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Heritage Science

RESEARCH ARTICLE

Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions. Part I: laboratory and field measurements

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Abstract

The area-specific emission rates of formic acid and acetic acid from heritage objects made of wood and paper were quantified for normal indoor room conditions (23 °C, 50% RH) as well as for cooler (10 °C) and drier (20% RH) conditions. At normal indoor conditions, the emission rate of formic acid and acetic acid together were in the range of 10 to 300 μg m^{-2} h^{-1}. The emission rate decreased by a factor of 2–4 from wood and paper when lowering the temperature from 23 to 10 °C. The emission rate decreased by more than a factor of 2 when reducing the relative humidity (RH) from 50% to 20%. This corresponds well with field measurements in real storage rooms containing heritage collections. In addition, 36 volatile organic compounds (VOCs) were identified to be released by four paper samples. All the VOCs detected can in general originate from several sources. Therefore, these substances cannot be used as unique degradation markers for paper but rather as an indication of emission sources present in the indoor environment.

Keywords: Indoor air pollution, Volatile organic compounds, Emission rate, Relative humidity, Temperature, Active sampling, Passive sampling, Wood, Paper degradation

Introduction

The main part of heritage collections is in storage. In storage buildings, beside the emissions from building interiors and people's activities, the collections themselves can be a source of air pollution. Gibson et al. [1] detected toluene, furfural, benzaldehyde, ethylhexanol, nonanal and decanal as the most abundant volatile organic compounds (VOCs) emitted from degrading paper, in the air of archives, and by direct sampling from between the pages of individual books. Risholm-Sundman et al. [2] and Ramalho et al. [3] pointed to acetic acid as one of the most abundant substance off-gassing from wood and paper. Acetic acid is formed due to the elimination of acetyl groups in hemicellulose and the side chains of lignin in wood [4] and has been proposed as a potential marker for the decay of paper [5]. Other emission substances such as vanillin, responsible for the vanilla-like smell in paper and possibly formed due to oxidation of lignin [6], has likewise been proposed as a potential marker for the degradation paper [7].

Acetic acid and to some extent formic acid can accelerate alkali leaching and cause efflorescence on limestone and ceramics [8–12] and corrosion on copper alloys, cadmium, zinc, magnesium and in particular lead [12–14]. Formic acid is also known to accelerate the formation of crystalline corrosion products on historic glass surfaces [15]. Robinet et al. [15] measured a concentration of 614 μg m^{-3} acetic acid and 220 μg m^{-3} formic acid in

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indoor air in a room previously used to store glass objects showing signs of deterioration.

This study quantifies the emission rates of formic acid and acetic acid from selected heritage objects made of wood and paper under indoor room conditions (23 °C, 50% RH) as well as for cooler (10 °C) and drier (20% RH) conditions. The results are compared to field measurements performed in real storage buildings during summer and winter. Furthermore, it determines the composition of VOCs released from paper and compares it with the emission profiles published in other studies.

Laboratory measurements

Samples

The area-specific emission rates of formic acid and acetic acid were quantified for four naturally aged paper samples (samples no. 1–4) together with two naturally aged wood samples (samples no. 5–6) and a newly produced wood packaging (sample no. 7) used to transport and store heritage collections in storage buildings. As an example of a well-known highly emissive material, the acetic acid emission from a cellulose acetate photographic negative (sample no. 8) was measured as well (Table 1).

Method

Experimental set-up

Formic acid and acetic acid emissions from the four paper and three wood samples (sample no. 1–7) were measured in an emission test chamber of 48 L volume at standard conditions (23 ± 2 °C; 50 ± 5% RH) as well as at cooler (10 ± 2 °C; 50 ± 5% RH), and drier (23 ± 2 °C; 20 ± 5% RH) conditions. A temperature of 23 °C was used as reference temperature in the present study. It is given as standard atmosphere according to EN 16516 [16] and originally dates from ISO 554 [17]. The cooler conditions were set to 10 °C to imitate the climate conditions in a storage building with semi-passive climate control. To have 20% RH in storage buildings with heritage collections is extreme but possible in unconditioned rooms in winter. The RH was set to an unusually low value in this experiment to warrant a measurable difference in emission rate. The emission of acetic acid from cellulose acetate negatives (sample no. 8) was only measured at standard conditions (23 ± 2 °C; 50 ± 5% RH). Sample size, mass and loading factor (*surface area of the sample per chamber volume*) are given in Table 2. The air exchange rate in the chamber was set to 1 h^{-1}.

The concentration in the empty test chamber was measured before each test. A sample was then placed in the test chamber and conditioned for 24 h before sampling. After sampling the test sample was removed and the test chamber heated up for several hours before another sampling interval started.

Active air sampling and analysis

Formic acid and acetic acid were trapped on silica gel tubes at standard (23 ± 2 °C; 50 ± 5% RH) and cooler (10 ± 2 °C; 50 ± 5% RH) conditions. Chamber air was sampled at 500 mL min^{-1} using a calibrated pump. The

Table 2 Surface area, mass and loading factor of samples 1–8

Sample no.	Material	Surface area (m^2)	Mass (g)	Loading (m^2 m^{-3})
1	Paper	0.57	30.2	12
2	Paper	0.57	13.2	12
3	Paper	0.57	22.0	12
4	Paper	0.57	11.2	12
5	Wood	0.07	990.9	1.5
6	Wood	0.08	558.8	1.7
7	Wood	0.17	1372.3	3.5
8	Cellulose acetate	0.15	18.2	3.1

Table 1 Description of the eight samples

Sample no.	Material	Description	Year
1	Paper	Handmade cotton rag paper	1795–1809[a]
2	Paper	Groundwood-containing newspaper	1914
3	Paper	Groundwood-containing paper	1993
4	Paper	Recycled newspaper	2017
5	Wood	Freeze-dried archaeological wood treated with 35–40% polyethylene glycol (PEG) 2000[b]	Viking Age (10th century)
6	Wood	Hardwood from the handle of a shoemakers tool	19th century
7	Wood	New softwood packaging	New
8	Cellulose acetate	Photographic negative	Mid-20th century

[a] Sample no. 1 is dated based on watermark identification. [b] The archaeological wood was treated with PEG from October 2013 to July 2016 and then freeze-dried from August 2016 to January 2017

total sampling volume was 75 L. Sampling of formic acid and acetic acid at drier (23 ± 2 °C; 20 ± 5% RH) conditions was done by passing 75 L of air with a flow rate of 125 L min^{-1} through a liquid absorber (20 mL of 0.1 M sodium hydroxide). The concentration from both sampling media was quantified by ion chromatography (IC) analysis (Methrom 881 Compact IC Pro). After elution with sodium carbonate solution, the compounds were separated on an anion separation column (Metrosep A Supp 7) coupled with a conductivity detector. The method has a limit of quantitation (LOQ) of 5 µg m^{-3} for formic acid and acetic acid, respectively, and was performed according to VDI 4301-7 [18]. This method allows a much more precise determination of C1-C2 carboxylic acids in chamber air and indoor air in comparison to the use of Tenax TA® and subsequent analysis by TD-GC/MS [19].

The area-specific emission rate SER_a (*amount (µg) of formic acid and acetic acid off-gassing per surface area and per hour*) was calculated from the measured formic acid and acetic acid concentrations:

$$\text{SER}_\text{a} = \text{C}_\text{i} * \text{n}/\text{L}$$

where C_i is the chamber concentration of formic acid and acetic acid (µg m^{-3}), n is the air exchange rate (h^{-1}) and L is the loading factor of the material in the chamber ($\text{m}^2\ \text{m}^{-3}$) [20].

Air sampling of VOCs was done with stainless steel desorption tubes filled with Tenax TA® (60/80 mesh). Sampling was performed actively by drawing the air through the sorbent bed by use of a pump with a flow rate of 125 mL min^{-1}. The sampling volume was 4 L. After sampling, the tubes were analysed by a coupled gas chromatography (GC)/mass spectrometry (MS)-system (Agilent 7890B/5975C) after thermal desorption (Markes TD 100). The compounds were separated on a DB-5 MS column (60 m × 0.25 mm, 0.25 µm). Qualifying was based on PBM library search [21]. Mass spectra and retention data were furthermore compared with those of reference compounds [22]. All identified substances were quantified using their own response factors. The areas of unidentified peaks were converted to concentrations using the toluene response factor. The linear regression model was used for calibration [23]. The described method has a LOQ of approximately 1 µg m^{-3} and was performed in accordance with DIN ISO 16000-6 [24].

Field measurements

Storage sites

The concentrations of formic acid and acetic acid were measured outside and inside two existing storage buildings with heritage collections. Storage I belongs to the Royal Library in Denmark (room volume: 600 m^3) and contains a 15th to 17th century book collection. The building is from 2008 and uses mechanical ventilation with air filtration. Storage II is part of the shared storage facility at the Centre for Preservation of Cultural Heritage in Vejle, Denmark. The building is from 2013 and contains one room with a paper-based archival collection (room volume: 3200 m^3) and another with museum objects made of mixed materials (room volume: 4800 m^3). Storage II uses semi-passive climate control with no heating and periodic dehumidification.

Method

The concentrations of formic acid and acetic acid were measured outside in nearby weather stations, and inside the two storage buildings in open room air with passive diffusion samplers placed in duplicates. Passive diffusion samplers have previously been used in museum environments to measure the concentrations of formic acid and acetic acid in air [25, 26]. The samplers collect the air pollutant on an adsorbent media placed inside a tube or badge. The concentration of air pollution is then determined from analysis of the mass collected in the sorbent media taking the diffusion velocity into account [25, 26]. As mentioned by Gibson et al. [1] events as the opening and closing of doors when staff enter the storage rooms could interfere with the measurements. In the present study the monitoring periods were 3 weeks each. During that time the stores were unoccupied except for a few, short visits by staff, which only lasted for a minor fraction of the total time. The interference by this was considered to be negligible. Measurements were conducted in February and again in August 2018. From previous years, these 2 months were known to represent the coolest and warmest periods inside the stores. The samplers were supplied and analysed by The Swedish Environmental Research Institute IVL. The limit of detection (LOD) is about 1.5 µg m^{-3} and the LOQ is 4 µg m^{-3} for formic acid and acetic acid respectively.

The concentration of an indoor generated air pollutant can be perceived as a proxy for the rate at which it is emitted to the room. Other factors as the loss of pollutants due to ventilation and deposition onto surfaces will also have an impact on the concentration in indoor air. The deposition onto interior surfaces is referred to as the surface removal rate (expressed as an air exchange rate) [27]. Emission tests are conducted in inert test chambers with a minimal uptake onto interior surfaces. In contrast, pollutant uptake by interior surfaces and collection objects in storage rooms might have a significant impact on the concentration of indoor air pollution. Especially in stores with a low air exchange rate. It can be difficult to calculate the exact emission rate due to the unknown magnitude between the air exchange rate and surface removal rate. The concentration of indoor air pollution still reflects however the level of emission rate.

The temperature and RH were measured using Tiny-Tag View 2 sensors (Gemini Dataloggers, UK), having an accuracy of ± 0.4 °C and ± 3% RH.

Results and discussion

Quantification of formic acid and acetic acid emissions under indoor room conditions (emission chamber tests)

The area-specific emission rates of formic acid and acetic acid from sample no. 1–7 are shown in Fig. 1 (the exact values are also tabulated as Additional file 1). The area-specific emission rates from the three wood samples ranged from archaeological wood with an emission rate of 145 µg m^{-2} h^{-1} up to newly produced softwood packaging with an emission rate of 303 µg m^{-2} h^{-1} at 23 °C and 50% RH. The emission rates from the four paper samples ranged from 10 to 33 µg m^{-2} h^{-1} at 23 °C and 50% RH.

The area-specific emission rates of formic acid and acetic acid from the three naturally aged wood samples measured in this study are in line with the results from other studies such as Risholm-Sundman et al. [2]. Risholm-Sundman et al. [2] quantified the area-specific emission rate of various VOCs including acetic acid from nine wood species used in parquet floor production. The wood samples were felled 0.5 to 1.5 year before the test. The emission rate spanned from birch emitting 10 µg m^{-2} h^{-1} to oak emitting 2800 µg m^{-2} h^{-1}.

A few authors have measured the emission rate from paper. Ramalho et al. [3] measured a mass-specific emission rate SER_m (*mass emitted per gram material, per hour)* of acetic acid from paper at indoor conditions after accelerated ageing. The mass-specific emission rate was 887 ng g^{-1} h^{-1} from a cotton rag paper and 4820 ng g^{-1} h^{-1} from a paper made of ground-wood pulp. Smedemark and Ryhl-Svendsen [28] measured the mass-specific emission rates of formic acid and acetic acid from four paper samples from the late 19th to the 20th century at indoor conditions. The emission rate in their study ranged from 45 ng g^{-1} h^{-1} from a book printed in 1864 up to 468 ng g^{-1} h^{-1} from a newspaper printed in 1946. The mass-specific emission rate from the four paper samples in our study were up to three times higher but still overlapping in range with the values reported by Smedemark and Ryhl-Svendsen [28]. The mass-specific emission rate of formic acid and acetic acid together ranged from 262 ng g^{-1} h^{-1} from the book printed in 1993 (sample no. 3) up to 1692 ng g^{-1} h^{-1} from the newspaper printed in 2017 (sample no. 4).

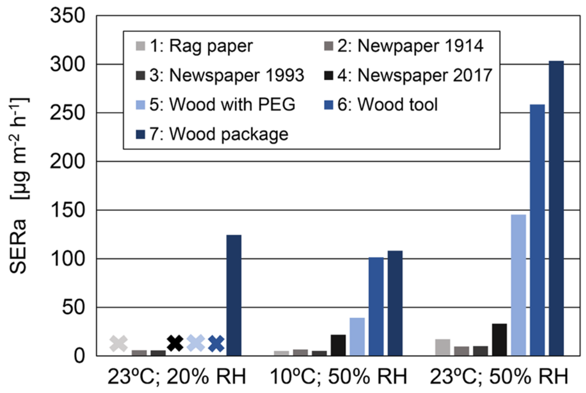

Fig. 1 Area-specific emission rates of formic acid and acetic acid at 20% RH and constant temperature (23 ± 2 °C) as well as at 10 and 23 °C with constant RH (50 ± 5% RH). The cross indicates measurements that are below the LOQ of 5 µg m^{-3}

Avoiding emissive construction materials and building interiors is used as an air pollution control strategy in order to reduce the concentrations of formic acid and acetic acid in storage buildings with heritage collections [29, 30 chapter 4]. The high emission rates of corrosive formic acid and acetic acid from newly produced softwood packaging quantified in our study could be used as an argument for selecting non-emissive transport and storage materials for the long-term storage of sensitive materials.

Another solution to reduce the concentrations of formic acid and acetic acid in air is to separate materials based on the source strength. The area-specific emission rate of formic acid and acetic acid together from the cellulose acetate negative (sample no. 8) was 3185 µg m^{-2} h^{-1} at 23 °C and 50% RH. Our measurements thus showed that the emission rate from cellulose acetate negatives was 10 times larger than the emission rate from the softwood packaging sample (no. 7) and more than 100 times larger than the emission from paper (sample no. 1–4). Cellulose acetate is therefore often stored in a separate area to avoid the deposition of acetic acid off-gassing from cellulose acetate onto other materials.

The impact of temperature and RH on the emission of formic acid and acetic acid

The emission rate of VOCs depend on temperature and an increase in temperature will often lead to an increase in the emission rate [31–33]. The area-specific emission rates of formic acid and acetic acid from all investigated samples (no. 1–7) depend on temperature. The emission rates from the four paper samples ranged from 5 to 22 µg m^{-2} h^{-1} and the emission rates from the three wood samples from 39 to 108 µg m^{-2} h^{-1} at 10 °C and 50% RH. The largest emission source remained the newly produced softwood packaging. Lowering the temperature from 23 to 10 °C thus reduced the emission rates of formic acid and acetic acid by a factor of 2–4 from the paper and wood samples. The measurements are in accordance with a study by Smedemark and Ryhl-Svendsen [28] showing that lowering the temperature from 22 to 10 °C gave rise to a decrease in the emission of formic acid and acetic acid by a factor of 2 from a book printed in 1864 and up to a factor of 16 for a highly emissive newspaper printed in 1946. Gibson and Watt [12] also showed that an increase in temperature from 20 to 45 °C increased the emission of acetic acid from wood by a factor of 7 to 11.

The emission rate will also depend on the RH [31, 32]. Reducing the RH from 50% to 20% reduced the emission rate to below 6 µg m^{-2} h^{-1} from all samples, except the softwood packaging. The emission rate from the softwood packaging was 124 µg m^{-2} h^{-1} at 23 °C and 20% RH. A decrease in RH from 50% to 20% thus lowered the emission of formic acid and acetic acid from all samples (no. 1–7) by a factor of 2 or more. A study by Gibson and Watt [12] have previously shown that increasing the RH from 54% to 100% increases the emission of acetic acid from hardwood by a factor of 2 to 3, while softwood is less affected.

Formic acid and acetic acid concentrations in storage buildings

Table 3 shows the concentration of organic acids (sum of formic acid and acetic acid) outdoor and inside Storage I and the two rooms in Storage II in winter and summer. The concentration outdoor was below the LOQ in winter and summer. The concentrations of formic acid and acetic acid were larger inside the storage buildings than outdoor. It is assumed that the heritage collections as well as paper and wood packaging materials are themselves internal sources that contribute to the concentrations of formic acid and acetic acid inside the storage buildings, as the storage rooms contain non-emissive construction materials and building interior such as concrete and metal that would not contribute significantly to its concentrations.

Table 3 Concentration of organic acids (sum of formic acid and acetic acid) in one storage building with mechanical ventilation (I), two rooms in another storage building with semi-passive climate control (II) and outdoor

Concentration (µg m^{-3})				
Season	**Storage I**	**Storage II –archival collections**	**Storage II –mixed materials**	**Outdoor**
Winter	7 (6 °C)	3 (9 °C)	28 (9 °C)	< LOQ
Summer	15 (14 °C)	9 (17 °C)	97 (15 °C)	< LOQ

The measurements were conducted in winter and summer. In parentheses the temperature is given for each occasion (monthly average), except for outdoors

The increase in temperature from winter to summer within each storage room is also shown in Table 3. In Storage I with mechanical ventilation the concentrations of formic acid and acetic acid increased by a factor of 2 from winter to summer whereas in Storage II with semi-passive climate control the concentrations increased by a factor of 3 in both rooms. Within the same period the temperature increased 7 ℃–8 ℃ whereas RH variations remained within the uncertainty of the sensor (± 3% RH). A study by Krupinska et al. [26] showed a similar trend where the concentrations of formic acid and acetic acid increased 5–6 times from winter to summer, and Smedemark and Ryhl-Svendsen [28] showed an 3–8 times increase in the concentrations of formic acid and acetic acid with a 7 °C increase in temperature from winter to summer within three storage buildings with archival and library collections in Denmark. Our study demonstrated how the emission rates of formic acid and acetic acid as well as its concentration in air inside real storage buildings with heritage collections depend on the temperature. The emission rate will also depend on other factors such as the difference in vapour pressure between the material surface and the surrounding air [34]. However, as the observed concentration in air never became extremely high we regard this of little influence on the emission rate. As mentioned above disturbance from people or air-handling equipment may also influence concentration levels, however, due to little operation time within these large storage rooms this was estimated to be of little impact.

VOC emissions from paper

Table 4 shows 36 VOCs detected as emissions during chamber tests from the four paper samples (no. 1–4). The recycled newspaper printed in 2017 emitted the largest number of VOCs. Almost all VOCs detected from the paper samples was measured in trace concentrations which was specified to below 10 µg m^{-3} in this specific experimental setup (shown in italic in Table 4). The area-specific emission rate (µg m^{-2} h^{-1}) for each compound has additionally been added. Identified substances released by the four paper samples detected in chamber air correspond with the VOC profile from paper made of rag and ground-wood pulp found in previous studies [1, 3, 6, 7, 35–39]. Compounds as toluene, ethylhexanol, nonanal and decanal were detected as emission substances from all four samples. Gibson et al. [1] detected the same compounds as emission substances from books.

Table 4 VOCs detected in chamber air from the four paper samples at 23 °C and 50% RH

Sample no.	1	2	3	4	References
C13 (Tridecane)				*0.1*	[7, 36, 39]
C14 (Tetradecane)				*0.3*	[6, 39]
C15 (Pentadecane)				*0.3*	[7, 36, 39]
C16 (Hexadecane)				*0.4*	[7, 36, 39]
C17 (Heptadecane)				*0.7*	[39]
C18 (Octadecane)				*0.2*	[7, 36, 39]
Benzaldehyde	*0.2*	*0.2*	*0.2*	*0.3*	[1, 6, 7, 36, 40]
Pentanal				*0.7*	[6, 37, 41]
n-Hexanal				***3.0***	[6, 37–41]
n-Heptanal				*0.3*	[6, 7, 36, 39, 40]
Octanal	*0.2*			*0.3*	[36]
n-Nonanal	*0.3*	*0.3*	*0.3*	*0.5*	[1, 6, 7, 36, 39, 40]
n-Decanal	*0.2*	*0.2*	*0.*	*0.2*	[1, 6, 7, 36]
Furfural		*0.1*	*0.1*		[1, 3, 6, 7, 41, 42]
2-ethyl-1-hexanol	*0.3*	*0.2*	*0.2*	*0.2*	[1, 6, 7, 36, 38, 39]
n-propanol				0.1	
1,2-Propanediol	***2.0***				
n-Butanol	*0.2*				[6, 39]
n-Pentanol				*0.5*	
Toluene	*0.1*	*0.1*	*0.1*	*0.1*	[1, 6, 7, 36, 37, 39–41]
Phenol		*0.1*			[6, 7, 36, 39]
Formic acid	***5.5***	***3.1***	***2.1***	***1.4***	[5, 41, 43]
Acetic acid	***11.9***	***6.7***	***8.0***	***31.7***	[1, 3, 5–7, 28–43]
Propanoic acid	*0.4*			*0.7*	[3, 6, 40]
Butanoic acid	*0.2*			***1.6***	[3, 6, 7, 36]
Pentanoic acid	0.3				[3, 6, 7, 35, 36]
Hexanoic acid	***0.8***	*0.2*	*0.3*	***0.8***	[3, 6, 7, 35, 36]
Acetone		*0.3*	*0.3*	*0.3*	[3, 6, 7, 35–37]
2,6-Diisopropylnaphthalene		*0.1*			
2,6-Di(tert-butyl)-1,4-benzoquinone				*0.2*	
Benzothiazole	*0.2*	*0.1*	*0.2*		
N,N-Dibutylformamide			*0.1*	*0.1*	
Vanillin		*0.2*			[3, 5–7, 35, 36]
Hexamethylcyclotrisiloxane			*0.1*		

The emphasis indicates the presence of the specific compound (italic indicates trace concentrations and bold italic concentrations above 10 µg m^{-3}). The area-specific emission rate (µg m^{-2} h^{-1}) for each compound has additionally been added. In addition, the right column contains references to other studies detecting the same VOC off-gassing from paper

Acetic acid was the most abundant compound detected in the emission profile from all paper samples and has also previously been detected as an emission substances from paper in several studies [3, 5–7, 36–39, 41–43]. All the 36 VOCs detected in chamber air can, however, arise from several sources present in nearly all indoor environments as constructions materials and building interior. Acetic acid can, among other things, arise from sources as fibreboards, particle boards, medium-density fibre boards, wood coatings, adhesives, paints and varnishes [44–47]. Emission substances such as acetic acid can therefore not be used as a unique marker for the degradation of paper but rather as an indication of emission sources present in the indoor environment.

Conclusion

The area-specific emission rates of formic acid and acetic acid from wood and paper ranged from 10 to 300 µg m^{-2} h^{-1} at normal indoor room conditions. A decrease in temperature from 23 to 10 °C reduced the emission rate 2–4 times from wood and paper whereas a decrease in the RH from 50% to 20% reduced the emission rate by a factor of 2 or more. The decrease in the emissions of formic acid and acetic acid from wood and paper with a decrease in temperature corresponds well with the reduction in concentration of formic acid and acetic acid in air from summer to winter in real storage rooms with heritage collections.

Furthermore, 36 VOCs were detected as emission substances from paper. Analysis of the VOC profiles from the four paper samples showed that acetic acid is the most abundant compound detected from all paper samples. All identified compounds can however, arise from multiple sources in the indoor environment making it difficult to use them as a unique marker for the degradation of paper.

Our study quantified the formic acid and acetic acid emission from eight wood and paper samples at normal indoor room conditions. Based on the results the area-specific emission rates from the samples were calculated. The measurements showed that lowering the temperature and RH will reduce the emission rates of formic acid and acetic acid. The results will be used in Part II of this study to model how air pollution control strategies such as temperature and the air exchange rate will impact on the concentrations of formic acid and acetic acid in a model storage room with heritage collections [48].

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s40494-020-00404-0.

Additional file 1: Laboratory measurements.

Abbreviations

RH: Relative humidity; VOC: Volatile organic compounds; IC: Ion chromatography; LOQ: Limit of quantitation; SERa: Area-specific emission rate; TD: Thermal desorption; GC: Gas chromatography; MS: Mass spectrometry; PEG: Polyethylene glycol; LOD: Limit of detection; SER_m: Mass-specific emission rate.

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Authors' contributions

SHS performed the laboratory work. All authors contributed to the data analysis and the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated during this study are included in this published article and its Additional file 1.

Competing interests

The authors declare that they have no competing interests.

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References

1. Gibson LT, Ewlad-Ahmed A, Knight B, Horie V, Mitchell G, Robertson CJ. Measurement of volatile organic compounds emitted in libraries and archives: an inferential indicator of paper decay? Chem Cent J. 2012;6:42–42.
2. Risholm-Sundman M, Lundgren M, Vestin E, Herder P. Emissions of acetic acid and other volatile organic compounds from different species of solid wood. Eur J Wood Wood Prod. 1998;56:125–9.
3. Ramalho O, Dupont A-L, Egasse C, Lattuati-Derieux A. Emission rates of volatile organic compounds from paper. ePRESERVATIONScience. 2009;6:53–9.
4. Fengel D, Wegener G. Wood. Berlin: Walter de Gruyter; 1989.
5. Dupont A-L, Egasse C, Morin 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. Carbohyd Polym. 2007;68:1–16.
6. Clark AJ, Calvillo JL, Roosa MS, Green DB, Ganske JA. Degradation product emission from historic and modern books by headspace SPME/GC-MS: evaluation of lipid oxidation and cellulose hydrolysis. Anal Bioanal Chem. 2011;399:3589–600.
7. Lattuati-Derieux A, Bonnassies-Termes S, Lavédrine B. Identification of volatile organic compounds emitted by a naturally aged book using solid-phase microextraction/gas chromatography/mass spectrometry. J Chromatogr A. 2004;1026:9–18.
8. Grzywacz CM, Tennent NH. Pollution monitoring in storage and display cabinets: carbonyl pollutant levels in relation to artifact deterioration. Stud Conserv. 1994;39:164–70.
9. Chiavari C, Martini C, Prandstraller D, Niklasson A, Johansson L-G, Svensson J-E, Åslund A, Bergsten CJ. Atmospheric corrosion of historical organ pipes: the influence of environment and materials. Corros Sci. 2008;50:2444–55.
10. Halsberghe L, Erhardt D, Gibson LT, Zehnder K. Simple methods for the identification of acetate salts on museum objects. In ICOM-CC 14th Triennial Conference Preprints, Hague, 12–16 September 2005; 2. pp. 39–647.
11. Robinet L, Coupry C, Eremin K, Hall C. The use of Raman spectrometry to predict the stability of historic glasses. J Raman Spectrosc. 2006;37:789–97.
12. Gibson L, Watt C. Acetic and formic acids emitted from wood samples and their effect on selected materials in museum environments. Corros Sci. 2010;52:172–8.
13. Thickett D, Odlyha M. Note on the identification of an unusual pale blue corrosion product from Egyptian copper alloy artifacts. Stud Conserv. 2000;45:63–7.
14. Tétreault J, Cano E, Van Bommel M, Scott D, Dennis M, Barthés-Labrousse M-G, Minel L, Robbiola L. Corrosion of copper and lead by formaldehyde, formic and acetic acid vapours. Stud Conserv. 2003;48:237–50.
15. Robinet L, Eremin K, Cobo Del Arco B, Gibson LT. A Raman spectroscopic study of pollution-induced glass deterioration. J Raman Spectrosc. 2004;35:662–70.
16. European Standard EN 16516. Construction products: assessment of release of dangerous substances—determination of emissions into indoor air. Berlin: Beuth Verlag; 2017.
17. International Standard ISO 554. Standard atmospheres for conditioning and/or testing. Specifications. Berlin: Beuth Verlag; 1976.
18. VDI-Richtlinie 4301 Blatt 7. Messen von Innenraumluftverunreinigungen—Messen von Carbonsäuren. Berlin: Beuth Verlag; 2018.

19. Schieweck A, Gunschera J, Varol D, Salthammer T. Analytical procedure for the determination of very volatile organic compounds (C3-C6) in indoor air. Anal Bioanal Chem. 2018;410:3171–83.
20. Salthammer T. Environmental test chambers and cells. In: Salthammer T, Uhde E (Ed.), Organic indoor air pollutants. WILEY-VCH, Weinheim, 2nd completely revised edition; 2009. pp. 101–115.
21. McLafferty FW, Turecek F. Interpretation of mass spectra. Mill Valley: University Science Books; 1993.
22. Hübschmann H-J. Handbook of GC-MS. 3rd ed. Weinheim: Wiley-VCH; 2015.
23. Massold E, Bähr C, Salthammer T, Brown SK. Determination of VOC and TVOC in air using thermal desorption GC-MS—practical implications for test chamber experiments. Chromatographia. 2005;62:75–85.
24. International standard ISO 16000-6:2011. Indoor air—part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FIDpart. 2011. pp. 1–10.
25. Ferm M, Karlsson A, Galle B. A multi-component diffusive sampler for acidic gases. Diffusive monitoring. 2002; 13.
26. Krupinska B, Van Grieken R, De Wael K. Air quality monitoring in a museum for preventive conservation: results of a three-year study in the Plantin-Moretus Museum in Antwerp, Belgium. Microchem J. 2013;110:350–60.
27. Sparks LE, Tichenor BA, Chang J, Guo Z. Gas-phase mass transfer model for predicting volatile organic compound (VOC) emission rates from indoor pollutant sources. Indoor Air. 1996;6:31–40.
28. Smedemark SH, Ryhl-Svendsen M. The contribution of formic and acetic acid from paper to indoor air pollution in archives and its dependence on temperature. Journal of Paper Conservation. Submitted 2019.
29. Schieweck A, Salthammer T. Schadstoffe in Museen. Stuttgart: Bibliotheken und Archiven. Fraunhofer IRB Verlag; 2014.
30. Tétreault J. Airborne pollutants in museums, galleries, and archives: risk assessment, control strategies, and preservation management. Canada: Canadian Conservation Institute; 2003.
31. Wolkoff P. Impact of air velocity, temperature, humidity, and air on long-term VOC emissions from building products. Atmos Environ. 1998;32:2659–68.
32. Qifan W, Jun S, Yang Z, Wanjun L. Influence of environmental factors on volatile organic compound emissions from plywood tested by a rapid detection method. Forest Prod J. 2017;67:120–5.
33. Wal JF, Hoogeveen AW, Wouda P. The influence of temperature on the emission of volatile organic compounds from pvc flooring, carpet, and paint. Indoor Air. 1997;7:215–21.
34. Myers GE. Effect on ventilation rate and board loading on formaldehyde concentration: a critical review of the literature. Forest Prod J. 1984;34(10):59–68.
35. Steckel V, Knoepfle A, Ohlmeyer M. Effects of climatic test parameters on acetic acid emission from beech (*Fagus sylvatica* L.). Holzforschung. 2013;67:47–51.
36. 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.
37. Lattuati-Derieux A, Ramalho O, Egasse C, Thao-Heu S, Dupont A-L. Evaluation of solid-phase microextraction on fiber derivatization for the analysis of paper degradation compounds. ePRESERVATIONScience. 2015;12:38–49.
38. Hrivňák J, Tölgyessy P, Figedyová S, Katuščák S. Solid-phase microcolumn extraction and gas chromatography–mass spectrometry identification of volatile organic compounds emitted by paper. Talanta. 2009;80:400–2.
39. Strlič M, Thomas J, Trafela T, Csefalvayova L, Cigic IK, Kolar J, Cassar M. Material degradomics: on the smell of old books. Anal Chem. 2009;81:8617–22.
40. Gaspar EM, Santana JC, Lopes JF, Diniz MB. Volatile organic compounds in paper—an approach for identification of markers in aged books. Anal Bioanal Chem. 2010;397:369–80.
41. Strlič M, Cigić IK, Možir A, De Bruin G, Kolar J, Cassar M. The effect of volatile organic compounds and hypoxia on paper degradation. Polym Degrad Stab. 2011;96:608–15.
42. Bembibre C, Strlič M. Smell of heritage: a framework for the identification, analysis and archival of historic odours. Herit Sci. 2017;5:1–11.
43. Pedersoli JL, Ligterink FJ, Van Bommel M. Non-destructive determination of acetic acid and furfural in books by Solid-Phase Micro-extraction (SPME) and Gas Chromatography-Mass Spectrometry (GC/MS). Restaurator. 2011;32:110–34.
44. Shahani CJ, Harrison G. Spontaneous formation of acids in the natural aging of paper. Stud Conserv. 2002;47:189–92.
45. Schieweck A, Salthammer T. Emission from construction and decoration materials for museum showcases. Stud Conserv. 2009;54:218–35.
46. Schieweck A, Salthammer T. Indoor air quality in passive-type museum showcases. J Cult Hert. 2011;12:205–13.
47. He Z, Zhang Y, Wei W. Formaldehyde and VOC emissions at different manufacturing stages of wood-based panels. Build Environ. 2011;47:197–204.
48. Smedemark S.H, Ryhl-Svendsen M. Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions—part II a model study. To be submitted 2020.

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