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Evaluating volatile organic compounds from Chinese traditional handmade paper by SPME-GC/MS

Li Ding^{*} , Qin Yang, Jianhui Liu and Zheng Lee

Abstract

Once printed, books are always accompanied by the smells of volatile organic compounds (VOCs) which are continuously emitted not only by inks but also by papers themselves throughout their lives. Although the VOCs from papers may bring mild discomfort to readers, they are considered as very important factors that feature the degradation of papers and show potential applications in cultural relic appraisal. In this study, an analytical approach based on solid phase microextraction combined with gas chromatography-mass spectrometry (SPME-GC/MS) was proposed for the evaluation of volatile organic compounds (VOCs) emitted by Chinese traditional handmade papers. The VOCs evaluations and artificial aging processes were both applied to recent-made papers and naturally aged papers from a traditional Chinese calligraphy and painting scroll (collected by the National Museum of China). To be noticed, a large number of aliphatic acids, aldehydes, ketones, furan derivatives, benzene series and terpenoid substances indicated that the VOCs signals not only reveal the degradation of paper but also tentatively reflect the storage environment along hundreds of years ago. The semi-quantitative evaluation of markers indicated that the historical paper is under a serious degradation due to the high capacity it releases. Our results provided a path way to get the degradation information of ancient paintings as well as potential realistic applications such as the conservation of paper-based relics and the environmental protection in libraries and museums.

Keywords: SPME-GC/MS, VOCs, Handmade paper, Degradation

Introduction

Paper, since invented thousands of years ago, have been considered as the vehicle of both knowledge and history of human civilizations. Compared with rock carvings and bamboo slips, writing on papers is of more convenience with greater information storages which quickly became mainstream of the data carriers before the age of information. Since obtained from organic materials, the degradation accompanies with the papers throughout their lives as long as they are produced. It is of great importance to evaluate papers to get their ageing situations by analyzing their degradations.

Compared with modern technologies for paper evaluations which are generally destructive with the need of grams of papers. No-invasive evaluation technologies such as pH, chromaticity, vibrational spectrometry is more acceptable in practical work especially for historical relics [1, 2] while these approaches can only provide either surficial information or functional group information [3–6]. Py-GC/MS (Pyrolysis gas chromatography-mass spectrometry) as a possible technique involving slight invasion (several micrograms), reflects the materials composition while the pyrolysis products are usually complicated and easy to be interfered. Therefore, it is still not applicable for quantitative analysis [7–9].

Recently, the volatile organic compounds (VOCs) emitted from the paper have aroused people's concern due to its strong influences on the storage environment and

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the life expectancy of the paper [10–14]. VOCs emitted from paper are the main odor source in the libraries and archives, and are recognized as a natural ageing feature of the papers. Matija Strlič proposed paper metabolomics theory, which described that the ageing behavior of paper is analogous to the metabolic behavior of organisms. The VOCs are metabolites which help others learn about the degradation behaviors [1, 12, 14, 15]. At the same time, the VOCs will accelerate the degradation of papers, which may in turn become the VOC absorbers [12].

Solid phase microextraction (SPME) combined with gas chromatography-mass spectrometry (GC/MS) is an effective no-invasive method for the collection, separation and detection of volatile organic compounds (VOCs) emitted by papers [12, 16–22]. Previous studies showed the SPME fiber with selected filler collected the aliphatic acid, aldehyde and furfural from natural and artificial aged wood pulp. Different VOCs were verified to be the degradation products of cellulose and lignin [12, 23–25]. With the help of this method, papers made from various materials including cotton/linen [25], wood pulp [25, 26], raw fibers [27] and even moldy paper with microorganisms [19, 28] have been intensively studied with applausive results in early European and Arab traditional papermaking technology. However, to our knowledge, VOCs emitted from Chinese traditional handmade papers is still unexplored.

The origin of Chinese handmade paper can be traced back to 2000 years ago, and it was the principal carrier for culture to spread and inherit. A large number of paper-based heritages are preserved due to the high mechanical property and high stability of the traditional handmade paper, such as the ancient book *The Records of the Three Kingdoms* and the earliest Chinese calligraphy *Pingfu Post* from the third century. The historical restoration is another critical factor to increase the lifetime expectancy of the paper in the past or present. Chinese handmade paper is widely applied to the conservation on paper-based heritage artifacts.

In this work, SPME-GC/MS was applied to evaluate the volatile organic compounds (VOCs) emitted from

three kinds of Chinese traditional handmade paper and a common mechanical newspaper. Our research aims to establish a list of VOCs from Chinese handmade papers as well as sorting out the degradation marker molecules. The SPME-GC/MS proved its practical applications in historical paper examination, the evaluation of the natural degradation papers which may further extend our understandings of no-invasive characterization of cultural relics.

Materials

Reference paper

Handmade papers were purchased from three different provinces in China, which boast famous producers of traditional Chinese handmade papers. The mechanical papers were selected as references in the control experiments. The information of the paper samples was listed in Table 1.

Agarwood and Mixiang paper

Vietnam agarwood was purchased from Aijia collection, Beijing.

Historical paper

Jiang Youzhu et al. *seven digging mounted painting scroll* is a traditional Chinese calligraphy and painting scroll from the Qing Dynasty (C.E 1636–1912) collected by the National Museum of China. The whole scroll can be divided into three parts: the upper part, the middle part and the lower part. P1 is a running script, signed by Chen Liangzhen (陈良箴), who was a calligrapher from Fujian province. P2 has no inscription. P3 is a painting which was inscribed by Jiang Youzhu (江友渚), who was a painter from the central Fujian province of the Qing Dynasty [29]. P4 has no inscription. P5 is the seal character which was contributed by Fan Can (范燦). P6 and P7 were scribed by Hong Ji (洪基), who was a folk artist from Fujian province [29]. According to the time documented, the “甲申菊秋” and “甲申小春” in P6 and P7, which hinted that the painting might be finished in C.E 1644, 1704 or 1764. Since the dates of birth and death of artists were not documented, the age of scroll

Table 1 Summary of the samples of known origins used in the course of the present studies

Product Name	Common name	Catalogue	Fiber origin	Year	Place	Paper grammage (g/m ²)
Gaoli	Mulberry paper	Handmade	<i>Morus alba</i>	2015	Qian'an, Hebei	29.2
Yukouzhi	Bamboo paper	Handmade	<i>Phyllostachys pubescens</i>	2011	Ninhua, Fujian	37.1
Xuan	Rice paper	Handmade	<i>Pteroceltis tatarinowii</i> Maxim and <i>Oryza sativa</i>	2017	Jingxian, Anhu	23.8
Wood pulp	Wood pulp paper	Mechanical	Wood pulp	2000	-	46.0

could not be clearly verified. The content of the running script and seal character were compliments to the generals of central Fujian province. In addition to the “奉祝清正” in the running script, the aim of the creation was to offer birthday congratulations to a general. The scroll was digging mounted with papers and badly damaged with stains and cracks around the mounting materials. The conservator decided to remount the scroll to extend the life of calligraphies and paintings. The substituted wrecked head margin paper was collected and further studied by SPME-GC/MS.

Experiments and methods

Artificial ageing

200 mg or 150 mg of reference paper sample was put into a 20 mL headspace bottle. 5 groups of papers were prepared, among which 1 group was taken as a control. The other 4 groups of samples underwent 1,2,3,4 ageing cycles, respectively. Each ageing cycle was 72 h. Three parallel samples were prepared for each group. The temperature and the humidity were controlled by the constant temperature humidity chamber following standard ISO 5630–3:1996. The ageing temperature was 80 °C and the relative humidity was 65%. Light was avoided inside the chamber. The brand and model of the constant temperature humidity chamber used is KBF-115 (Binder, Germany). The total ageing time was listed in Table 2. Historical paper at sampling location 5 (Fig. 1) were manipulated under the same artificial ageing process. The photographs and mass records of reference sample and historical paper were attached in Additional file 1: Figure S1 and Table S1.

Paper fiber observation

Paper samples were stained with Graff “C” reagent to assess the presence of color and morphology of fiber. The paper samples were observed under the Leica Dmrx2 microscope.

The scanning electron microscope images of paper fibers were obtained via FEI Quanta 650.

SPME-GC/MS

The VOCs emitted by reference papers (200 mg/150 mg) at different ageing stages and historical paper (200 mg) were collected by solid phase microextraction fiber. The SPME extraction was performed automatically on each aged sample in the headspace bottle using 120 µm ARR11-DVB/CWR120/20 (Divinylbenzen-Carboxen/Poly (Dimethylsiloxane), SPME arrow fiber. The filler is suitable for a wide

Table 2 Total ageing time for different ageing stage

Ageing stage	Fresh	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Ageing total time (h)	0	72	144	216	288



Fig. 1 The photograph of “Jiang Youzhu et al. seven digging mounted painting scroll”. The location of samples for SPME-GC/MS and fiber observation was labeled

range of chemicals and was successfully used for studies on paper-based materials [25]. The extraction was performed according to the adapted methods available in literatures [23, 26, 30, 31]. The fiber was pre-conditioned in the GC injection port at 230 °C for 3 min before extraction. Then the vial with paper sample was placed in the incubation block at 60 °C for 30 min. The fiber was inserted into the vial at a depth of 32 mm to extract the analyte for 30 min at 60 °C. After that, the analyte was then immediately desorbed by insertion of the fiber into the injector port of chromatograph at a depth of 45 mm for 5 min at 230 °C. All

the above processes were completed on three-in-one automatic pretreatment platform (Zhida, Guangzhou). In addition, an empty vial without a paper sample was also tested as a blank.

The volatile compounds were identified by gas chromatography-mass spectrometry (GC/MS) analysis with a 7890A-5975C (Agilent, USA). The chromatograph was equipped with a DB-5MS capillary column, 30 m × 0.25 mm, 0.25 μm film thickness. The temperature of chromatographic elution was programmed as follows: isothermal at 35 °C for 10 min, then from 35–250 °C at a rate of 5 °C/min, and isothermal hold at 250 °C for 30 min. The split/splitless injector was used in splitless mode and its temperature was maintained at 230 °C. The interface temperature was set at 270 °C. Mass spectra were acquired under electron ionization mode (EI) at 70 eV and recorded from *m/z* 33–700 amu. TIC mode was used for peak analysis of the total ion current spectrum, and the peak with S/N above 3 was extracted and compared with the NIST 2014 spectrum library.

For targeted monitoring and semi-qualitative measurement, the chromatograph was equipped with a HP-INNOWax capillary column, 30 m × 0.25 mm, 0.25 μm film thickness. The temperature of chromatographic elution was programmed as follows: isothermal at 50 °C for 2 min, then from 50 to 240 °C at a rate of 10 °C/min, and isothermal hold at 240 °C for 2 min. The split/splitless injector was used in splitless mode and its temperature was maintained at 230 °C, while the interface temperature was set at 260 °C. Mass spectra were acquired under electron ionization mode (EI) at 70 eV and recorded from *m/z* 15–300 amu. Deconvolution mode was used for peak analysis of the total ion current spectrum.

External standard

10, 20, 30, 40, 50, 60, 70, 80, 90, 100 (10^{−6} g/mL) of Acetic acid in methanol were prepared to obtain the linear calibration curves. The GC/MS injection volume of external standard was 0.5 μL.

Semi-quantitative calculation

In this study, the trend of VOC emission was evaluated semi-quantitatively by dealing with the analyte absorbed by the SPME arrow fiber. The amount of analyte extracted onto the coating is linearly proportional to the analyte concentration in the bottle [32].

The semi-quantitative calculation was as follows:

$$C_R \left(\frac{\text{ng}}{\text{g paper}} \right) = \frac{M_f}{M_p} = \frac{C_0 (10^{-6} \text{ g/mL}) \times 0.5 (\mu\text{L})}{M_p (\text{g paper})}$$

M_f is the mass of adsorbed substance on the SPME arrow fiber. M_p is the mass of the paper. C_0 is the calibrated

concentration. C_R is the emission rate of targeted compounds. The diameter of SPME arrow fiber was 1.5 mm. The DI liner tube with inner diameter with 2 mm was applied to ensure the injection efficiency of SPME and liquid injection was near 95% [33]. M_f is the mass of adsorbed substance on the SPME arrow fiber.

Results and discussion

Morphologies of fibers

As shown in Fig. 2a, Mulberry paper is composed of mulberry bark fiber and Eulens binata fiber. The mulberry bark fiber turns wine red after being dyed with Graff "C" reagent. The fiber is cylindrical with smooth surface and oblique transverse node stripes. Amorphous wax attached to the fiber wall can be observed. As shown in Fig. 2b, the Bamboo paper is composed of bamboo fibers, which are characterized by tapering of the fiber ends and reticulated vessel element. As shown in Fig. 2c, Rice paper consists of a small amount of bark and straw. Straw fiber at both ends is tiniest and with transverse section lines on the cell wall. In addition, the serrated epidermal cells of the straw were shown in the Figure inserted. As shown in Fig. 2d, the Wood pulp paper is made of mechanical softwood groundwood paper pulp, since the Graff "C" stain creates a vivid yellow color. It is basically consistent with the information of labels of the products. The SEM images of fibers were also shown in Additional file 1: Figure S2.

Non targeted screening of VOCs

Solid-phase micro-extraction was carried out following a non-invasive analytical method previously proposed for the determination of VOCs in paper samples [23, 26, 30, 31]. The SPME fiber with Divinylbenzen-Carboxen/Poly (Dimethylsiloxane) fillers were tested to be suitable for absorbing a wide range of VOCs from the paper materials [25, 26]. In this work, the arrow SPME fiber with the same filler was applied. Owing to the larger adsorption surface area, the arrow SPME fiber could achieve higher extraction efficiency. In Fig. 3, the typical chromatograms obtained in Mulberry, Bamboo, Rice and Wood pulp paper were reported. The peak identification was performed by the corresponding mass spectra compared with the NIST2014 database. 87 compounds were clearly identified (Table 3) compared with a blank chromatogram, where these compounds were not detected.

Peaks labeled with asterisks in Fig. 3 were identified to be derivatives of siloxane as contaminants which are likely derived from SPME fibers. These 87 compounds comprise the aliphatic acid, aldehyde, ketone, alkane, furan derivative and benzene series. The aliphatic acids, like acetic acid, propanoic acid, butanoic acid and pentanoic acid, are notorious for acidification of paper [13,

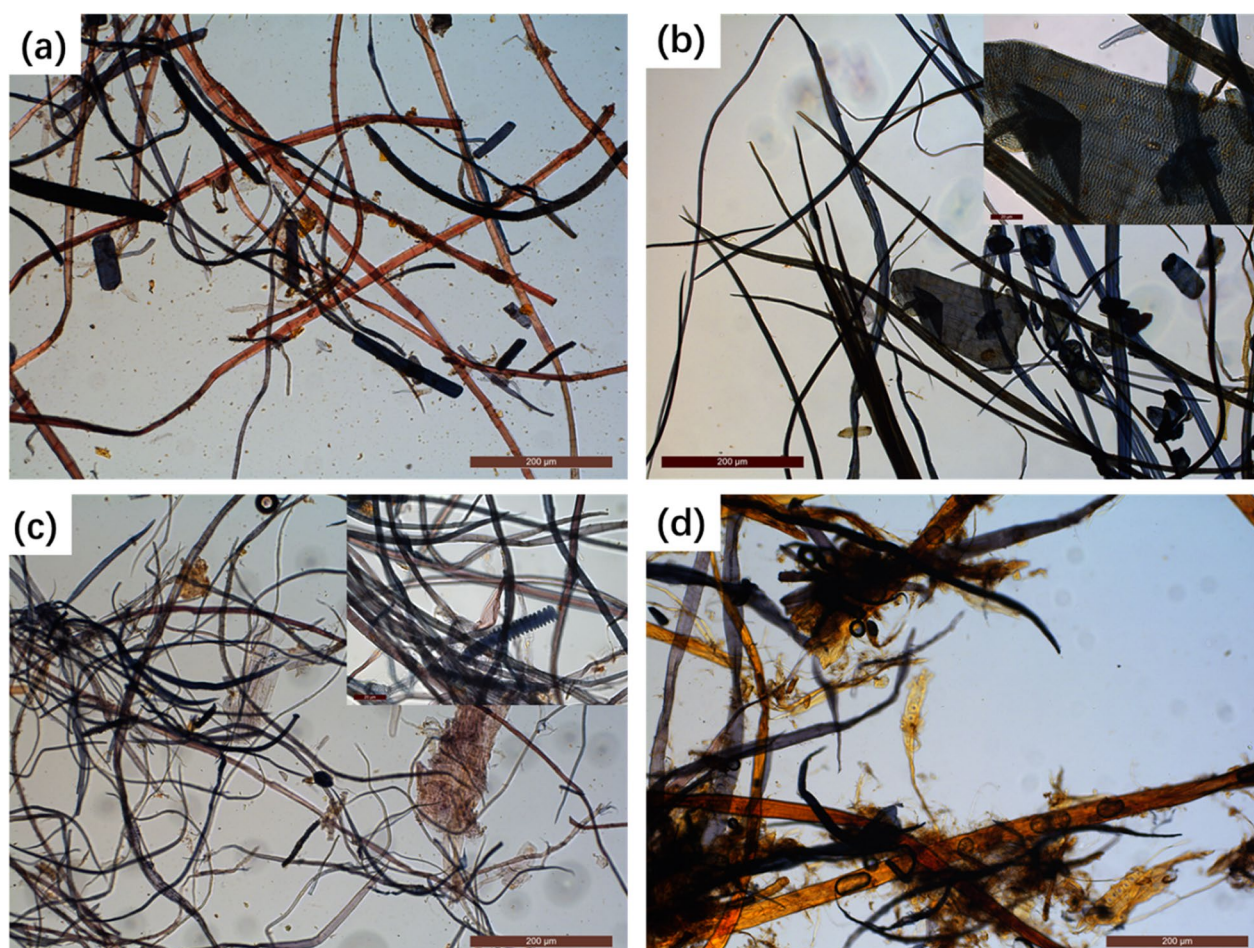
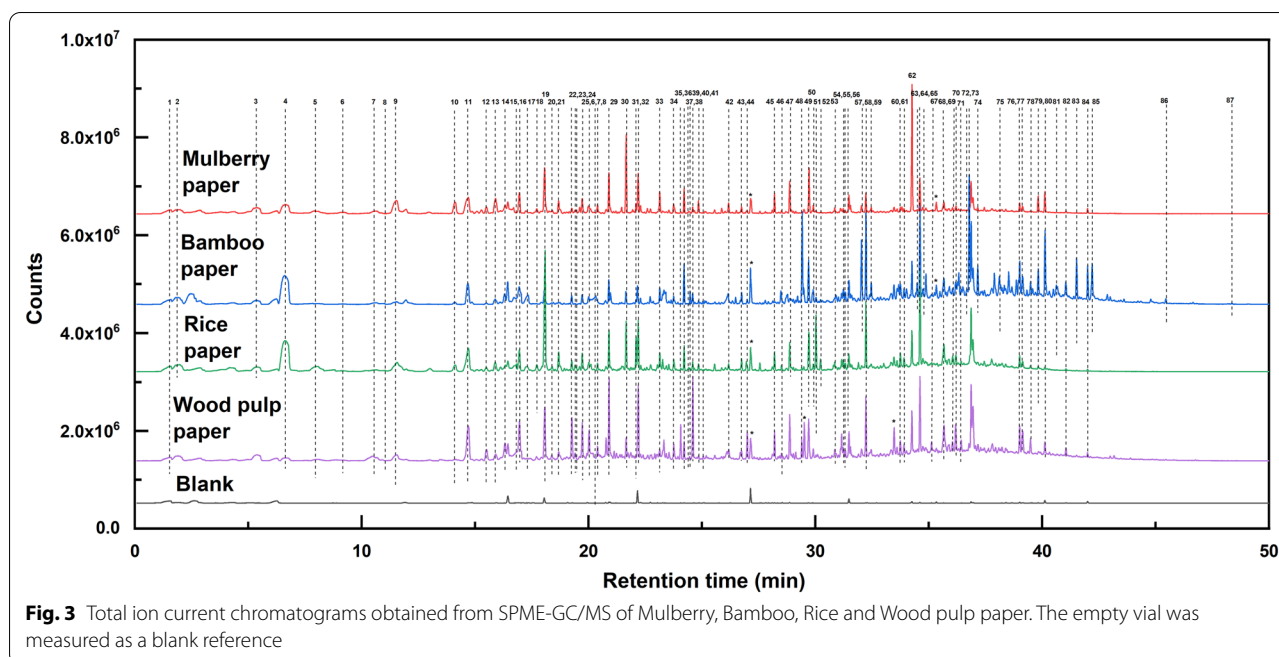


Fig. 2 The optical microscopy images of the fiber from **a** Mulberry paper, **b** Bamboo paper, **c** Rice paper and **d** Wood pulp paper

30]. These short chain acids could be emitted from various degradation of the paper, such as the deep degradation of cellulose and oxidation of lipid [2, 30]. However, several long chain aliphatic acids ($C_n > 10$) were also detected in our studies. For instance, C_{14} and C_{16} were found in the Bamboo paper which is made from *Phyllostachys pubescens* fibers. The straight chain aldehyde (C_6 – C_{18}) and Ketone (C_7 – C_{15}) identified in the samples are convenient markers for the autoxidation of aliphatic acids, which naturally exist as residual resins known to be dominated by the 18 carbon unsaturated acids oleic, linoleic and linolenic acids [24, 30]. Alkane mainly originated from waxy residue on the surface of fibers or degradation of lipid and unsaturated hydroperoxides [30, 34–36]. Furan derivatives are typical products of degradation due to the acid hydrolysis of five- to six-carbon sugar in cellulose and hemicellulose. The representative compound was furfural. Besides, 2-Furanmethanol, 2-pentyl-Furan, 5-ethyldihydro-5-methyl-2(3H)-Furanone, 5-ethyldihydro-5-methyl-2(3H)-Furanone and

dihydro-5-pentyl- 2(3H)-Furanone were also detected. Monomethoxylated phenolic compounds (such as vanillin, guaiacol or other benzene series) with a smoky aroma arising from lignin degradation can be considered as a degradation compound of groundwood pulp paper [23]. In this investigation, vanillin and guaiacol were prominently screened out in Bamboo and Wood pulp paper. It might be due to the high concentration of lignin in the *Phyllostachys pubescens* fibers and wood pulp. In addition, some plant markers were identified. For instance, the cedrene was unique to be found in the Rice paper, which indicated that the essential oil might be the additive. The camphor was found in the Mulberry, Rice and Wood pulp paper, which might be due to the additive of camphor for expelling parasites. However, until further verification, these are only speculations. The environmental contaminations would contribute as well. Therefore, the evaluation of VOCs from papers could not only give the information of the degradation but also help with looking into manufacturing technology or the storage



environment during the past years. The VOCs emitted from paper and their corresponding sources are listed in Table 4.

Monitoring of artificial ageing process

The VOCs related to the degradation were selected to monitor the artificial ageing process of paper. Typically, aliphatic acids, furan derivatives, aldehyde and ketone were surveyed independently. In order to evaluate the products of degradation semi-quantitatively, the PEG (polyethylene glycol) column with strong polarity was employed. The peak patterns of acids, furan derivatives and aldehyde were improved as shown in Additional file 1: Fig. S4. The amount of absorbed substance on the SPME fiber (M_f) was calculated by the external standard curve and further calibrated on the paper mass (C_R). Even though the response factors of targeted compounds are various, this result clearly showed the applicability of SPME for identifying and semi-quantifying VOCs emitted from paper, the original data were supplied in Additional file 2.

As shown in Fig. 4, the continuous growth of VOCs from Mulberry paper was observed as more artificial ageing cycles were applied. To be mentioned, not all the compounds were ideally suited for indicating the ageing progress of paper. In Fig. 4a the content of most acids kept increasing with ageing. Typically, the concentration of acetic acid and hexanoic acid is 12.7 and 15.1 ng/g at cycle 4, respectively. The concentration of 2-ethyl-Hexanoic acid showed a decline in Cycle 4, which is not

proper to be an indicator. As for furan derivatives, furfural was known as an important degradation marker for paper and its accumulation was clearly monitored by the SPME-GC/MS as shown in Fig. 4b. The concentration of furfural is 33.8 ng/g at cycle 4. Accumulation of other furan derivatives was relatively slow. In Fig. 4c, straight chain aldehyde (C_9 – C_{10}) experienced a consumption during the ageing, which might be due to the limitation degradation of the unsaturated acid. However, octanal showed conspicuous formation after the first ageing cycle and increased until Cycle 4. Abundant ketone compounds were detected (including C_8 – C_{15}), whose contents went through a slight increment. As shown in Fig. 4d, benzene series such benzaldehyde, acetophenone are highly relative to the degradation of lignin. Since benzaldehyde comprehensively exists in the plant stems and leaves in the form of glycoside, it is not surprising to find them in the Mulberry paper. As the degradation proceeds, the benzaldehyde continues to be sent out, which might account for the hydrolysis of its glycoside, such as amygdalin [37, 38]. In conclusion, for Mulberry paper, acetic acid and hexanoic acid, furfural and benzaldehyde were demonstrated to be the degradation molecular markers.

Bamboo paper has emerged since the Song Dynasty (C.E 960–1279). Compared with other handmade papers, Bamboo paper usually has poor anti-ageing performance. As shown in Fig. 5a acetic acid and hexanoic acid as the most important degradation markers increased remarkably during ageing. The concentrations of acetic acid and

Table 3 The assignment of VOCs detected from the Mulberry, Bamboo, Rice and Wood pulp paper

No	t _R /min	Assignment	Score	No	t _R /min	Assignment	Score
1	1.60	2-Propanamine	78	45	28.12	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	89
2	1.87	Acetic acid	76	46	28.50	dihydro-5-pentyl- 2(3H)-Furanone	93
3	5.37	Hexanal	96	47	28.85	Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-trimethylpentyl ester	98
4	6.59	Furfural	99	48	29.39	Vanillin	98
5	8.01	2-Furanmethanol	86	49	29.71	6,10-dimethyl-2-Undecanone	97
6	9.09	1-Hexanol	91	50	29.89	Dodecanal	97
7	10.60	2-Heptanone	82	51	30.02	α-Cedrene	97
8	11.00	Pentanoic acid	70	52	30.22	β-Cedrene	94
9	11.51	Heptanal	97	53	30.85	Geranyl acetone	94
10	14.12	3-Ethyl-4-methylpentan-1-ol	91	54	31.21	2,6,10-Trimethyltridecane	91
11	14.68	Benzaldehyde	97	55	31.32	2-methyl-Tetradecane	87
12	15.49	1-Heptanol	94	56	31.55	Cyclododecane	91
13	15.89	Phenol	89	57	32.03	1-Pentadecene	98
14	16.30	2-pentyl-Furan	89	58	32.22	Pentadecane	98
15	16.83	Hexanoic acid	91	59	32.47	Tetradecanal	85
16	16.94	Octanal	97	60	33.74	2-methyl-Pentadecane	90
17	17.23	1H-Pyrrole-2-carboxaldehyde	95	61	33.90	3-methyl-Pentadecane,	85
18	17.71	5-ethyldihydro-5-methyl-2(3H)-Furanone	86	62	34.25	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	98
19	18.05	2-ethyl-1-Hexanol	98	63	34.48	2-Tetradecanone	86
20	18.37	2-hydroxy-Benzaldehyde,	79	64	34.60	Hexadecane	98
21	18.67	4,6-dimethyl-2-Heptanone	86	65	34.73	Cedrol	90
22	19.25	Acetophenone	87	66	35.12	Benzophenone	89
23	19.39	4-methyl- Benzaldehyde	95	67	35.67	2,6,10-trimethyl-Pentadecane	90
24	19.46	2-Acetonycyclopentanone	82	68	36.04	2-methyl-Hexadecane	88
25	19.71	1-Octanol	99	69	36.18	2,2',5,5'-tetramethyl-1,1'-Biphenyl	90
26	20.02	Guaiacol	92	70	36.42	3,4-diethyl- 1,1'-Biphenyl,	85
27	20.32	Heptanoic acid	74	71	36.69	E-15-Heptadecenal	82
28	20.39	2-Nonanone	91	72	36.77	2-Pentadecanone	96
29	20.89	Nonanal	99	73	36.86	Heptadecane	91
30	21.64	1-methyl-4-(1-methylethyl)-,cis-Cyclohexanol	85	74	37.15	Pentadecanal	92
31	22.08	(R,S)-5-Ethyl-6-methyl-3E-hepten-2-one	98	75	38.10	Tetradecanoic acid	91
32	22.18	Camphor	98	76	38.99	Octadecane	94
33	23.13	1-Nonanol	95	77	39.12	2,6,10,14-tetramethyl-Hexadecane	92
34	23.75	2-Decanone	87	78	39.47	Isopropyl myristate	93
35	24.06	Dodecane	98	79	39.81	6,10,14-trimethyl-2-Pentadecanone	96
36	24.21	Decanal	99	80	40.12	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	96
37	24.41	2-propyl- 1-Heptanol	85	81	40.62	n-Nonadecanol-1	86
38	24.47	2,3-dihydro-Benzofuran	93	82	40.89	4-Octadecenal	62
39	24.58	Benzothiazole	94	83	41.51	Hexadecanoic acid, methyl ester	98
40	24.84	Undecanal	88	84	42.00	Dibutyl phthalate	95
41	25.04	Isophthalaldehyde	92	85	42.20	n-Hexadecanoic acid	97
42	26.02	Nonanoic acid	95	86	45.45	(Z)-18-Octadec-9-enolide	89
43	26.74	2-Undecanone	97	87	48.36	10-methyl-Eicosane	79
44	26.99	Tridecane	97				

hexanoic acid are 14.6 and 15.1 ng/g at cycle 4, respectively. In addition, the amount of other acids gradually increased as well. With regard to furfural, it maintained

a stable rising tendency as expected (Fig. 5b). The concentration of furfural is 12.5 ng/g at Cycle 4. The variations of aliphatic aldehyde and ketone were complicated

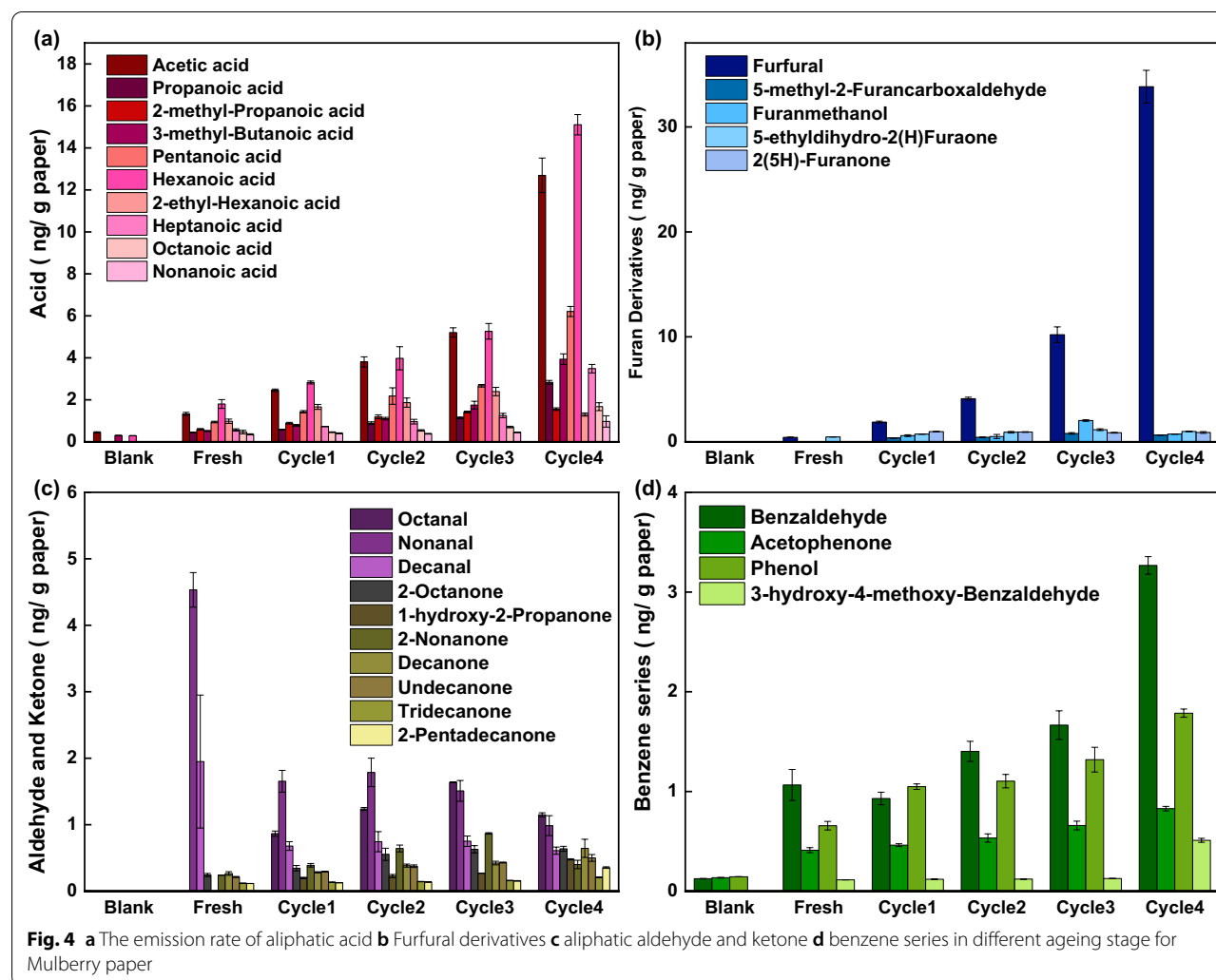
Table 4 The VOCs emitted from paper and their corresponding sources

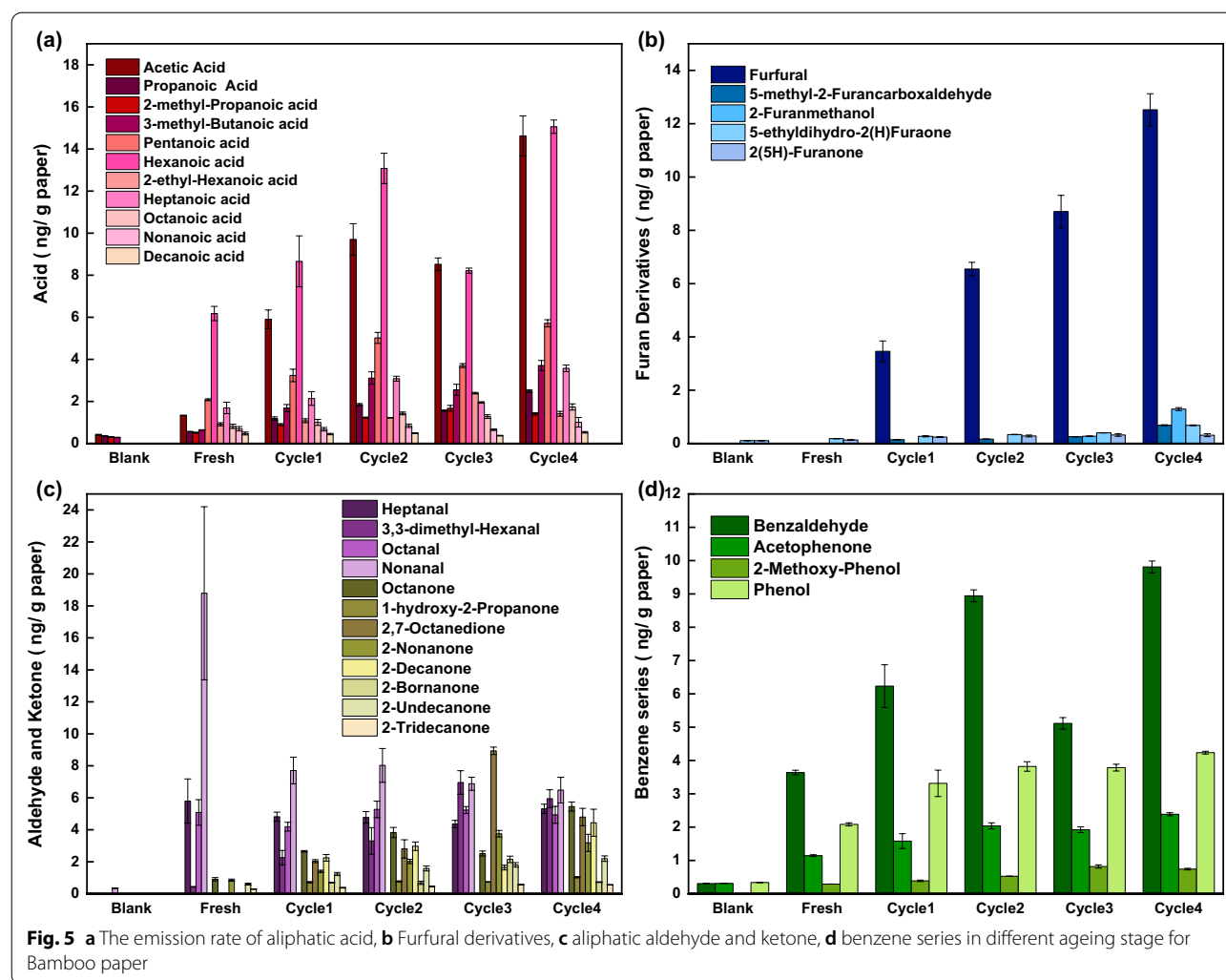
Source	VOCs
Cellulose and Hemicellulose	Furan derivatives, short chain aliphatic acids
Lignin	Vanillin, guaiacol, benzene series
Lipid	Straight chain aldehyde Ketone, Alkane
Wax	Alkane
Plant markers	Camphor, Cedrene

for the Bamboo paper. As shown in Fig. 5c, aliphatic aldehyde (C_7 – C_9) showed freshly high content and experienced a decline during the ageing. ketone compounds ranging from C_8 to C_{13} were detected and the content of them went through a slight increase. As for emission rate of benzene series in Fig. 5d, Bamboo paper showed relative high level. It is 9.8 ng/g for benzaldehyde at cycle

4, which hints a high lignin content of Bamboo paper. Hence for Bamboo paper, acetic acid and hexanoic acid, furfural and benzaldehyde were demonstrated to be the degradation molecular markers.

Rice paper, mostly made of mixed *Pteroceltis tatarinowii* Maxim and *Oryza sativa*, are produced from Jinxiang, Anhui, and considered as the most famous paper for mounting and repairing traditional Chinese painting and calligraphy. In Fig. 6a the amount of aliphatic acid, such as acetic acid, hexanoic acid increase as the degradation progress, which is similar to the Mulberry and Bamboo paper. The concentrations for acetic acid and hexanoic acid are 12.1 and 11.4 ng/g at cycle 4, respectively. It is shown in Fig. 6b, furfural maintained a stable rising tendency and the emission rate was up to 68.9 ng/g, which demonstrated the high furfural release capacity of Rice paper. Concerning the aldehyde and ketone compounds, as shown in Fig. 6c, a relative high concentration of aliphatic aldehyde with C_7 , C_9 , C_{10} , C_{11} was detected



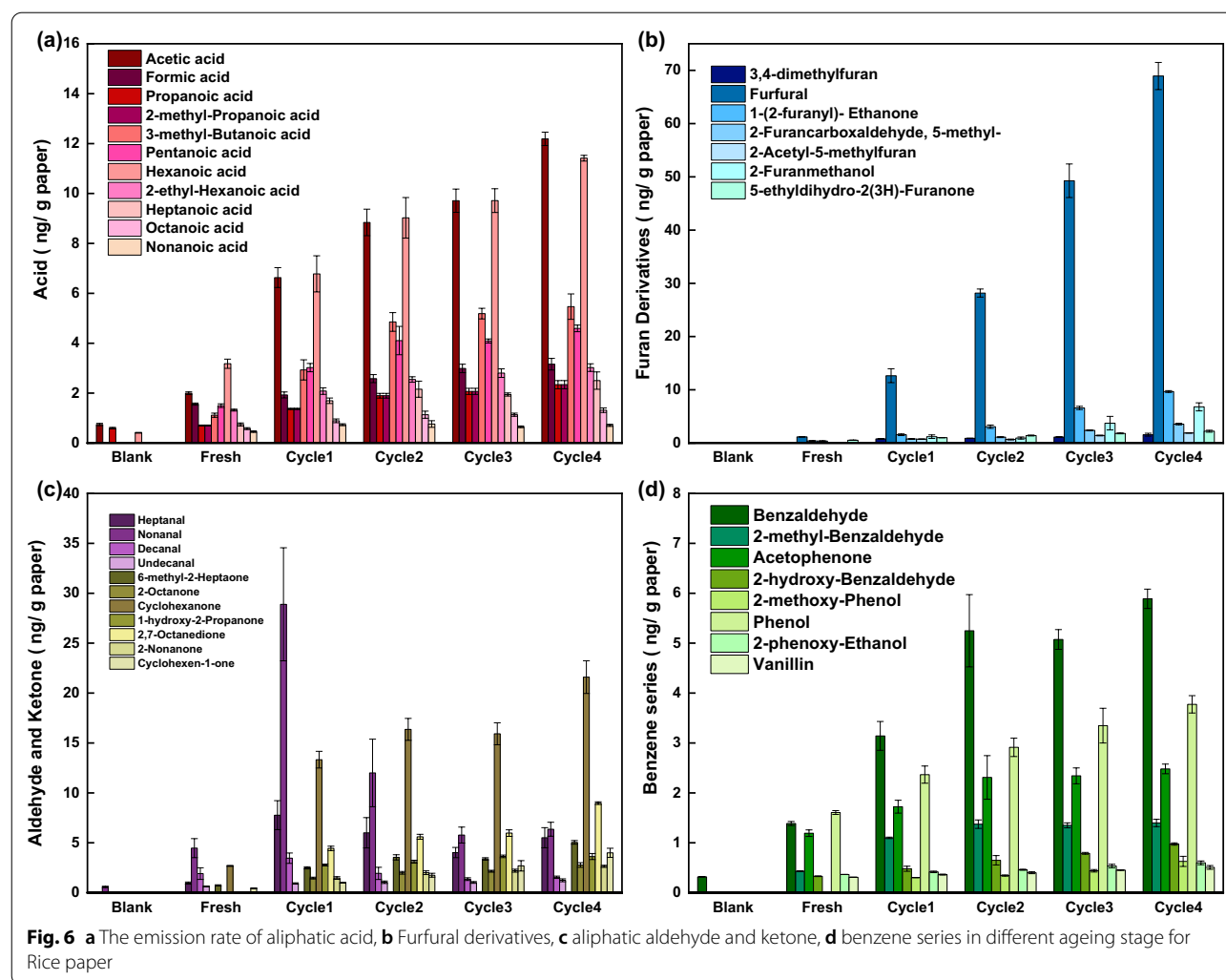


for the first cycle ageing, as the ageing proceeded the concentration of aliphatic aldehyde gradually reduced. However, the content of ketones showed distinct positive correlation with the degradation process. Rich benzene series compounds were found in Rice paper showing in Fig. 6d. The degradation of its glucoside was monitored by the emission of benzaldehyde and the emission rate is 5.9 ng/g at ageing cycle 4. In conclusion, the degradation markers for Rice paper are acetic acid, hexanoic acid, furfural and benzaldehyde.

In addition to the typical handmade paper, the ageing process of mechanical paper was also studied as the control experiment. Since modern and contemporary paper cultural relics were widely made from wood pulp, it is important to get to know the degradation of mechanical wood pulp paper. As shown in Fig. 7a, the amount of acetic acid, hexanoic acid observably increased with degree of ageing process and went up to 12.4 and 13.5 ng/g at Cycle 4, respectively. Concerning furfural Fig. 7b, it

maintained a stable rising tendency as expected. The concentration of furfural is 5.7 ng/g at cycle 4. In Fig. 7c, the content of aldehyde (C_8 , C_9) showed an increment in the first cycle then went through a decline in the further ageing stage. The content of ketones showed distinct positive correlation with the degradation process. As shown in Fig. 7d, various benzene series compounds were detected and their performance agrees with the degradation process, typically the emission rate of benzaldehyde was 3.6 ng/g at cycle 4. Therefore, the degradation markers for wood pulp paper are acetic acid, hexanoic acid, furfural and benzaldehyde.

By comparing the results above, the representative degradation compounds for 3 handmade papers and a mechanical paper were selected. The emission rate of these compounds at ageing Cycle 4 was listed in Table 5. The value provides semi-quantitative comparison for the releasing capacity of VOCs of the paper. The acid releasing capacities are similar to Mulberry, Bamboo, Rice



and Wood pulp paper ranging from 12.1 to 14.6 ng/g in terms of acetic acid and ranging from 11.4–15.1 ng/g in terms of hexanoic acid, which were generated by the spontaneous reactions with oxygen of aldehyde end-groups. The furfural releasing capacity is the key factor for evaluating the stability of the cellulose and hemicellulose. As shown in Table 5, the stability of paper in terms of furfural releasing capacity is Wood pulp paper > Bamboo paper > Mulberry paper > Rice paper. Benzaldehyde releasing capacity reflects the lignin degradation, which for Bamboo paper is highest (9.8 ng/g). It might be due to the high concentration of lignin in the *Phyllostachys pubescens* fibers [23].

Case study

Jiang Youzhu et al. seven digging mounted painting scroll is a traditional Chinese calligraphy and painting scroll from the Qing Dynasty (C.E 1636–1912) collected by the National Museum of China. The scroll was digging

mounted with paper and badly damaged with stains and cracks around the mounting materials. As shown in Fig. 8e, the scroll underwent several historical restorations and treatments. The head margin was repaired at least by three different materials, which are indicated by the number 1, 2, 3 in the Figs. 1 and 8e. Each of the repairing papers were stained with Graff “C” reagent to assess the presence of color and morphology of fiber. The representative images were shown in Fig. 8a–d. The repairing paper 1, 2 and 3 shows the features of bark fiber, since the fibers were wine red and cylindrically straight in shape. Besides, the paper 3 was mixed with bamboo fiber which showed the blue color after dyeing with tapering ends. The original paper of head margin was taken from location 4. As shown in Fig. 8d, the vessel members with pits were unique to bamboo fiber. Therefore, the base paper was bamboo paper and the repairing papers were bark papers. The SEM images of historical paper fibers were also shown in Additional file 1: Fig. S3. Sample

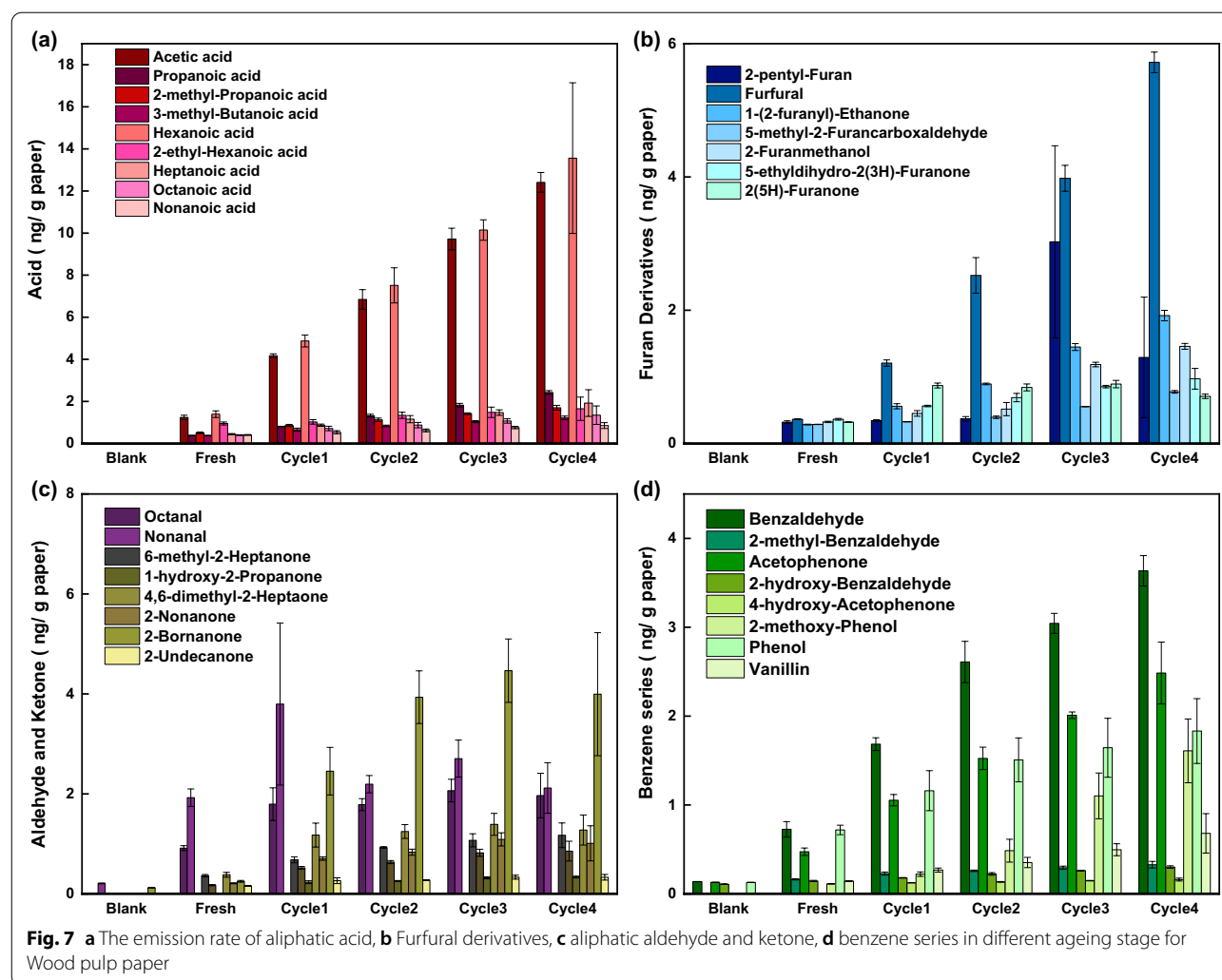


Table 5 The emission rate of representative compounds in the ageing Cycle 4 of different papers

ng/g	Acetic acid	Hexanoic acid	Furfural	Benzaldehyde
Mulberry	12.7	15.1	33.8	3.2
Bamboo	14.6	15.1	12.5	9.8
Rice	12.1	11.4	68.9	5.9
Wood pulp	12.4	13.5	5.7	3.6

1–4 was further taken to be evaluated by SPME-GC/MS. Even though the fibers were different among the samples, the TIC of profiles shows the same fingerprint peaks. The representative TIC profile is shown in Fig. 9.

As shown in Fig. 9, 55 compounds were screened out from the head margin paper of *Jiang Youzhu* et al. *seven digging mounted painting scroll*. These compounds comprise the aliphatic acid, aldehyde, alkane, benzene

series and terpenoid substances (Table 6). The aliphatic acid (C_2 – C_9), aldehyde (C_8 – C_{10}) and benzene series originated from the degradation of cellulose, hemicellulose, lipid and lignin. Even though, typical degradation marker such as furfural was not found in the TIC mode. However, by carefully checking with the EIC, the furfural was shown at $t_R = 6.73$ min and the qualitative ion $m/z = 95$ and $m/z = 96$ were obtained (Additional file 1: Fig. S5). In addition, Bornanone, endo-Borneol and Isosafrol were detected. These compounds are volatile constituents of the camphor tree and usually the raw material to produce the mothball. The mothball is widely applied in the storage room to keep moths and other insects away. Besides, the camphorwood furniture and storage rack were manipulated in the warehouse of the museum. Therefore, camphor related markers are highly likely originated from the mothball and the camphorwood shelf. Due to the high adsorption ability of the paper, the accumulation of VOCs might almost

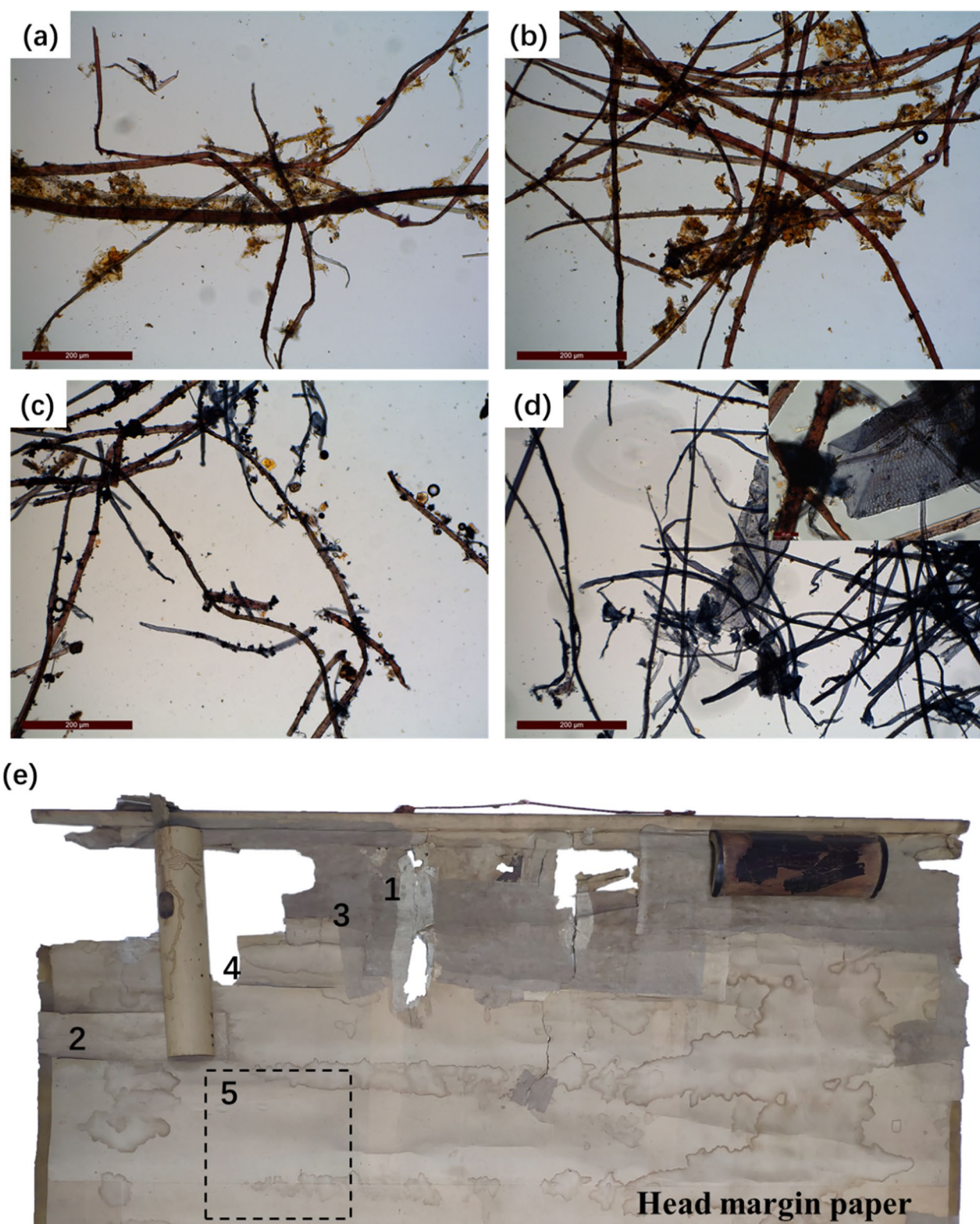


Fig. 8 The optical microscopy image of the paper fibers originated from “Jiang Youzhu et al. seven digging mounted painting scroll” (a), (b), (c), (d) for sampling location 1,2,3,4, respectively, e the photograph of sampling location of Head margin paper

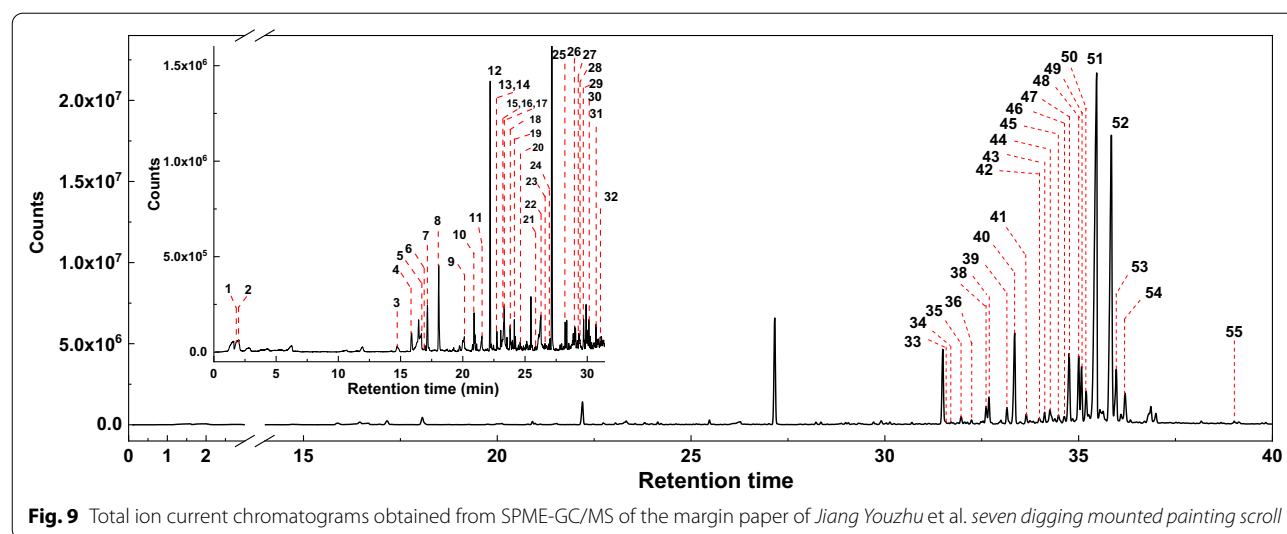


Table 6 The assignment of VOCs detected from head margin paper of Jiang Youzhu et al. *seven digging mounted painting scroll*

No	t _R	Assignment	Score	No	t _R	Assignment	Score
1	1.87	Acetic acid	96	29	29.71	Tetradecane	94
2	2.01	Methylal	96	30	30.13	Caryophyllene	83
3	14.70	Benzaldehyde	87	31	30.70	isolekene	93
4	15.87	Phenol	96	32	31.05	Humulene	79
5	16.68	Hexanoic acid	95	33	31.57	1-Dodecanol	95
6	16.96	Octanal	84	34	31.71	α-Curcumene	86
7	17.16	Benzene, 1,3-dichloro-	98	35	31.97	(+)-Valencene	97
8	18.07	1-Hexanol, 2-ethyl-	98	36	32.23	Pentadecane	96
9	20.13	Heptanoic acid	89	37	32.61	δ-Cadinene	92
10	20.91	Nonanal	99	38	32.69	trans-Calamenene	94
11	21.54	Hexanoic acid, 2-ethyl-	96	39	33.15	α-Calacorene	93
12	22.20	(+)-2-Bornanone	99	40	33.35	Elemol	98
13	22.73	Benzaldehyde, 3-ethyl-	98	41	33.65	β-Calacorene	88
14	22.76	endo-Borneol	82	42	33.98	Caryophyllenyl alcohol	86
15	23.28	Benzaldehyde, 4-ethyl-	85	43	34.12	Caryophyllene oxide	94
16	23.32	Octanoic acid	84	44	34.25	Gleenol	86
17	23.34	Naphthalene	90	45	34.48	Guaiaol	92
18	23.81	α-Terpineol	85	46	34.63	Hexadecane	95
19	24.22	Decanal	93	47	34.75	Cedrol	97
20	24.61	1,2-Benzisothiazole	88	48	35.00	α-Eudesmol	90
21	25.77	Ethanone, 1-(4-ethylphenyl)-	86	49	35.07	γ-Eudesmol	97
22	26.27	Nonanoic acid	93	50	35.19	Di-epi-1,10-cubenol	97
23	26.60	1,3-Benzodioxole, 5-(1-propenyl)-	88	51	35.46	Agarospinol	95
24	27.00	Tridecane	88	52	35.84	(+)-Valerianol	96
25	28.23	α-Cubebene	93	53	35.97	7-epi-α-Eudesmol	96
26	28.99	Copanen	87	54	36.19	Cadalene	97
27	29.32	(+)-Calarene	90	55	39.01	Octadecane	92
28	29.42	p-Anisaldehyde, 2-hydroxy-	88				

come from the environment. However, it is very hard to evaluate how long paper can hold onto past absorbed VOCs before releasing them. It is also worth noticing that at 27 to 39 min, in other words, between the n-alkane of C_{13} and C_{18} , abundant terpenoid substances are eluted, like α -cubebene, copanen, (+)-calarene, 2-hydroxy-p-anisaldehyde, caryophyllene, caryophyllenyl alcohol, agarospirol and so on. Among them, the agarospirol is a typical plant marker of the agarwood, and the other terpenoids were reported to be found in the VOCs constituents of the agarwood as well depending on its place of origin [39]. The Vietnam agarwood were obtained and the SPME–GC–MS result was collected to ensure the existence of agarospirol as shown in Additional file 1: Fig. S6. This result hints that the scroll somehow had a relationship with the agarwood. It might be from the raw material of paper or be contaminated from the storage environment. However, it needs further studies to clarify. In order to evaluate the releasing capacity of the degradation marker molecule, historical paper was processed with the ageing program the same as reference paper. At ageing cycle 4, compared to the fresh reference paper sample, the historical paper releases a large amount of degradation products. As shown in Table 7, at ageing cycle 4, the acid releasing capacities is 32.9 ng/g in terms of acetic acid and 43.7 ng/g in terms of hexanoic acid, which are around 2 and 3 times of the reference bamboo paper. The releasing capacity of furfural and benzaldehyde is 162.8 ng/g and 19.2 ng/g, which is 13 times and 2 times of the reference bamboo paper, respectively. Chain scission of cellulose, hemicellulose and lignin is a key step of paper degradation, which leads to producing various monosaccharide and benzene series [2]. These small molecule compounds are precursors to produce the VOCs, such as furan derives, short chain aliphatic acids. Since the historical paper experienced more than 100-year natural ageing, a large number of small molecules were accumulated, which are easier to be given off as VOCs products during the artificial ageing process. Meanwhile, consideration of brittle paper with low DP (degree of polymerization), more end-groups exposure and lead to the faster monomer generation. Therefore, due to its high releasing capacity of the degradation

markers, the historical paper is under a serious degradation situation.

Conclusions

Solid phase microextraction combined with gas chromatography-mass spectrometry (SPME–GC/MS) has been applied and proved to be useful to evaluate volatile organic components (VOCs) emitted from the Chinese traditional handmade papers. The artificial ageing processes were applied to 3 different handmade papers in addition to a mechanical paper as the control experiments. 87 compounds were identified using the Total Ion Current and attributed to originate from cellulose, hemicellulose, lignin, lipid, wax and plant markers. Compounds with 5 different functional groups (aliphatic acid, aldehyde, ketone, furan derivatives and benzene series) were evaluated semi-quantitatively during the aging process. It was found that the aldehydes are not accumulated as aging products of paper, which has not been demonstrated before. Further, VOCs were evaluated in historical paper from a traditional Chinese calligraphic and painting scroll, which was collected by the National Museum of China. A large number of terpenoids showed that the VOCs emitted from the paper not only originated from the paper itself but also could be generated from the substance absorbed on paper, which gives information about the historical storage environment. The artificial ageing process provided the releasing capacity of the degradation markers, which quantitatively illustrate the severe condition of the historical paper. Therefore, SPME–GC/MS provided a powerful tool for study of the VOCs of paper-based heritages and allowed the assessment of the degradation products, which is critical for the paper ageing evaluation and of great significance for contemporary conservation.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-021-00626-w>.

Additional file 1. Additional figures and tables.

Additional file 2. Original data of semi-quantifying VOCs from artificial ageing paper.

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Authors' contributions

L. Ding designed experiments, analyzed experimental data and was a major contributor in writing the manuscript. Q. Yang analyzed paper fibers via scanning electron microscope. Jh. Liu provided the reference paper samples. Zh. Lee provided the historical paper samples. All authors read and approved the final manuscript.

Table 7 The emission rate of representative compounds in the ageing Cycle 4 of historical paper

ng/g	Acetic acid	Hexanoic acid	Furfural	Benzaldehyde
Historical paper	32.9	43.7	162.8	19.2

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Availability of data and materials

Not applicable.

Declarations

Competing interests

No potential conflict of interest was reported by the author(s).

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