paper surface; pH<sub>E</sub>, pH of aqueous paper extract; FA, formic acid; AA, acetic acid; XYL, D-xylose; GAL, D-galactose; ARA, L-arabinose; MAN, D-mannose; GLC, D-glucose; HOL, holocellulose; LIG, lignin; BW, basis weight; BL, breaking length; B, brightness; ASH, ash content

Strlič *et al.* (2007) studied paper documents from 1870, which were composed of 70% cotton and 30% year-old wheat and straw. The authors found that the  $pH_E$  of these paper samples was acidic (pH 4.7). This was also the case for paper samples from 1874, which consisted of 50% wood pulp and 50% sulphite pulp. An alkaline pH (pH 8.8) was recorded in paper samples originating from 2002, which were composed of 70% bleached kraft pulp and 30% bleached sulphite pulp.

#### *Changes in the amount of acetic and formic acids*

The greatest amounts of carboxylic acids were found in the oldest examined paper document from 1762 (Table 1), in which the content of acetic acid reached  $3.8 \text{ mg g}^{-1}$  and formic acid reached  $5.8 \text{ mg g}^{-1}$ .

High values of carboxylic acids were also found in paper documents from 1807. Jablonsky *et al.* (2012b) measured  $4.8 \text{ mg g}^{-1}$  of acetic acid in paper documents that were subjected to an accelerated ageing period of 60 days. Formic acid penetrates deeper inside stacks of papers than acetic acid, which reveals its potential for degradation in archives and libraries (Tétreault *et al.* 2013). The removal of volatile organic compounds has a significant positive effect on paper stability and can, in certain cases, double their lifetime expectancy (Strlič *et al.* 2011). In addition, in the present work it was found that the contents of acetic and formic acid were mutually correlated (see supplementary Table S1).

#### *Changes in contents of saccharides, lignin, and ash*

A significant proportion of paper is composed of saccharides. Based on the quantitative results of neutral saccharides in paper documents from the 18<sup>th</sup> and 19<sup>th</sup> centuries, these samples contained the highest proportion of glucose, very small amounts of other hemicellulose components (*i.e.*, galactose, mannose, and arabinose), and no xylose (Table 1).

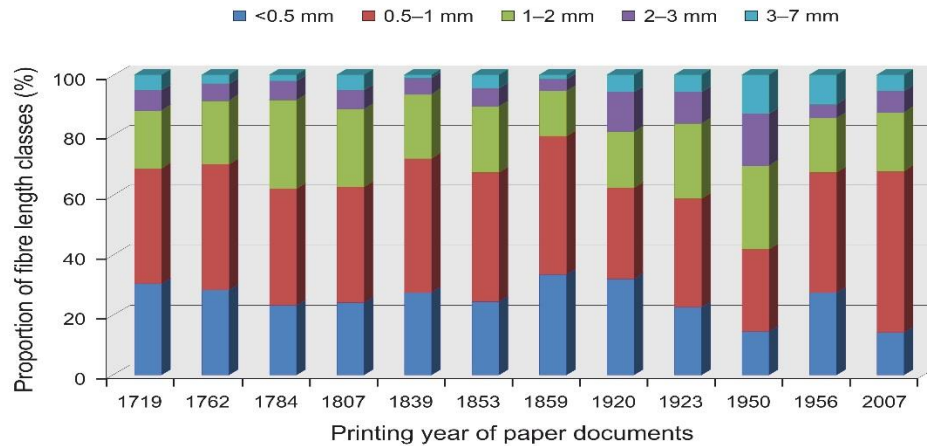
The degradation of hemicellulose begins with deacetylation, forming acetic acid that catalyzes both the hydrolysis of glycosidic bonds in polysaccharides and the subsequent reactions of arising monosaccharides (Nuopponen *et al.* 2004; Esteves and Pereira 2009). Until 1859, the amount of glucose ranged from about 87 to 91%. In 1920, the amount of glucose dropped to 35.4% because wood pulp at the time was an important component of printing paper.

Paper documents from 1920 and 1923 were made from softwood pulp, as is evidenced by the high content of both lignin and glucomannan in their paper samples. These documents also had low values for breaking length and brightness.

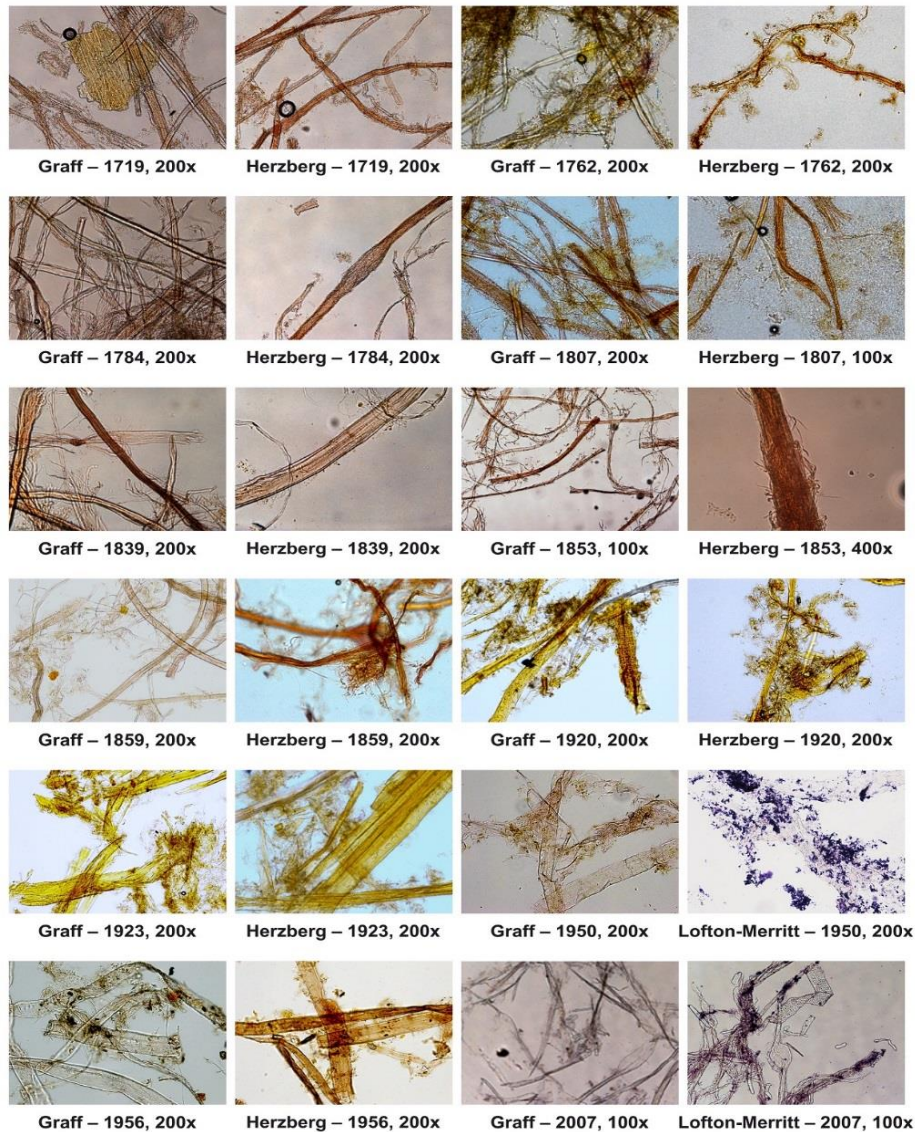
The presence of lignin chromophores in the examined paper samples resulted in a significant yellowing of the paper. Paper documents from 1920 contained a high content of ash (21.9%), which may explain their low strength, *e.g.*, in comparison to the paper document from the same period (1923), which contained a lower ash content. The 1923 document's breaking length was almost twice as high. High filler content has an indirect effect on the surface strength and the stiffness of paper (Ciullo 1996).

#### *Changes in fibre length distributions*

The results of fibre length distributions (Fig. 1) showed that the largest proportion of fibres in the oldest examined paper documents (until 1859) were in the 0.5 to 1.0 mm length class (ranging from 38.5 to 46.0%).



**Fig. 1.** Proportion of fibre length classes across the examined paper documents



**Fig. 2.** Light microscopy images of fibres present in the examined paper documents. Some images are adapted from Gojny *et al.* (2014)



These paper samples also contained a relatively high proportion of fibres longer than 1 mm. The microscopic analysis of fibres (Fig. 2) revealed that the paper documents from the 18<sup>th</sup> and 19<sup>th</sup> centuries were primarily made from rag pulp (cotton, flax, hemp). According to Kilpinen (1994), shorter cotton fibres (3 to 5 mm) were used in the past to make paper. Microscopic analyses provided by Collings and Milner (1984) concerning paper specimens made in Europe between 1400 and 1800 primarily showed mixtures of hemp and flax fibres with higher concentrations of hemp (*e.g.*, 75%) in earlier paper samples. While both cotton and cotton-containing fabrics were available in Europe during this period, they were not commonly used to generate substantial cotton-rag material for papermaking until the 19<sup>th</sup> century. Significant quantities of cotton fibre are therefore rare in paper documents before 1800.

Paper documents from the 20<sup>th</sup> century contained fibres within the 0.5 to 1.0 mm length class, from 28% (1950) to 40% (1956), with a large proportion of fibres longer than 2 mm (from 16% to 30%). The microscopic analysis of paper documents from 1920 and 1923 confirmed that these paper samples were made mostly from softwood pulp.

Paper documents from 1950 and 1956 consisted mainly of bleached softwood pulp, whereas paper samples from 2007 were produced from bleached hardwood pulp (Fig. 2). The latter paper documents contained the largest proportion of fibres at a length class of 0.5 to 1.0 mm (53.8%). Pulp fibre-length distribution that is observed after pulping and/or papermaking is a function of both the original fibre length distribution and the effects of processing. Because fibre length distributions affect tensile strength, tear, opacity, porosity, and many other paper properties, papermakers have developed many techniques to measure fibre length averages (Clark 1985). Other studies have also reported on the significant relationship between fibre length and the strength of paper (*e.g.*, breaking length and tear index) (Seth and Page 1988; Niskanen 1998; Molteberg and Høibø 2006).

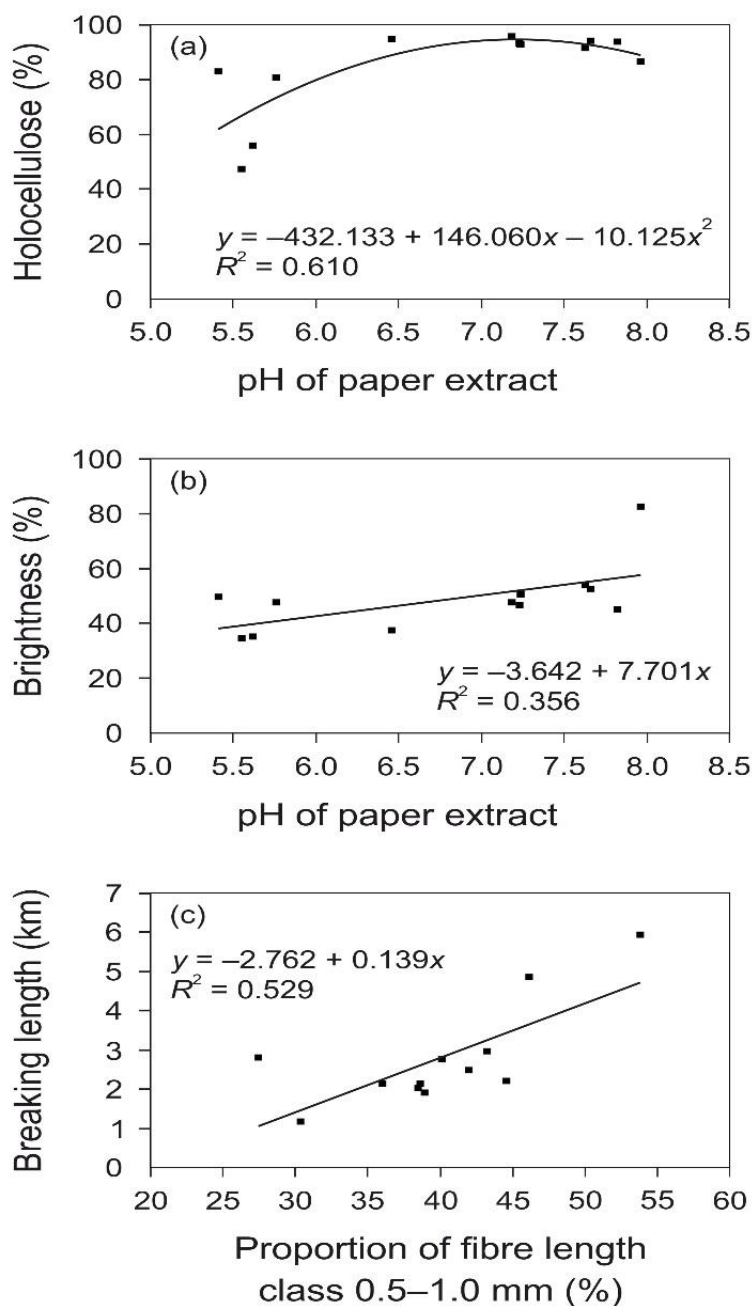
### *Correlated traits*

Statistical analysis of the examined trait linkages revealed that some traits affected other characteristics, either positively or negatively. Correlation coefficients among the examined traits are presented in the supplementary Table S1.

Within the examined paper documents, there were significant relationships between the pH and the contents of mannose, glucose, total yield of saccharides (*i.e.*, holocellulose), and lignin. Figure 3a shows the correlation of p<sub>H<sub>E</sub></sub> on the amount of holocellulose, which peaked at a p<sub>H<sub>E</sub></sub> of 7.18. The data was fitted with a second-order polynomial, and the measurements of the p<sub>H<sub>E</sub></sub> explained 61% of the variation in the content of holocellulose ( $R^2 = 0.610$ ,  $P = 0.014$ ).

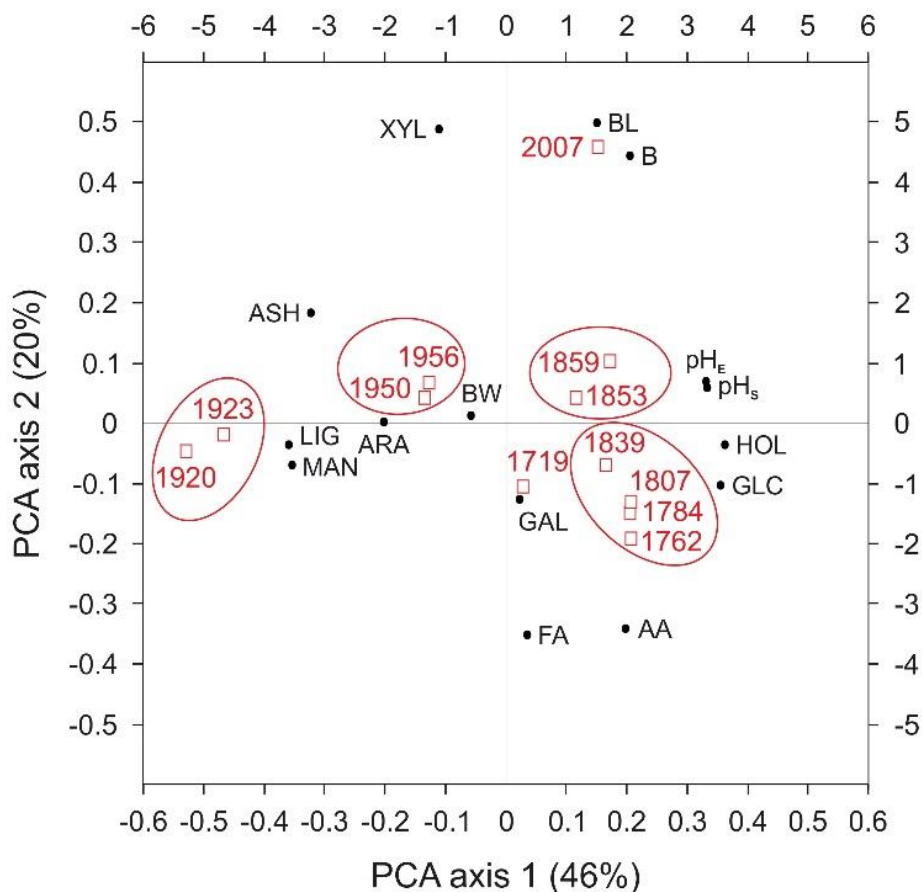
Paper brightness was also related to the p<sub>H<sub>E</sub></sub> (Fig. 3b), whereby the measurements of the p<sub>H<sub>E</sub></sub> explained 36% of the variation in the brightness of the paper documents ( $R^2 = 0.356$ ,  $P = 0.040$ ). Previous studies have shown that acidity accelerates the degradation of cellulose, holocellulose, and paper *via* acid-catalyzed hydrolysis (Wilson and Parks 1983). Weak, discoloured, and brittle paper correlated with low pH, while neutral and alkaline papers were generally in a much better state of preservation (Sobucki and Drewniewska-Idziak 2003).

Furthermore, there was a positive relationship between the breaking length and the proportion of fibre length class 0.5 to 1.0 mm (Fig. 3c). Measurements of the proportion of fibre length class 0.5 to 1.0 mm explained 53% of the variation in the breaking length of paper documents ( $R^2 = 0.529$ ,  $P = 0.007$ ).



**Fig. 3.** Relationships between the pH of aqueous paper extract and the content of holocellulose (a) and to paper brightness (b); the relationship of the proportion of fibre length class 0.5 to 1.0 mm to the breaking length of paper documents (c)

Greater fibre length and higher fibre strength supports higher paper strength (Fišerová *et al.* 2009). In this study, the fibre length class 0.5 to 1.0 mm was clearly the predominant proportion for the majority of the examined paper documents, and was thus primarily responsible for the strength of the paper samples. In addition, the amount of mannose negatively influenced the brightness of the paper because lignin, the major lignocellulosic component responsible for reducing brightness (Chen *et al.* 2012), correlated well with the mannose content (see supplementary Table S1).



**Fig. 4.** Positions of 15 paper traits on the first and second axes of the principal component analysis (PCA). The bottom and left-hand axes refer to the paper traits, whereas the top and right-hand axes refer to the printing year for the examined paper documents.

#### *Associations among paper traits*

A principle component analysis (PCA) was conducted to evaluate how the examined traits were associated (Fig. 4). The first axis explained 46% of the variation and showed strong positive loadings for the contents of holocellulose and glucose, as well as for the pH<sub>S</sub> and pH<sub>E</sub>. The negative side of the axis indicated strong loadings for the contents of lignin, mannose, and ash.

The second axis explained 20% of the variation and showed strong positive loadings for the breaking length, brightness, and xylose content. The negative side of the axis indicated strong loadings for the contents of both formic and acetic acids.

In addition, four groups of compact homogeneous clusters could be distinguished in a multivariate paper trait analysis that were clearly segregated from each other. Paper documents printed in 1762, 1784, 1807, and 1839 formed the first cluster, followed by clusters of paper documents printed in 1853 and 1859, then 1920 and 1923, and finally 1950 and 1956. The paper sample printed in 1719 formed a single segregated specimen; the same case was also observed for the paper document originating from 2007. The latter paper document was the most segregated specimen from all of the other groups, and traits such as breaking length and brightness were closely associated solely with this document.

## CONCLUSIONS

1. Paper documents originating from the 18<sup>th</sup> and 19<sup>th</sup> centuries were characterized by slightly acidic to neutral pH values, those from the 20<sup>th</sup> century by acidic values, and those from 2007 by slightly alkaline values. The contents of mannose, glucose, holocellulose, and lignin were significantly affected by the pH value of paper.
2. Paper documents from the 18<sup>th</sup> and 19<sup>th</sup> centuries were made from non-wood fibres (rag), those from the 1920s from softwood pulp, those from the mid of the 20<sup>th</sup> century from softwood bleached pulp, and lastly those from 2007 from bleached hardwood pulp.
3. Breaking length was influenced by both the fibre length class of 0.5 to 1.0 mm, and the degree of delignification as represented by brightness.
4. The lowest strength value was associated with 1920 paper documents made from wood fibres and containing very high amounts of both lignin and ash (fillers). Paper documents from 1920 and 1923 also had the lowest percentage of brightness. Therefore, paper documents originating from this period deserve very special attention and protection in public archives and libraries.
5. The paper document printed in 2007 was the most segregated specimen from all of the other groups of paper document clusters with regards to a multivariate paper trait analysis.
6. To make the paper more resistant to aging it is crucial to keep alkaline pH values, lower the air humidity and the temperature of the environment where the books are kept.

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**Table S1.**  
Pearson Correlation Coefficients for the Examined Paper Traits

Trait	pH <sub>s</sub>	pH <sub>E</sub>	FA	AA	XYL	GAL	ARA	MAN	GLC	HOL	LIG	BW	BL	B	ASH	FL1	FL2	FL3	FL4	FL5
pH <sub>s</sub>	—	<b>0.884</b>	0.007	0.447	-0.062	0.372	-0.458	<b>-0.727</b>	<b>0.712</b>	<b>0.766</b>	<b>-0.792</b>	0.018	0.377	0.559	<b>-0.651</b>	-0.128	<b>0.704</b>	0.076	<b>-0.615</b>	<b>-0.591</b>
pH <sub>E</sub>	<b>0.884</b>	—	0.037	0.477	-0.103	0.397	-0.489	<b>-0.717</b>	<b>0.666</b>	<b>0.703</b>	<b>-0.695</b>	-0.312	0.484	<b>0.597</b>	<b>-0.690</b>	-0.060	<b>0.728</b>	-0.035	<b>-0.587</b>	<b>-0.655</b>
FA	0.007	0.037	—	<b>0.772</b>	-0.261	-0.130	0.093	-0.056	0.096	0.054	-0.061	-0.306	-0.427	-0.178	-0.067	0.051	-0.322	0.338	0.077	0.051
AA	0.447	0.477	<b>0.772</b>	—	-0.414	0.194	-0.325	-0.388	0.441	0.401	-0.393	-0.225	-0.284	0.038	-0.436	0.165	0.078	0.279	-0.291	-0.467
XYL	-0.062	-0.103	-0.261	-0.414	—	-0.141	0.140	0.217	-0.509	-0.382	0.229	0.078	0.562	<b>0.608</b>	<b>-0.623</b>	<b>-0.615</b>	0.266	-0.116	0.278	0.382
GAL	0.372	0.397	-0.130	0.194	-0.141	—	-0.109	0.253	-0.085	-0.079	0.170	-0.073	-0.156	-0.169	-0.210	0.255	0.268	0.051	-0.262	<b>-0.762</b>
ARA	-0.458	-0.489	0.093	-0.325	0.140	-0.109	—	0.424	-0.408	-0.396	0.407	0.033	-0.096	-0.301	0.407	0.270	-0.271	-0.429	0.273	0.294
MAN	<b>-0.727</b>	<b>-0.717</b>	-0.056	-0.388	0.217	0.253	0.424	—	<b>-0.900</b>	<b>-0.913</b>	<b>0.957</b>	0.040	-0.452	<b>-0.584</b>	<b>0.676</b>	0.047	-0.544	0.128	0.548	0.232
GLC	<b>0.712</b>	<b>0.666</b>	0.096	0.441	-0.509	-0.085	-0.408	<b>-0.900</b>	—	<b>0.988</b>	<b>-0.945</b>	-0.030	0.205	0.295	<b>-0.899</b>	0.055	0.441	0.044	<b>-0.619</b>	-0.338
HOL	<b>0.766</b>	<b>0.703</b>	0.054	0.401	-0.382	-0.079	-0.396	<b>-0.913</b>	<b>0.988</b>	—	<b>-0.972</b>	-0.017	0.308	0.407	<b>-0.876</b>	-0.043	0.528	0.033	<b>-0.629</b>	-0.317
LIG	<b>-0.792</b>	<b>-0.695</b>	-0.061	-0.393	0.229	0.170	0.407	<b>0.957</b>	<b>-0.945</b>	<b>-0.972</b>	—	-0.059	-0.373	-0.533	<b>0.745</b>	0.111	-0.571	0.015	<b>0.614</b>	0.239
BW	0.018	-0.312	-0.306	-0.225	0.078	-0.073	0.033	0.040	-0.030	-0.017	-0.059	—	-0.326	-0.153	0.222	-0.172	-0.225	0.147	0.274	0.263
BL	0.377	0.484	-0.427	-0.284	0.562	-0.156	-0.096	-0.452	0.205	0.308	-0.373	-0.326	—	<b>0.870</b>	-0.124	-0.348	<b>0.727</b>	-0.395	-0.279	-0.041
B	0.559	<b>0.597</b>	-0.178	0.038	<b>0.608</b>	-0.169	-0.301	<b>-0.584</b>	0.295	0.407	-0.533	-0.153	<b>0.870</b>	—	-0.121	-0.492	<b>0.770</b>	-0.211	-0.305	-0.071
ASH	<b>-0.651</b>	<b>-0.690</b>	-0.067	-0.436	<b>-0.623</b>	-0.210	0.407	<b>0.676</b>	<b>-0.899</b>	<b>-0.876</b>	<b>0.745</b>	0.222	-0.124	-0.121	—	-0.107	-0.400	-0.156	<b>0.590</b>	0.521
FL1	-0.128	-0.060	0.051	0.165	<b>-0.615</b>	0.255	0.270	0.047	0.055	-0.043	0.111	-0.172	-0.348	-0.492	-0.107	—	-0.029	<b>-0.590</b>	-0.417	-0.507
FL2	<b>0.704</b>	<b>0.728</b>	-0.322	0.078	0.266	0.268	-0.271	-0.544	0.441	0.528	-0.571	-0.225	<b>0.727</b>	<b>0.770</b>	-0.400	-0.029	—	-0.432	<b>-0.771</b>	-0.554
FL3	0.076	-0.035	0.338	0.279	-0.116	0.051	-0.429	0.128	0.044	0.033	0.015	0.147	-0.395	-0.211	-0.156	<b>-0.590</b>	-0.432	—	0.400	0.215
FL4	<b>-0.615</b>	<b>-0.587</b>	0.077	-0.291	0.278	-0.262	0.273	0.548	<b>-0.619</b>	<b>-0.629</b>	<b>0.614</b>	0.274	-0.279	-0.305	<b>0.590</b>	-0.417	<b>-0.771</b>	0.400	—	<b>0.661</b>
FL5	<b>-0.591</b>	<b>-0.655</b>	0.051	-0.467	0.382	<b>-0.762</b>	0.294	0.232	-0.338	-0.317	0.239	0.263	-0.041	-0.071	0.521	-0.507	-0.554	0.215	<b>0.661</b>	—

Note: Correlation coefficients presented in bold are significant at  $P < 0.05$ .

pH<sub>s</sub>, pH of paper surface; pH<sub>E</sub>, pH of aqueous paper extract; FA, formic acid; AA, acetic acid; XYL, D-xylose; GAL, D-galactose; ARA, L-arabinose; MAN, D-mannose; GLC, D-glucose; HOL, holocellulose; LIG, lignin; BW, basis weight; BL, breaking length; B, brightness; ASH, ash content; FL1, fibre length class <0.5 mm; FL2, fibre length class 0.5–1 mm; FL3, fibre length class 1–2 mm; FL4, fibre length class 2–3 mm; FL5, fibre length class 3–7 mm.