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Trouble in Storage?

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Publication date:
2020

Document Version:
Publisher's PDF, also known as Version of record

[Link to publication](#)

Citation for pulished version (APA):
Hjerrild Smedemark, S. (2020). *Trouble in Storage? Understanding the dynamics of airborne organic acids in storage buildings and its consequences for the air quality, energy use, and preservation of heritage collections.* The Royal Danish Academy of Fine Arts, Schools of Architecture, Design and Conservation.

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Trouble in Storage?

Understanding the dynamics of airborne organic acids in storage buildings and its consequences for the air quality, energy use, and preservation of heritage collections

Ph.D. Thesis 2020

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Trouble in Storage?

Understanding the dynamics of airborne organic acids in storage buildings and its consequences for the air quality, energy use, and preservation of heritage collections

Ph.D. Thesis 2020

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Thesis for the degree of Doctor of Philosophy in Conservation-Restoration

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February 28th 2020

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Printed in Denmark by PrininfoDenmark A/S, February 2020.

Preface

This Ph.D. thesis assembles the results from a three-year interdisciplinary Ph.D. project between the Royal Danish Academy of Fine Arts Schools of Architecture, Design and Conservation (KADK), School of Conservation and the Technical University of Denmark (DTU), Department of Civil Engineering. The project was funded by the Independent Research Fund Denmark (DFR-6121-00003).

The project was conducted between March 2017 and February 2020 under supervision from Associate Professor Morten Ryhl-Svendsen (KADK) and co-supervision from Professor Jørn Toftum (DTU).

Outline of the dissertation

This Ph.D. thesis is based on one review paper, five research journal papers and two conference proceeding papers. The thesis contains an introduction to the development and principles for semi-passive climate control of storage buildings (Chapter 1), which together with Paper I provides state-of-the-arts. The research questions, methodology, and significance are presented in Chapter 2. The methodology consists of three parts. Part I measures the area-specific emission rates of formic acid and acetic acid from heritage collections under normal indoor room conditions in a laboratory. Part II includes field measurements in one storage building with a heating, ventilation and air-conditioning (HVAC) system, and one with semi-passive climate control. Part III examines the removal efficiency of two commercially available activated carbon filters, a desiccant silica gel rotor as well as passive adsorption onto a clay brick wall. Chapter 3 describes the two storage buildings examined in Part II.

The results from the laboratory and field measurements in Part I-III are summarized in Chapter 4. All data is collated into a Monte Carlo simulation in Chapter 5. The simulation examines the concentrations of formic acid and acetic acid in indoor air, and determine the fraction of organic acids that is removed through active air filtration and the fraction that deposit back onto interior surfaces. Chapter 6 contains a discussion of the methods used to control organic acids in storage buildings and their energy use. Finally the thesis ends with a conclusion in Chapter 7.

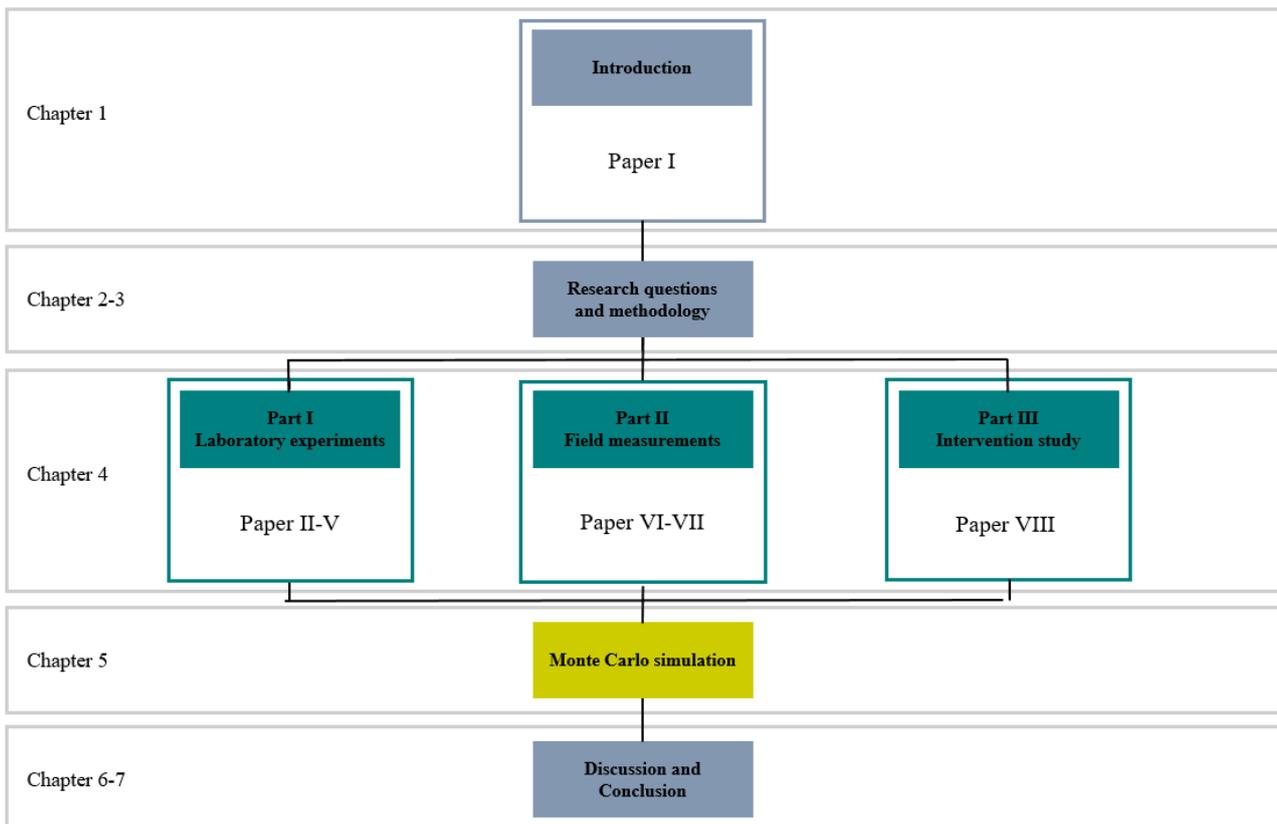


Figure 1. Graphical outline of the thesis.

Summary

Formic acid and acetic acid are among the most critical indoor air pollutants known to cause damage to heritage collections. This Ph.D. project examined the route of organic acids in storage buildings from emission sources, such as the collections themselves, to the removal through air exchange with ambient, air filtration in mechanical ventilation systems, and deposition onto interior surfaces. The aim was to establish the fate of formic acid and acetic acid in storage buildings and to determine control methods for the protection of heritage collections from corrosive organic acids.

The area-specific emission rates of formic acid and acetic acid from six naturally aged wood and paper samples and from a wood packaging material used to transport and storage collections were measured at laboratory conditions. The emission rate ranged from 10 to 300 $\mu\text{g m}^{-2} \text{h}^{-1}$ at indoor room conditions (23°C, 50% RH). The study also demonstrated that a decrease in temperature from normal room conditions to 10°C reduced the emission rate of organic acids 2-4 times from wood and paper, whereas a decrease in the RH from 50% to 20% reduced the emission rate with a factor 2 or more. A similar organic acid behaviour was observed in unoccupied storage buildings where the decrease in temperature from summer to winter led to a reduction in the concentration of organic acids in air.

The spatial distribution in temperature, moisture and organic acids were measured in one storage building belonging to the Royal Library in Denmark (with a mechanical ventilation system), and in two rooms in the shared storage facility at the Centre for Preservation of Cultural Heritage in Vejle (with semi-passive climate control). The spatial temperature and moisture distribution were almost uniform except for a weak vertical temperature gradient causing a RH gradient opposite to that of temperature. The spatial organic acid distribution showed areas in the storage building with semi-passive climate control where incomplete mixing caused a local accumulation of organic acids. However, the survey demonstrated that both storage buildings provided acceptable temperature and moisture distributions without problematic microclimates, and with an acceptable air quality performance irrespective of the ventilation form.

An intervention study was additionally carried out in the two buildings, in order to measure the removal efficiency of two commercially available activated carbon filters *in situ*. The organic acid removal efficiency of a desiccant silica gel rotor used for dehumidification, and the passive adsorption onto a clay brick wall, were also measured. The intervention study demonstrated that the organic acid removal efficiency of the filters depend on the airflow through the filter and that the performance varies considerably *in situ* from the removal efficiency obtained in a laboratory. The desiccant silica gel rotor efficiently removed 98-100% acetic acid from the air while the clay brick wall reduced the concentration of acetic acid close to the wall with 56%.

The storage buildings examined in this project maintained almost the same temperature and RH conditions indoor however, the store with a mechanical ventilation system consumed almost 60 times more energy for outdoor air filtration and climate control than the store with semi-passive climate control. The results underlined that storage buildings with semi-passive climate control provide acceptable climate and air quality conditions and reduces the energy use for the preservation of collections in storage.

All data was collated into a Monte Carlo simulation to examine the fate of organic acids in heritage collection storage buildings. The simulations showed that formic acid and acetic acid would deposit onto interior surfaces despite the use of active air filtration, and with the continued risk of causing damage to heritage collections.

Dansk resumé

Organiske syrer i museumsmagasiner og deres konsekvens for luftkvalitet, energiforbrug og bevaringen af vore kulturarvssamlinger

De organiske forbindelser, myresyre og eddikesyre, er blandt de mest skadelige luftforureningsstoffer indendørs i forhold til nedbrydningen af vore kulturarvssamlinger. Dette ph.d.-projekt har undersøgt tilstedeværelsen og fordelingen af organiske syrer i indeklimaet i magasinbygninger til opbevaring af kulturarv, fra kilde til bortfjernelse. Selve samlingerne, samt træholdigt pakkemateriale og inventar, kan være en væsentlig kilde til luftforureningen indendørs. Bortfjernelse sker igennem luftsiftet, luftfiltrering i mekaniske ventilationsanlæg samt ved deponering på indvendige overflader. Målet med ph.d.-projektet var at kortlægge forureningsstoffernes rute, for at kunne udpege de mest effektive kontrolmetoder til beskyttelse af vore kulturarvssamlinger mod nedbrydning.

Afgasningsraten af myresyre og eddikesyre fra seks naturligt ældede træ- og papirprøver, og fra træemballagen, der anvendes til transport og opbevaring af genstande på magasinernes kompaktreoler, blev målt i et laboratorium. Emissionsraten varierede fra 10 til 300 $\mu\text{g m}^{-2} \text{h}^{-1}$ under normale indendørs klimaforhold (23°C, 50% RF). Undersøgelsen viste desuden, at et fald i temperatur fra normale indendørs klimaforhold til 10°C formindsker emissionsraten af organiske syrer 2-4 gange, mens et fald i den relative luftfugtighed fra 50% RF til 20% RF formindsker emissionsraten 2 gange eller mere. Den samme tendens blev observeret i magasinbygninger uden komfortopvarmning, hvor en sænkning i temperaturen fra sommer til vinter medførte et 2-3 gange fald i koncentrationen af organiske syrer i luften.

Den rumlige fordeling og variation i temperatur, luftfugtighed og koncentration af organiske syrer blev målt detaljeret over et år for magasinrum beliggende i to forskellige magasinbygninger. Det ene magasin tilhører Det Kongelige Bibliotek (styret med et mekanisk ventilationsanlæg), mens det andet magasin tilhører Center for Bevaring af Kulturarv i Vejle (semi-passiv klimastyret). I magasinet i Vejle blev to magasinrum undersøgt. Den rummæssige temperatur- og fugtfordeling var næsten ensartet i de to bygninger, bortset fra en svag lodret temperaturgradient, der forårsager en omvendt gradient i relativ luftfugtighed. Den rumlige fordeling af organiske syrer viste en uensartet luftopblending i det ene rum i bygningen med semi-passiv klimakontrol. Dette gav anledning til luftlommer med lokale ophobninger af organiske syrer. På trods af dette viste undersøgelsen, at uanset ventilationsform, opretholder begge bygninger en acceptabel temperatur- og fugtfordeling uden problematisk mikroklima, og med en acceptabel luftkvalitet.

Effektiviteten af luftrensning med kulfiltrering blev afprøvet i et interventionsstudie *in situ* i begge bygninger. To forskellige kulfilter-typer blev testet. Desuden blev en silica-gel adsorptionsaffugters evne til at fjerne eddikesyre fra luften afprøvet i laboratoriet, og passiv luftrensning ved adsorption på en lervæg blev afprøvet i et testrum. Interventionsstudiet viste, at effektiviteten af filtrene afhænger af luftstrømningshastigheden gennem filteret, og at den varierer betydeligt *in situ* fra effektiviteten målt under kontrollerede laboratorieforhold. Affugteren kunne fjerne stort næsten alt (98-100%) eddikesyre fra luften, mens lervæggen reducerede luftens koncentration af eddikesyre med 56% i umiddelbar nærhed af vægoverfladen.

De klimamæssige forhold var næsten ens i de to magasinbygninger undersøgt i dette projekt. Energiforbruget var til gengæld næsten 60 gange større i bygningen med et mekanisk ventilationsanlæg, til udendørsluftfiltrering og klimastyring, end i bygningen med semi-passive klimakontrol. Resultaterne

understreger at bygninger med semi-passiv klimastyring sikrer acceptable klima- og luftkvalitetsforhold og et lavere energiforbrug til bevaringen af kulturarvssamlinger.

Alt data fra projektet blev samlet i en Monte Carlo simulering for at analysere og illustrere variationen i koncentrationen af organiske syrer i indeklimaet i kulturarvsmagasinbygninger. Simuleringerne viste, at myresyre og eddikesyre deponeres på indvendige overflader trods brugen af aktiv luftfiltrering, hvilket medfører en forsat risiko for at forårsage skade på kulturarvssamlinger.

Acknowledgement

I am extremely grateful to the Independent Research Fund Denmark who financially supported this project and the Kalmer foundation for supporting a three-month research stay at Fraunhofer WKI in Braunschweig, Germany.

Firstly, I wish to express my deep gratitude to my Ph.D. supervisor Morten Ryhl-Svendsen from the School of Conservation at KADK and co-supervisor Jørn Toftum from the Department of Civil Engineering at DTU. Thank you for introducing me to this unique interdisciplinary research field and for sharing your knowledge and contacts. I am very grateful for your advice and feedback throughout the project. My warmest thanks also goes to Charles J. Weschler for invaluable discussions and ideas.

The first part of the laboratory tests were carried out at Fraunhofer WKI, Department of Material Analysis and Indoor Chemistry in Germany where I spend my research stay in the autumn 2017. I wish to thank especially Tunga Salthammer and Alexandra Schieweck for giving me this opportunity, as well as the laboratory staff for their help and for making me feel welcome. The second part of the laboratory tests were carried out at the National Museum of Denmark, Department for Environmental Archaeology and Material Science. I am very grateful for the assistance given by especially Martin Mortensen and Janne Winsløw.

The field measurements were carried out at the Royal Library of Denmark and the Centre for Preservation of Cultural Heritage in Vejle, Denmark. I wish to acknowledge the staff in both places for their help especially Birgit Vinther Hansen, Tine Rauff, and Niels Danielsen at the Royal Library, and Knud Lund Mortensen at the Centre for Preservation of Cultural Heritage in Vejle.

Special thanks goes to my colleagues and my fellow Ph.D. students Camilla Jul Bastholm, Kathrine Segel, Louise Maria Husby, Mette Midtgård Madsen, and Tine Louise Slotsgaard from KADK, and Maria Bivolarova from DTU.

I am extremely grateful for the Revit and Illustrator assistance given by Søren and Marie Hjerrild Smedemark.

List of papers

Paper I: Smedemark, S.H. 2018, 'The dynamics and control of indoor air pollution in repositories without mechanical ventilation for cultural heritage collections. A literature review', *ePRESERVATIONScience*, **15**, 17-28.

Paper II: Smedemark, S.H. and 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* (accepted 18.09.2019).

Paper III: Smedemark, S.H., Ryhl-Svendsen, M. and Schieweck, A. 'Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions – Part I: laboratory and field measurements', *Heritage Science* (submitted 21.01.2020).

Paper IV: Smedemark, S.H. and Ryhl-Svendsen, M. 'Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions – Part II: a model study', *Journal of Cultural Heritage* (submitted 27.01.2020).

Paper V: Smedemark, S.H., Ryhl-Svendsen, M. and Schieweck, A. 2018, 'The effect of temperature on emissions of carboxylic acids in passive climate controlled repositories with cultural heritage collections'. In Proceedings from the *15th Conference of the International Society of Indoor Air Quality & Climate (Indoor Air 2018)*, 22-27 July 2018, Philadelphia, USA.

Paper VI: Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J. 'Distribution of temperature, moisture and organic acids in storage facilities with heritage collections', *Building and Environment* (submitted 12.12.2019).

Paper VII: Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J. 'Comparing the air quality performance in unoccupied storage buildings with mechanical ventilation and semi-passive climate control'. In Proceedings from the *19th International Council of Museums - Committee for Conservation (ICOM-CC) Triennial Conference*, 14-18 September 2020, Beijing, China (submitted 15.11.2019).

Paper VIII: Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J. 'Removal of organic acids from indoor air in museum storage rooms by active and passive sorption techniques', *Studies in Conservation* (submitted 29.01.2020).

In addition, part of the work has been presented at international conferences:

Poster I: Smedemark, S.H. and Ryhl-Svendsen, M. 2018, ‘An examination of the emission of carboxylic acid from cultural heritage collections dependence on temperature – can a decrease in temperature reduce the demand for air filtration?’, at the *4th International Conference on Science and Engineering in Arts, Heritage and Archaeology (SEAHA)*, 4-6 June 2018, London, UK.

Presentation I: Smedemark, S.H. and Ryhl-Svendsen, M. 2017, ‘Presentation of the Ph.D. project: Trouble in store? Understanding the dynamics of air pollution and its consequences for the conservation of cultural heritage collections’, at the *9th Nordic Conservation Ph.D. Student Colloquium*, 10 November 2017, Oslo, Norway.

Presentation II: Smedemark, S.H., Ryhl-Svendsen, M. and Schieweck, A. 2018, ‘The effect of temperature on emissions of carboxylic acids in passive climate controlled repositories with cultural heritage collections’, at the *15th Conference of the International Society of Indoor Air Quality & Climate (Indoor Air 2018)*, 22-27 July 2018, Philadelphia, USA.

Presentation III: Smedemark, S.H. and Ryhl-Svendsen, M. 2018, ‘Trouble in store? Presentation of a Ph.D. project examining the dynamics of air pollution in repositories with cultural heritage collections and its consequences for air filtration’, at the *13th International Conference on Indoor Air Quality in Museums and Archives*, 10-12 October 2018 Krakow, Poland.

Presentation IV: Smedemark, S.H. and Ryhl-Svendsen, M. 2019, ‘Presentation of the Ph.D. project: Trouble in store? Understanding the dynamics of air pollution and its consequences for the conservation of cultural heritage collections – final stage’, at the *10th Nordic Conservation Ph.D. Student Colloquium*, 21-21 November 2019, Copenhagen, Denmark.

Upcoming conferences:

Presentation V: Smedemark, S.H. and Ryhl-Svendsen, M. 2020, ‘Adsorption of formic acid and acetic acid onto paper and books’, at the *14th International Conference on Indoor Air Quality in Heritage and Historic Environments (IAQ)*, 30 March – 1 April 2020, Antwerp, Belgium.

Presentation VI: Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J. 2020, ‘Comparing the air quality performance in unoccupied storage buildings with mechanical ventilation and semi-passive climate control’, at the *19th The International Council of Museums - Committee for Conservation (ICOM-CC) Triennial Conference*, 14-18 September 2020, Beijing, China.

Abbreviations

ASHRAE: American Society of Heating, Refrigeration, and Air-Conditioning Engineers

BMS: building management system

CADR: clean air delivery rate

CFD: computational fluid dynamics

DTU: The Technical University of Denmark

GC: gas chromatography

HVAC: heating, ventilation, and air-conditioning system

IC: ion chromatography

IIC: International Institute for Conservation

ICOM-CC: International Council of Museums - Committee for Conservation

IMPACT: innovative modelling of museum pollution and conservation threshold model

KADK: The Royal Danish Academy of Fine Arts School of Architecture, Design and Conservation

LOAD: lowest-observed adverse effect level

LOD: limit of detection

LOQ: limit of quantification

MS: mass spectrometry

NOAL: no-observed adverse effect level

PAN: peroxyacetyl nitrate

PEG: polyethylene glycol

PFT: perfluorocarbon tracer gas

POC: photocatalytic oxidation air purifier

RH: relative humidity

RNG: renormalization group theory model

TD: thermal desorption

TVOC: total volatile organic compounds

UN: United Nations

UNESCO: United Nations Educational, Scientific and Cultural Organization

VOC: volatile organic compounds

Nomenclature

A: surface area of a material (m^2)

CADR: clean air delivery rate ($\text{m}^3 \text{h}^{-1}$)

$C_{\text{downstream}}$: concentration of air pollution in the airstream after an air cleaning device ($\mu\text{g m}^{-3}$)

C_i : concentration of air pollution indoor at steady-state ($\mu\text{g m}^{-3}$) or (ppb)

C_{upstream} : concentration of air pollution in the airstream before an air cleaning device ($\mu\text{g m}^{-3}$)

D: diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)

dc: fraction of air pollution that is removed in a desiccant silica gel rotor (-)

E: energy use ($\text{kWh m}^{-3} \text{year}^{-1}$)

F: flux, the deposition rate of air pollution on a surface ($v_d C$)

fc: fraction of air pollution that is removed using active air filtration (-)

G: generation rate of pollutant ($\mu\text{g h}^{-1}$)

L: loading ($\text{m}^2 \text{m}^{-3}$)

m: mass (g)

Mw: molar weight (g mol^{-1})

n: air exchange rate (h^{-1})

$n_{\text{recirculation}}$: internal recirculation (h^{-1})

η : removal efficiency (%)

p: pressure (Pa)

Q: heat loss (kWh)

q_v : airflow ($\text{m}^3 \text{h}^{-1}$)

S: surface removal rate (h^{-1})

SER_a : area-specific emission rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)

SER_m : mass-specific emission rate ($\text{ng g}^{-1} \text{h}^{-1}$)

T: temperature ($^{\circ}\text{C}$)

t: time (h)

τ : mean age of air (h)

U-value: thermal transmittance ($\text{W m}^{-2} \text{K}^{-1}$)

V: volume of air (m^3)

v_d : deposition velocity (m h^{-1})

v: air velocity (m s^{-1})

Terminology

Absolute humidity: the amount of water per cubic metre of air (g m^{-3}).

Adsorbent: material used to remove air pollution e.g. activated carbon.

Adsorption: a surface-based process where compounds from the air physically adhere to the surface of a material.

Active air filtration: passing the air actively through air-filters to remove particles and gases using a fan.

Active sampling: passing the air actively at a specified airflow rate through an adsorbent media using a calibrated pump.

Age of air: the mean age of air is a measure of the average time air spent inside an enclosure.

Air-conditioning: the use of heating, cooling, humidification and/or dehumidification to control the indoor climate conditions.

Air exchange rate: a measure of the rate at which air in an enclosure is replaced with ambient air.

Air pollution: a contaminant causing damage to cultural heritage materials.

Area-specific emission rate: the emission rate per surface area per hour.

Buf (B): the buffer capacity of a material defined as the quantity of water vapour exchange. It can be expressed, as the volume of storage space that will experience the same change in RH with the change in amount of water vapour.

Building envelope: the physical outer construction of a building that separates the conditioned inside air from the outside environment.

Building Management System (BMS): computer-based control system that controls and monitors the buildings' mechanical and electrical equipment such as ventilation, lighting, power systems, fire systems and security systems.

Chemical adsorption: an irreversible chemical reaction between an air pollutant and the surface of an adsorbent material.

Clean air delivery rate (CADR): a measure which combines the removal efficiency with the airflow rate through the filter ($\text{m}^3 \text{h}^{-1}$).

Concentration: the mass or volume of a substance divided by the total volume of air, expressed as either ppb (parts-per-billion) or $\mu\text{g m}^{-3}$. The equation $[\text{ppb}] = ([\mu\text{g m}^{-3}] * 24.04)/M_w$ is used to convert between the units at room temperature, where M_w is the molar weight of the pollutant.

Cool conditions – used in here as a synonym for 10°C and 50% RH.

Dead-spaces: areas with air stratification in a room that can lead to an accumulation in the concentration of indoor air pollution.

Deposition velocity: the flux of pollutant to a surface divided by its concentration in air.

Desorption: the opposite process of adsorption where adsorbed compounds are released to the air.

Dosimeter: a material that deteriorate in a way similar to objects found within the collections.

Dry conditions: used in here as a synonym for 23°C and 20% RH.

Emission rate: the release of air pollution from a material.

Enclosure: a separate defined entity e.g. display case, room or a building.

Exfiltration: airflow out of a building through unintentional openings in the building envelope.

Exposure: the time a cultural heritage object is exposed to air pollution multiplied by the concentration of pollution.

Flux: the deposition rate of air pollution on a surface.

Hygroscopic materials: materials that adsorbs and desorbs moisture with changes in the RH of the surrounding environment.

Indoor air: air inside a building or room.

Indoor atmospheric corrosivity: the ability of the atmosphere to cause corrosion.

Indoor air pollution: pollutants generated from sources inside a building.

Infiltration: unintentional airflow into a building through openings in the building envelope.

Loading factor: the ratio between the surface area of interior surfaces including the cultural heritage collection and the volume of the enclosure.

Mass-specific emission rate: amount emitted per mass per hour.

Mean age of air: see age of air.

Mechanical ventilation: ventilation driven by a fan, e.g. in a HVAC system.

Microclimate: climate in one area that differs from the surrounding climate.

Moisture buffer capacity: the materials ability to moderate RH variations.

Monte Carlo simulation: a simulation used to obtain numerical results from a model with random variables.

Natural ventilation: airflow through intentional ventilation openings in the building envelope.

Normal indoor room conditions: used in here as a synonym for 23°C and 50% RH.

Off-gassing: see emission rate.

Operational threshold: the concentration where the degradation due to other mechanisms become more significant than the deterioration due to air pollution.

Organic acids: sum of formic acid and acetic acid.

Outdoor air pollution: pollutants generated outside the building.

Passive climate control: using the properties of the building structure and fabric to control the climate conditions and air quality.

Passive sampling: the air pollution is adsorbed passively through diffusion onto an adsorbent media placed in a tube or a badge.

Physical adsorption: the process where molecules in air adhere to the surface of an adsorbent material by reversible weak Van der Waals forces.

Relative humidity (RH): the ratio between the partial water vapour pressure in air and the water vapour pressure at saturation given as a percentage.

Removal efficiency: the difference between the concentration of air pollution before and after an air cleaning device given as a percentage.

Removal mechanisms: mechanisms as active air filtration, the air exchange rate and the surface removal rate that removes air pollution from the indoor environment.

Repository: storage building with heritage collections.

Residence time: the theoretical time a pollutant in air is in contact with the adsorbent medium while the air flows through an air-filter.

Semi-passive climate control: a building that uses the principles of passive climate control (see definition above) with some mechanical ventilation e.g. dehumidification.

Sink-effect: the adsorption of air pollution onto interior surfaces in a building.

Sorbent: see adsorbent.

Stack effect: airflow in an enclosure caused by vertical temperature differences.

Steady-state concentration: the equilibrium concentration between the generation rate and removal rate of pollution in air.

Surface removal rate: a measure of the rate of adsorption of air pollutants on a surface. The surface removal rate is defined as the deposition velocity multiplied by the surface-to-volume ratio of the enclosure.

Surface-specific emission rate: see area-specific emission rate.

Total volatile organic compounds (TVOC): sum of volatile organic compounds.

Ventilation: intentional process of supplying or removing air to or from a building.

Ventilation effectiveness: the ventilation systems ability to remove air pollution from the indoor environment.

Very volatile organic compound (VVOC): organic compound whose boiling point is the range from $<0^{\circ}\text{C}$ to $50\text{-}100^{\circ}\text{C}$. This classification system has been defined by the World Health Organization (WHO, 1989).

Volatile organic compound (VOC): organic compound whose boiling point is in the range from $50\text{-}100^{\circ}\text{C}$ to $240\text{-}260^{\circ}\text{C}$. This classification system has been defined by the World Health Organization (WHO, 1989).

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1. Introduction

Heritage institutions are responsible for collecting tangible and intangible evidence of cultural, religious, and historical importance. The evidence is considered essential to the understanding and appreciation of our diverse culture and history in a time with *'fake news'*, it serves as an undisputable testimony of our common past and an invaluable source for future research. Heritage institutions are additionally responsible and often legally mandated to make collections accessible to the public and pass it on to future generations. At the United Nations Educational, Scientific and Cultural Organization's (UNESCO) general conference in 1972 a convention concerning the protection of tangible cultural and natural heritage was adopted: *'Considering that deterioration or disappearance of any item of the cultural or natural heritage constitute a harmful impoverishment of the heritage of all the nations in the world'* (UNESCO, 1972).

The main part of heritage collections about 90 – 95% are in storage (Ryhl-Svendsen, 2007a) and the preservation of collections therefore largely depends on the climate and air quality conditions in storage buildings. Johnson and Horgan wrote already in 1979 that *'probably more harm has been done to museum collections through improper storage than by any other means'*. A report on the preservation conditions in heritage institutions in Denmark from 2003 continues to cite inadequate storage conditions as one of the primary reasons for the degradation of collections (KUM, 2003).

1.1 The development of semi-passive climate control

Until recently, the dogma has been to use the *'best available technology'* to maintain constant climate conditions to improve the preservation of collections. The development of HVAC systems made it possible to set increasingly strict specifications for allowable fluctuations in climate conditions leading to an accompanying increase in energy use (Padfield, 2013).

The challenge to preserve heritage collections is to control climate conditions and air quality in storage buildings while at the same time reducing the energy use for a sustainable future. A declaration by the International Institute for Conservation (IIC) and the International Council of Museums - Committee for Conservation (ICOM-CC) published in 2014 states that: *'Museums and collecting institutions should seek to reduce their carbon footprint and environmental impact to mitigate climate change, by reducing their energy use and examining alternative renewable energy sources'*. The United Nations (UN) defines a sustainable development as one that meets the needs of the present without compromising the ability of future generations to meet their own needs (UN, 2015).

A blueprint was signed in 2015 by 193 heads of state in the UN to address global challenges and transform our world for a better and more sustainable future. The blueprint contains a goal to *"strengthen efforts to protect and safeguard the world's cultural and natural heritage"* (UN, 2015, Goal 11.4). UN's framework furthermore strives to create affordable and clean energy as well as reduce climate change due to human activities (UN, 2015, Goal 7 and 13).

Energy use is a dominant contributor to global climate change and accounts for about 60% of the total greenhouse gas emissions (UN, 2015, Goal 7). It is therefore essential to reduce the energy use for a sustainable future. The declaration from IIC and ICOM-CC (2014) also states that: *'Care of collections should be achieved in a way that does not assume air conditioning (HVAC)'* and *'passive methods, simple technology that is easy*

to maintain, air circulation and lower energy solutions should be considered'. The new guidelines from the American Society of Heating, Refrigeration and Air-Conditioning Engineers' (ASHRAE) for museums, libraries and archives additionally advocates for strategies and solutions that preserve heritage collections in an economic, social and environmentally sustainable way (ASHRAE, 2019).

The shift from 'best available technology' towards more sustainable collection management include the development of unoccupied storage buildings with semi-passive climate control. A storage with semi-passive climate control consumes 2% of the energy use in a storage with a HVAC system. Furthermore, the 2% can be delivered from green energy sources making the building almost CO₂ neutral (Christensen *et al.*, 2016; Ankersmit and Stappers, 2017).

Large investments are now being made in heritage institutions to improve the preservation conditions in storage buildings and reduce the energy use. Examples of major storage buildings under construction in Denmark include the shared storage facility between the National Museum and the Royal Library (Figure 2) and the shared storage facility between local museums in Sønderjylland (Figure 3).



Figure 2. Sketch of the new storage facility using semi-passive climate control belonging to the National Museum and the Royal Library of Denmark. (© Drawing by Gottlieb Paludan Architects from <https://www.gottliebpaludan.com>).



Figure 3. Sketch of the new storage facility using semi-passive climate control belonging to Museum Sønderjylland. (© Visualisation by Friis & Moltke Architects and BASE Erhverv from <https://www.faod.dk/friis-moltke-vinder-konkurrencen-om-magasinbygning/>).

1.2 The concept of semi-passive climate control

The concept of passive climate control is to build an airtight hygrothermal inert building envelope on an un-insulated concrete floor. The building envelope will even out daily fluctuations in the outside climate. The un-insulated concrete floor will act as a heating surface in winter and a cooling surface in summer (Christensen *et al.*, 2016, Padfield *et al.*, 2018). As the storage is unoccupied, no heating to comply with human comfort requirements is needed. Simulations using COMSOL Multiphysics® modelling software have shown that the temperature in a storage building with passive climate control changes slowly from 7°C in winter up to 15°C in summer in a temperate climate as Northern Europe (Figure 4) (Padfield, 2013). Smedemark *et al.* (2019a) measured a temperature from 7°C in winter up to 19°C in summer in a storage building with passive climate control in Denmark.

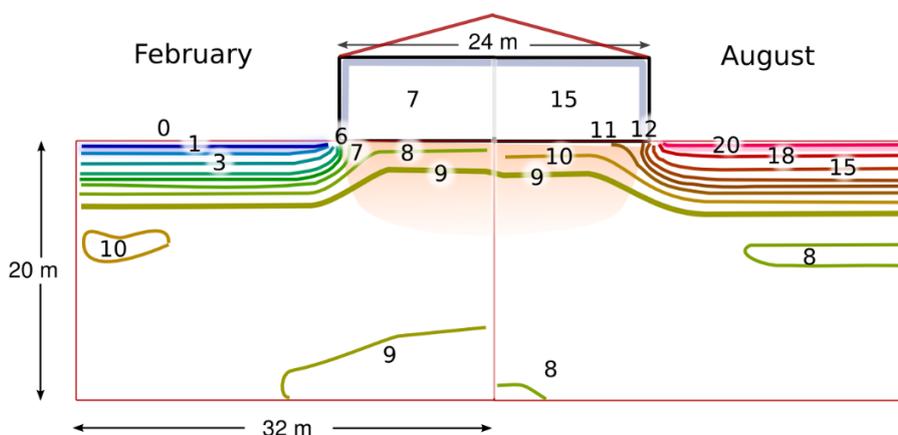


Figure 4. Computer simulation of the temperature in a storage building with passive climate control during winter and summer in a temperate climate as in Northern Europe. (Reproduced with permission by T. Padfield (2013) based on a simulation by Bøhm and Ryhl-Svendsen (2011) using the COMSOL Multiphysics® Modelling Software).

The most prominent source of water vapour in storage buildings with passive climate control is infiltration from outside (Janssen and Christensen, 2013). Water vapour will infiltrate the building envelope, particularly in summer where the outside temperature is higher than inside, producing an excess of water. A reduction in the air exchange rate will evidently reduce the need for dehumidification. Building Simulation (BSim) computer modelling by Janssen and Christensen (2013) showed that periodic dehumidification is necessary to maintain an acceptable relative humidity (RH) about 50% within a storage building with passive climate control (*semi-passive climate control*). Smedemark *et al.* (2019a) measured an average RH about 37% in a room with a paper-based archival collection in a store with semi-passive climate control and mechanical dehumidification in Denmark. The set point conditions for the dehumidification system was 40% RH.

Hygroscopic materials as construction materials, building interior and the collections themselves have a considerable potential to buffer the RH in indoor air (Padfield and Larsen, 2004). The moisture buffer capacity is the materials ability to moderate RH variations (Rode *et al.*, 2007). The buffer capacity (*buf*) can be expressed, as the volume of storage space that will experience the same change in RH with the change in amount of water vapour (Padfield and Jensen, 2010). Padfield and Jensen (2010) evaluated the buffer capacity of construction materials as cellular concrete, wood and unfired clay brick. Unfired perforated clay brick had the best buffer capacity with 27 cubic meter per square meter of material surface.

The collections themselves can also buffer the RH in the indoor environment. A full storage with paper collections will have a buf around 200 cubic meter of space per square meter of material surface (Ryhl-Svendsen *et al.*, 2011). Kupczak *et al.* (2017) converted the three-dimensional adsorption and desorption of moisture in paper and wood into a one-dimensional transfer with COMSOL Multiphysics® modelling software and used WUFI® Plus software to model the climate and energy use in a storage building. The model showed that the buffer capacity of a paper collection will reduce the energy use for humidification and dehumidification by 38% compared to an empty storage.

1.3 The concern with semi-passive climate control

A widespread concern in connection with the application of semi-passive climate control is that the airtight building envelope in combination with emissive collections stored densely packed on movable shelves can lead to thermal stratification and a local accumulation in indoor air pollution. Figure 5 show general museum collections stored densely packed on movable shelves in a large storage room at the shared storage facility with semi-passive climate control at the Centre for Preservation of Cultural Heritage in Vejle, Denmark.



Figure 5. A storage room with semi-passive climate control at the shared storage facility at the Centre for Preservation of Cultural Heritage in Vejle, Denmark. The store contains general museum collections stored closely packed on movable shelves with a large amount of collection materials in a small space.

Christoffersen (1995) recommends to maintain an air exchange rate below 0.1 h^{-1} to provide stable climate conditions in unoccupied stores with semi-passive climate control. The air exchange rate with ambient have been measured in several storage buildings with semi-passive climate control in Denmark and typically range from 0.05 down to 0.01 h^{-1} (Ryhl-Svendsen *et al.*, 2014; Smedemark *et al.*, 2019a).

Formic acid and acetic acid are among the most critical indoor air pollutants known to cause damage to sensitive materials in heritage collections (Brimblecombe and Grossi, 2012). The concentrations of formic acid and acetic acid have previously been measured in one or a few locations within storage buildings however, the spatial distribution in temperature, moisture and organic acids remains unknown. It is therefore crucial to establish the air distribution in storage buildings with semi-passive climate control in order to assess the preservation conditions and determine the necessary control methods to preserve heritage collections.

Paper I in this thesis provides a thorough literature review with state-of-the-arts on the dynamics and control of indoor air pollution in non-mechanical ventilated storage buildings (Smedemark, 2018).

2. Project summery

2.1 The problem

Active air filtration in ventilation systems is commonly used to remove air pollution inside buildings. Research on the formic acid and acetic acid removal efficiency of active air filtration *in situ* in storage buildings with heritage collections is however scarce. On the one hand it is clear that active air filtration can remove a large fraction of formic acid and acetic acid from the indoor air. The deposition which also occurs onto interior surfaces as construction materials, building interior, and the collections themselves can however, not be overlooked. The uncertainty in whether formic acid and acetic acid are removed through active air filtration or deposition onto interior surfaces has implication for the installation cost, operational cost and energy use for HVAC systems in storage buildings. More importantly it has direct implications for the preservation of heritage collections in storage.

It is crucial to determine the fate of formic acid and acetic acid in storage buildings with heritage collections in order to be able to select the most effective control methods that provide acceptable climate and air quality conditions for the preservation of collections in storage buildings without excessive energy use.

2.2 Hypothesis

The hypothesis for this Ph.D. project is that active air filtration only removes a fraction of the formic acid and acetic acid from indoor air while a fraction will deposit back onto interior surfaces.

2.3 Research aim and questions

The overall aim of this Ph.D. project is to understand the route of organic acids in storage buildings from emission sources, such as the collections themselves, to removal through air exchange with ambient, active air filtration and deposition onto interior surfaces. This leads to three research questions:

1. What are the area-specific emission rates of formic acid and acetic acid from heritage collections under normal indoor room conditions and how does it depend on temperature and RH?
2. What is the spatial distribution in temperature, moisture, and organic acids in unoccupied storage buildings, with a HVAC system or with semi-passive climate control?
3. What is the organic acid removal efficiency of commercially available activated carbon filters and other HVAC components such as dehumidifiers, as well as interior surfaces?

2.4 Research design and methodology

This Ph.D. project consist of three parts. Part I measured the area-specific emission rates of formic acid and acetic acid from heritage collections under normal indoor room conditions and its dependence on temperature

and RH in a laboratory. Part II measured the climate and air quality conditions in two storage buildings with heritage collections. Part III was an intervention study examining the organic acid removal efficiency of activated carbon filters, a desiccant silica gel rotor as well as passive adsorption onto a clay brick wall.

Part I measured the emission rates of formic acid and acetic acid from six paper samples in a pilot study. The measurements were conducted in a climate controlled test chamber at normal indoor room conditions (22°C, 50% RH) as well as at cooler (10°C) conditions for three samples and dry (0% RH) conditions for one paper sample.

The area-specific emission rates of formic acid and acetic acid were also measured from seven naturally aged wood, paper, and cellulose acetate film samples as well as a newly produced wood packaging material used to transport and storage collections. The area-specific emission rates were measured in a climate controlled test chamber at normal indoor room conditions (23°C, 50% RH) as well as at cooler (10°C) and drier (20% RH) conditions.

The volatile organic compound (VOC) emission profile from four naturally aged paper samples were also determined in the test chamber under normal indoor room conditions (23°C and 50% RH). The total volatile organic compound (TVOC) emission were also measured in the climate controlled test chamber at normal indoor room conditions (23°C, 50% RH) and at cooler (10°C) conditions.

Formic acid and acetic acid were trapped on silica gel tubes or in a 0.1 M sodium hydroxide solution and the concentration of organic acids determined using ion chromatography (IC) analysis. The VOCs were sampled on Tenax TA® sorbent tubes with thermal desorption (TD) gas chromatography - mass spectrometry (GC-MS) analysis.

The area-specific emission rates of formic acid and acetic acid were used to model the concentration of organic acids in a model storage room under normal indoor room conditions. The impact of changes in the room temperature, the air exchange rate with ambient and the surface removal rate were furthermore modelled as three separate cases and the results compared with the energy use.

Part II measured the climate and air quality conditions in one storage building with a HVAC system, and in two rooms in another storage building with semi-passive climate control (see description in Chapter 3). The mean age of air and the air exchange rate with ambient were measured in both stores with perfluorocarbon (PFT) tracer gas. The concentration of ozone, nitrogen dioxide and organic acids were measured in one location inside and outside each storage building in summer and winter using passive diffusion samplers. The indoor atmospheric corrosivity was measured gravimetrically as the mass increase of copper, zinc, and lead coupons and in real-time as the increase in the electrical resistance on a 400 nm lead sensor with an AirCorr™ monitoring system from February 2018 to January 2019 (one year).

A sensor grid with 74 measurement locations were placed in a horizontal and vertical grid in both storage buildings. A climate sensor was placed in each location and the spatial distribution in temperature and RH measured for one year from February 2018 to January 2019. The spatial distributions in formic acid and acetic acid were additionally measured in each location as an average over three weeks in August 2018 using passive diffusion samplers.

Part III measured the formic acid and acetic acid removal efficiency of two commercially available activated carbon filters *in situ* in the same stores examined in Part II. One filter was designed for outdoor type pollutants (Filter A), while the other was designed for organic acids in indoor air (Filter B). The activated carbon filters

were tested using the HVAC system and mobile stand-alone filter units. Duplicate passive diffusion samplers were placed in the middle and in the corner of each storage room during the intervention study to examine the effect of active air filtration on the concentrations of formic acid and acetic acid close to the collections stored densely packed on shelves. The acetic acid removal efficiency of a desiccant silica gel rotor was also measured in a laboratory at different RH levels. The concentrations of formic acid and acetic acid in the air upstream and downstream of the activated carbon filters and the desiccant silica gel rotor were measured using active sampling in a 0.1 M sodium hydroxide solution with IC analysis.

The passive adsorption of acetic acid onto dry silica gel and unfired clay brick were measured with passive diffusion samplers in a test chamber and for clay brick in a test room as well.

All data from the laboratory and field measurements conducted in Part I-III will be merged into a Monte Carlo simulation in Chapter 5 to simulate the fraction of formic acid and acetic acid that deposit onto interior surfaces despite the use of active air filtration.

2.5 Significance

Several heritage institutions internationally and in Denmark will within the next couple of years invest in storage buildings with semi-passive climate control to improve the long-term preservation of heritage collections held in trust for future generations and reduce the energy use for climate control. Examples include the shared storage facility between the National Museum and the Royal Library of Denmark and the shared storage facility between local museums in Sønderjylland, Denmark.

The results from this Ph.D. project will increase our knowledge on the climate and air quality performance in these special indoor environments and can be used to select an appropriate air distribution and filtration system in storage buildings with semi-passive climate control to ensure economic and environmentally sustainable storage solutions with acceptable climate and air quality conditions for the preservation of collections.

3. The storage buildings

This Ph.D. project examined the climate and air quality conditions in one storage building with a HVAC system (Storage I) and two rooms in another storage building with semi-passive climate control (Storage II).

3.1 Storage I

Storage I belongs to the Royal Library in Denmark. The storage building is from 2008 and located in central Copenhagen surrounded by heavy traffic. The room is about 600 m³ and holds a book collection from the 15th to the 17th century. The books are stored on movable compact shelves on each side of a central passage (Figure 6).



Figure 6. Storage I seen from the outside (left). The store contains a book collection stored on compact movable shelves (right).

All walls are interior walls that connect to services areas or other storage rooms (Figure 7). Light sensors turn the light on when people enter the store. The entrance has a double door airlock.

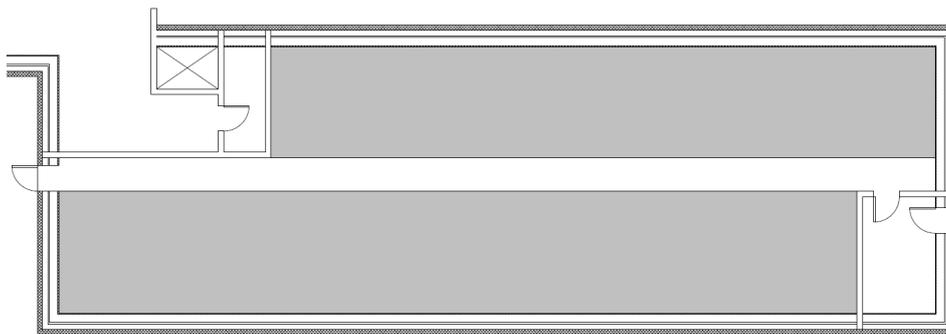


Figure 7. Floor plan for Storage I. The areas with movable compact shelves are marked in grey.

A HVAC system with heating, cooling, humidification, dehumidification and air filtration service the storage room (Supplementary information 1). The HVAC system contain F8 particle filters as well as two consecutive activated carbon filters. A building management system (BMS) control the intake of outdoor air, the internal recirculation rate and the climate conditions. Air is supplied to the storage room to maintain a constant overpressure and reduce infiltration from outside.

The RH is kept constant about 50% RH throughout the year while the room temperature is allowed to change from 6°C in winter up to 19°C in summer to reduce the energy use for climate control. The HVAC system

The RH is kept constant about 50% RH throughout the year while the room temperature is allowed to change from 6°C in winter up to 19°C in summer to reduce the energy use for climate control. The HVAC system consume 67 kWh m⁻³ year⁻¹ for climate and air quality control (Danielsen, personal communication, October 9th 2019).

3.2 Storage II

Storage II is part of the shared storage facility at the Centre for Preservation of Cultural Heritage located in a rural area outside Vejle in Denmark. The storage building is part of an extension from 2013. One storage room contain a paper-based archival collection (3200 m³) while the other room contain a mixed material collection (4800 m³). The collections are stored on movable compact shelves in both rooms (Figure 8).



Figure 8. Storage II seen from the outside (left) and the room with a mixed material collection stored on compact movable shelves seen from the inside (right).

The storage room with a paper-based archival collection has two external walls as well as one wall facing a central hall and one facing another storage room. The storage room with a mixed material collection has one external wall, one wall facing a central hall and two walls facing other storage rooms (Figure 9). The entrance has a double door airlock. A detailed description of the wall construction is given in Supplementary information 2. Light sensors are activated when the storage rooms are in use.

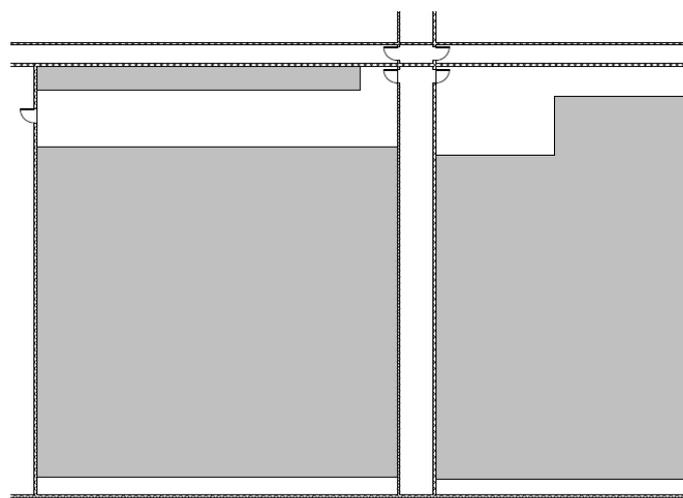


Figure 9. Floor plan for Storage II. The storage room with a paper-based archival collection is on the right and the room with a mixed material collection is on the left. The areas with movable compact shelves are marked in grey.

Storage II is unheated with periodic dehumidification using a Munters MLT 800 (Ryhl-Svensen *et al.*, 2012) (Supplementary information 1). The room temperature change from 7°C in winter up to 19°C in summer. The set point conditions for the dehumidification system is 40% RH for the room with a paper-based archival collection and 50% RH for the room with a mixed material collection. The ventilation system also contain a heater used to dry out the storage building during the construction process. The silica gel rotor consume 1.1 kWh m⁻³ year⁻¹ for periodic dehumidification (Knudsen, personal communication, August 22nd 2018).

The information is collected in Table 1.

Storage	Location	Year	Ventilation form	Energy use (kWh m ⁻³ year ⁻¹)	Volume (m ³)	Collection
I	City centre	2008	HVAC system	67	600	Books
II	Rural area	2013	Semi-passive climate control	1.1	3200	Paper
					4800	Mixed

Table 1. Information about Storage I and the two rooms in Storage II.

4. Summary of results

The results from Part I-III are summarized below.

4.1 Part I - laboratory measurements

Part I measured the VOC, formic acid and acetic acid emission rates from wood, paper, and cellulose acetate films present in heritage collections at normal indoor room conditions as well as cooler and drier conditions. The results were used to model the organic acid concentration in a storage room.

Analysis of the VOC emission profile from the four paper samples showed that acetic acid was the most abundant compound detected from all samples. All the 36 VOCs detected can arise from multiple sources in the indoor environment making it difficult to use them as a unique marker for the degradation of paper.

The mass-specific emission rates of formic acid and acetic acid from the six paper samples ranged from 12 to 468 ng g⁻¹ h⁻¹ at normal indoor room conditions (22°C, 50% RH). A decrease in temperature from normal indoor room conditions to 10°C reduced the emission rate 2-16 times from the three paper samples tested while a decrease in the RH from 50% to 0% reduced the emission rate with a factor 43 from the one paper sample tested.

The area-specific emission rates of formic acid and acetic acid from the six naturally aged wood and paper samples as well as the wood packaging material used to transport and store collections ranged from 10 to 300 µg m⁻² h⁻¹ while cellulose acetate emitted above 3000 µg m⁻² h⁻¹ at normal indoor room conditions (23°C, 50% RH). A decrease in temperature from normal indoor room conditions to 10°C reduced the TVOC emission. A decrease in temperature also reduced the emission rate of organic acids with a factor 2-4 from wood and paper while a decrease in the RH from 50% to 20% reduced the emission rate with a factor 2 or more.

A similar organic acid behaviour was observed in Storage I and II where the decrease in room temperature from summer to winter reduced the concentration of organic acids 2-3 times in indoor air.

The model study demonstrated that the area-specific emission rate from heritage collections can be used to model the concentrations of formic acid and acetic acid in indoor air at different conditions as well as the impact of removal mechanisms such as the air exchange rate. A decrease in temperature from indoor room conditions to cool conditions reduced the concentration of organic acids in indoor air. The concentration decreased from 508 to 204 µg m⁻³ in the model storage room with a wood collection and from 43 to 24 µg m⁻³ in the model storage room with a paper collection under the specified conditions. A decrease in temperature will also reduce the energy use for heating in temperate climates as in Northern Europe. To achieve the same reduction in the concentration of organic acids under normal indoor room conditions, as is possible with a decrease in temperature, would require an increase in the air exchange rate with 3.8 h⁻¹ in the model room with a wood collection and 1.6 h⁻¹ in the model room with paper. An increase in the air exchange rate with ambient will, however, also increase the energy use for outdoor air filtration and climate control.

The results from the laboratory measurements are presented and discussed in detail in Paper II-V.

4.2 Part II - field measurements

Part II measured the mean age of air and the air exchange rate in two storage buildings. The concentration of outdoor air pollution and the indoor atmospheric corrosivity were also measured together with the spatial distribution in temperature, moisture, and organic acids.

The mean age of air was four hours in Storage I with a HVAC system and up to 151 hours in Storage II with semi-passive climate control. This corresponds to an air exchange rate of 0.25 h^{-1} in Storage I and down to 0.01 h^{-1} in Storage II. Despite the difference in the air exchange rates both storage buildings protected the collections well against outdoor air pollution. The concentration of ozone and nitrogen dioxide diminished to below 9% from outdoor and the indoor atmospheric corrosivity was very low for zinc and copper in both stores.

The spatial temperature and moisture distributions throughout the horizontal measurement grids were uniform in Storage I and II. However, there was a weak vertical temperature stratification with 2.7°C difference between the floor and 2.5 m height in Storage I and 3.8°C between the floor and 5 m height in Storage II from late spring through the summer. The vertical temperature gradient caused a RH gradient opposite to that of temperature. The field measurements demonstrated that both ventilation forms upheld an acceptable climate performance with appropriate temperature and moisture distributions and without air pockets producing problematic microclimates.

In Storage I (HVAC system) with a book collection the concentration ranged from 2 to $19 \mu\text{g m}^{-3}$. In Storage II (semi-passive climate control) the concentration of organic acids ranged from 2 to $21 \mu\text{g m}^{-3}$ in the room with a paper-based archival collection and 45 to $134 \mu\text{g m}^{-3}$ in the room with a mixed material collection. The difference in the concentrations of formic acid and acetic acid between the two rooms in Storage II with semi-passive climate control indicated that, besides the ventilation form other parameters, as the material type and amount, also affected the concentration level.

The spatial organic acid distribution in Storage I was controlled by the HVAC system. The concentration of organic acids increased with up to five times from the air supply across the room to the exhaust. The horizontal grid in the room with a mixed material collection in Storage II contained areas where incomplete mixing caused a local accumulation of organic acids. The organic acid level additionally increased up to three times from the ceiling to the floor in both rooms within Storage II. The indoor atmospheric corrosivity towards lead corresponded to a pure atmosphere despite the higher concentration of organic acids in some areas of Storage II. This study demonstrated that both storage buildings provided an acceptable air quality performance irrespective of the ventilation form.

The corrosion thickness on the AirCorr™ monitoring system increased with higher temperature and RH. The result underlined that control of these parameters can be used to improve the air quality performance in storage buildings with heritage collections.

The results from the field measurements are presented and discussed in detail in Paper VI-VII.

4.3. Part III - intervention study

Part III measured the removal efficiency of activated carbon filters *in situ* during an intervention study in the two storage buildings with heritage collections. The removal efficiency of a desiccant silica gel rotor was also measured in a laboratory and the passive adsorption onto dry silica gel and clay brick in a test chamber and for clay brick in a test room as well.

The intervention study demonstrated that the formic acid and acetic acid removal efficiency of activated carbon filters varied considerably *in situ* from the removal efficiency obtained under laboratory conditions. Filter B designed to remove formic acid and acetic acid in heritage institutions performed better than Filter A designed for outdoor pollutants. The organic acid removal efficiency of the filters depended on the airflow through the filters. An increase in the airflow from normal ventilation conditions (50% fan power) to full ventilation (100% fan power) reduced the removal efficiency from 77% to 7% for Filter A, and from 92% to 24% for Filter B. The measurements showed that the clean air delivery rate (CADR), that combines the removal efficiency with the airflow through the filter, could be a more useful measure, than the removal efficiency alone, to evaluate the performance of filters *in situ* in heritage institutions.

Active air filtration did not have a significant impact on the organic acid concentration measured in the middle and in the corner of the storage buildings close to the collections and away from the ventilation inlets. The organic acid concentration measured during the intervention study didn't stand out from the natural variation. Natural variation was expected due to a decrease in the emission rate from interior surfaces following a decreasing room temperature from summer to winter.

The desiccant rotor used for dehumidification in storage buildings efficiently removed 98-100% acetic acid from the air. The removal efficiency was independent of the RH in the range from 25% to 70%. The desiccant rotor will, however, only be running when there is a need for dehumidification and as a result will only periodically remove pollutants.

Dry silica gel reduced the acetic acid concentration in the test chamber with more than 92% while the clay brick only reduced the acetic acid concentration by 37%. The passive adsorption capacity of dry silica gel might have been overestimated due to the possible decrease in acetic acid emission from the emission source at low RH. The clay brick wall established a concentration gradient across the test room. The organic acid concentration was 56% lower close to the clay brick wall compared to at the emission source. Passive adsorbents as clay brick will remove organic acids continuously from indoor air without consuming energy. Adsorbents as dry silica gel can however not be used to remove air pollutants in heritage institutions without considering its impact on the RH in indoor air.

The results from the intervention study are presented and discussed in detail in Paper VIII.

5. Monte Carlo simulation

A Monte Carlo simulation can be used to obtain numerical results from a model that depend on random variables. The simulation often contains several variables and the variables are also often difficult to determine experimentally. A probability distribution is assigned to each variable and the results obtained from repeated random sampling.

Monte Carlo simulations have been used in several previous studies on air pollution indoors (Aldred *et al.*, 2019; Gall *et al.*, 2011; Johnson *et al.*, 2011). Aldred *et al.* (2016) for example used a Monte Carlo simulation to predict the fate of ozone in residential buildings with and without commercially available activated carbon filters. Their model was based on several variables such as the outdoor ozone concentration, the air exchange rate with ambient and filter efficiency.

The fate of organic acids in storage buildings depend on several variables. A Monte Carlo simulation was therefore used to predict the formic acid and acetic acid concentrations inside the storage buildings. The results were validated by comparing the model predictions with concentrations found in the literature. The Monte Carlo simulation was then used to predict the fraction of organic acids that deposit back onto interior surfaces despite the use of active air filtration.

5.1 Model description

The concentrations of formic acid and acetic acid in indoor air depend on the strength and amount of emission sources present as well as the removal mechanisms. A mass-balance model was developed inspired by previous models from Ryhl-Svendsen (2007b) and Aldred *et al.* (2016) to calculate the steady-state concentration C_i ($\mu\text{g m}^{-3}$) of organic acids in indoor air:

$$C_i = (\text{SER}_a * L) / (n + S + fc * n_{\text{recirculation rate}} + dc * n_{\text{recirculation rate}}) \quad (1)$$

where, SER_a is the area-specific emission rates of formic acid and acetic acid ($\mu\text{g m}^{-2} \text{h}^{-1}$), L is the loading factor of emissive materials ($\text{m}^2 \text{m}^{-3}$), n is the air exchange rate with ambient (h^{-1}), S is the surface removal rate (h^{-1}), fc is the fraction of formic acid and acetic acid that is removed using active air filtration (-), dc is the fraction of formic acid and acetic acid that is removed in a desiccant rotor, and $n_{\text{recirculation rate}}$ is the recirculation rate through the filter or the desiccant rotor (h^{-1}).

The mass-balance ignores the contribution of organic acids from outside.

5.2 Method

The Monte Carlo simulations were done in Excel using the supplementary program Oracle Crystal Ball (<https://www.oracle.com/applications/crystalball/>). The simulations were done with 100.000 iterations.

The results from the measurements conducted in Part I-III were used as input data together with results found in the literature. All input data are collected in Table 2.

The Monte Carlo simulation ignores the contributions of formic acid and acetic acid from construction materials, building interior and people's activities. The simulation only accounts for the formic acid and acetic acid emissions from heritage collections.

Parameter	Value	Reference
SER _a paper (10°C)	5-22 µg m ⁻² h ⁻¹	Smedemark <i>et al.</i> , 2020a.
SER _a paper (23°C)	10-33 µg m ⁻² h ⁻¹	Smedemark <i>et al.</i> , 2020a.
SER _a mixed materials (10°C)	5-101 µg m ⁻² h ⁻¹	Smedemark <i>et al.</i> , 2020a.
SER _a mixed materials (23°C)	10-259 µg m ⁻² h ⁻¹	Smedemark <i>et al.</i> , 2020a.
L collection	3-5 m ² m ⁻³	Ryhl-Svendsen and Clausen, 2009.
SER _a wood packaging (23°C)	303 µg m ⁻² h ⁻¹	Smedemark <i>et al.</i> , 2020a.
L wood packaging	0.5-1 m ² m ⁻³	Estimate.
n	0.01–1 h ⁻¹	Smedemark <i>et al.</i> , 2019a, Thickett <i>et al.</i> , 2007; Ryhl-Svendsen <i>et al.</i> , 2014; Mašková <i>et al.</i> , 2017.
S	0.2–2 h ⁻¹	Ryhl-Svendsen and Clausen, 2009.
fc	0.24–0.92	Smedemark <i>et al.</i> , 2020b.
dc	0.98-1	Smedemark <i>et al.</i> , 2020b.
n recirculation	2 h ⁻¹	Estimate.
C	0-1019 µg m ⁻³	Smedemark <i>et al.</i> , 2019a; Robinet <i>et al.</i> , 2004; Schieweck <i>et al.</i> , 2005; Lopez-Aparicio and Grasiene, 2013; Ryhl-Svendsen <i>et al.</i> , 2014; Mašková <i>et al.</i> , 2017.

Table 2. The Monte Carlo simulation model parameters and input data.

The area-specific emission rate (SER_a) from heritage collections was used to simulate the concentration in a storage building at normal indoor room conditions and cool conditions (Smedemark *et al.*, 2020a). A loading factor (L) between 3 and 5 m² m⁻³ was used to simulate collections stored densely packed on shelves in the storage building. The loading factor was based on an estimate found in the literature (Ryhl-Svendsen and Clausen, 2009).

The area-specific emission rates of formic acid and acetic acid from the newly produced wood packaging used to transport and store collections were used to examine its contribution to the organic acid concentration in indoor air (Smedemark *et al.*, 2020a). The wood packaging was estimated to have a loading factor between 0.5 and 1 m² m⁻³ based on observations in the room with a mixed material collection in Storage II.

Only a few studies have measured the air exchange rate (n) in storage buildings with heritage collections. The air exchange rate found in the literature ranged from 0.01 to about 1 h⁻¹ (Thickett *et al.*, 2007; Ryhl-Svendsen *et al.*, 2014; Mašková *et al.*, 2017; Smedemark *et al.*, 2019a).

The surface removal rate (S) was set to between 0.2 and 2 h⁻¹ based on an estimate found in the literature (Ryhl-Svendsen and Clausen, 2009).

The effectiveness of active air filtration (fc) was simulated using a formic acid and acetic acid removal efficiency between 24-92% (Filter B) measured *in situ* in storage buildings with heritage collections (Smedemark *et al.*, 2020b). The recirculation rate ($n_{\text{recirculation}}$) through the filter was set to 2 h⁻¹.

An organic acid removal efficiency between 98-100% was used to simulate the impact of a desiccant silica gel rotor (dc) on the concentrations of formic acid and acetic acid in air (Smedemark *et al.*, 2020b). The recirculation rate ($n_{\text{recirculation}}$) through the dehumidifier was set to 2 h⁻¹.

Several previous studies have measured the concentrations (C_i) of formic acid and acetic acid in one or a few locations in storage buildings with heritage collections (Robinet *et al.*, 2004; Schieweck *et al.*, 2005; Lopez-Aparicio and Grasiene, 2013; Ryhl-Svendsen *et al.*, 2014; Mašková *et al.*, 2017; Smedemark *et al.*, 2019a; Smedemark *et al.*, 2019b; Smedemark and Ryhl-Svendsen, 2019). The concentration found in the literature was used to validate the model and then to simulate the fraction of formic acid and acetic acid that deposit onto interior surfaces.

Altogether nine scenarios were simulated (Table 3). The probability distribution for the variables are difficult to establish as the input data are based on either an estimate or a few measurements. A uniform probability distribution was therefore assigned to each variable in this study.

Scenario	Collection	Climate conditions	Description
1	Paper collection	10°C; 50% RH	Cool conditions
2		23°C; 50% RH	Normal indoor room conditions
3		23°C; 50% RH	Active air filtration
4		23°C; 50% RH	Dehumidification using a desiccant rotor
5	Mixed collection	10°C; 50% RH	Cool conditions
6		23°C; 50% RH	Normal indoor room conditions
7	Mixed collection stored on wood packaging	23°C; 50% RH	Normal indoor room conditions
8		23°C; 50% RH	Active air filtration
9		23°C; 50% RH	Dehumidification using a desiccant rotor

Table 3. The nine scenarios modelled in the Monte Carlo simulation.

5.3 Results and discussion

5.3.1 Organic acid concentration

The nine scenarios simulated result in nine probability density plots. The plots show the expected formic acid and acetic acid concentrations in storage buildings with heritage collections. Two examples are shown in

Figure 10 and 11. The blue color show the empirical probability distribution from repeated random sampling in the Monte Carlo simulation while the green line indicate the theoretical distribution.

Figure 10 show the Monte Carlo simulations prediction of the organic acid concentration in a store with a mixed material collection at normal indoor room conditions. Figure 11 show the same store with the collections stored on wood packaging.

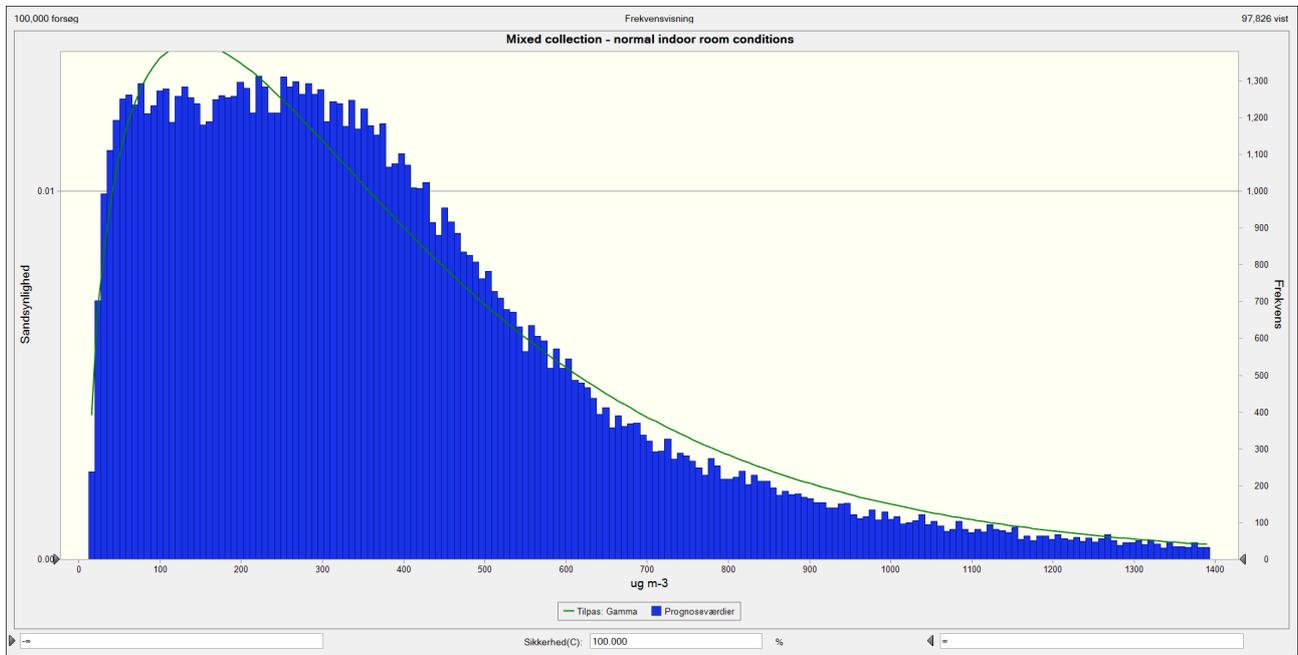


Figure 10. The Monte Carlo simulations prediction of the formic acid and acetic acid concentrations in a storage building with a mixed material collection at normal indoor room conditions.

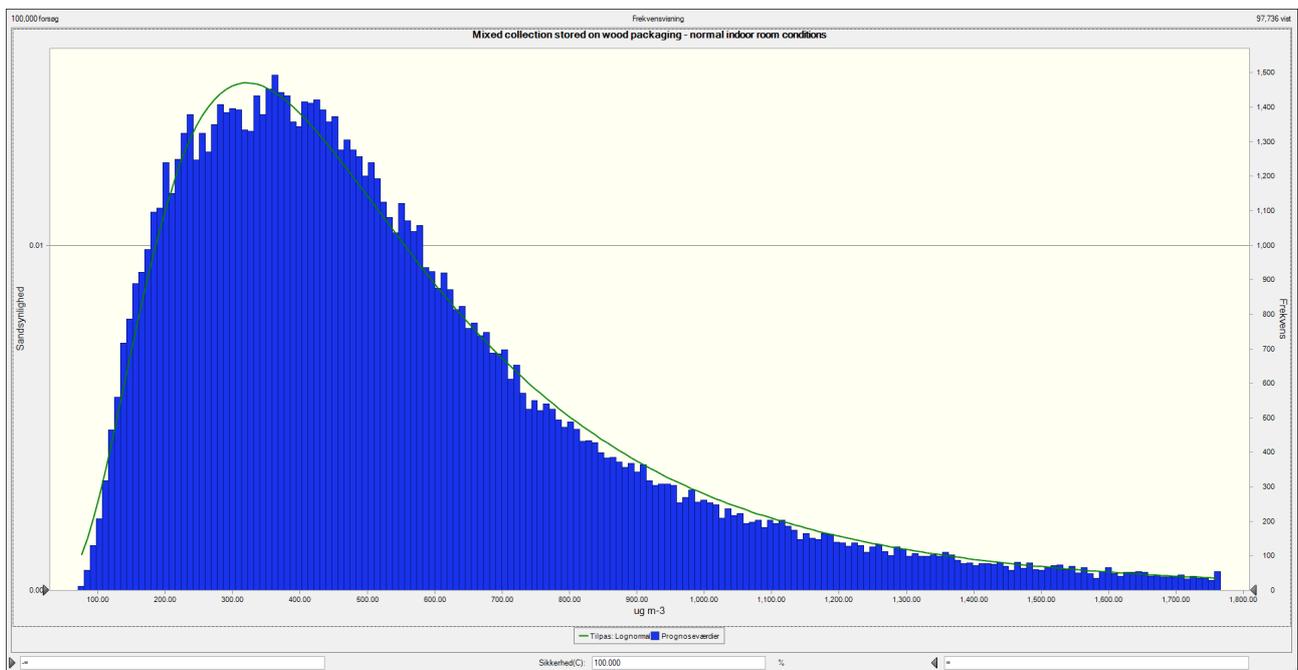


Figure 11. The Monte Carlo simulations prediction of the formic acid and acetic acid concentrations in a storage building with a mixed material collection stored on wood packaging at normal indoor room conditions.

All nine probability density plots have a similar shape. They are all clearly right skewed. To exclude extremely unlikely high concentrations the 95% quartile were used as the maximum concentration expected. Table 4 show the average predicted concentrations and the standard deviation. The average concentration indicates where the distribution is centered. The standard deviation show the large concentration interval obtained from the Monte Carlo simulations and thereby the uncertainty in the predictions.

Scenario	Description	Organic acid concentration ($\mu\text{g m}^{-3}$)			
		Min.	95%	Max.	Average
1.	Paper collection (10°C, 50% RH)	5	95	441	41 ±30
2.	Paper collection (23°C, 50% RH)	11	148	674	65 ±45
3.	Paper collection (23°C, 50% RH) with filtration	7	64	187	34 ±16
4.	Paper collection (23°C, 50% RH) with dehumidification	7	42	69	25 ±10
5.	Mixed collection (10°C, 50% RH)	6	405	2120	161 ±137
6.	Mixed collection (23°C, 50% RH)	12	1040	4807	408 ±352
7.	Mixed collection stored on wood packaging (23°C, 50% RH)	71	1354	5138	575 ±396
8.	Mixed collection stored on wood packaging (23°C, 50% RH) with filtration	48	589	1749	299 ±156
9.	Mixed collection stored on wood packaging n (23°C, 50% RH) with dehumidification	40	394	671	220 ±97

Table 4. The minimum and maximum organic acid concentration predicted in the Monte Carlo simulations for the nine scenarios. The 95% quartile and the average concentration predicted together with the standard deviation are also given.

The average organic acid concentration and the standard deviation from the Monte Carlo predictions are also shown in Figure 12.

The Monte Carlo simulations predicted an organic acid concentration between 11 and 148 $\mu\text{g m}^{-3}$ in a store with paper collections and between 12 and 1040 $\mu\text{g m}^{-3}$ in a store with mixed collections at normal indoor room conditions. The formic acid and acetic acid concentration interval predicted in the Monte Carlo simulations corresponded with the concentration measured in several previous field measurements (see review Smedemark, 2018).

Wood packaging used to transport and store collections led to a 29% increase in the average organic acid concentration predicted from the Monte Carlo simulations. The result underlined that non-emissive alternatives to transport and store collection will reduce in the organic acid concentration in indoor.

The average organic acid concentration predicted from the Monte Carlo simulations decreased with 37% in a store with paper collections and 61% in a store with a mixed material collection with a decrease in temperature from normal indoor room conditions to cool conditions. The Monte Carlo simulations showed that reducing the temperature in storage buildings with heritage collections from normal indoor room conditions to cool conditions can be used as a control method to reduce the concentrations of formic acid and acetic acid in indoor air.

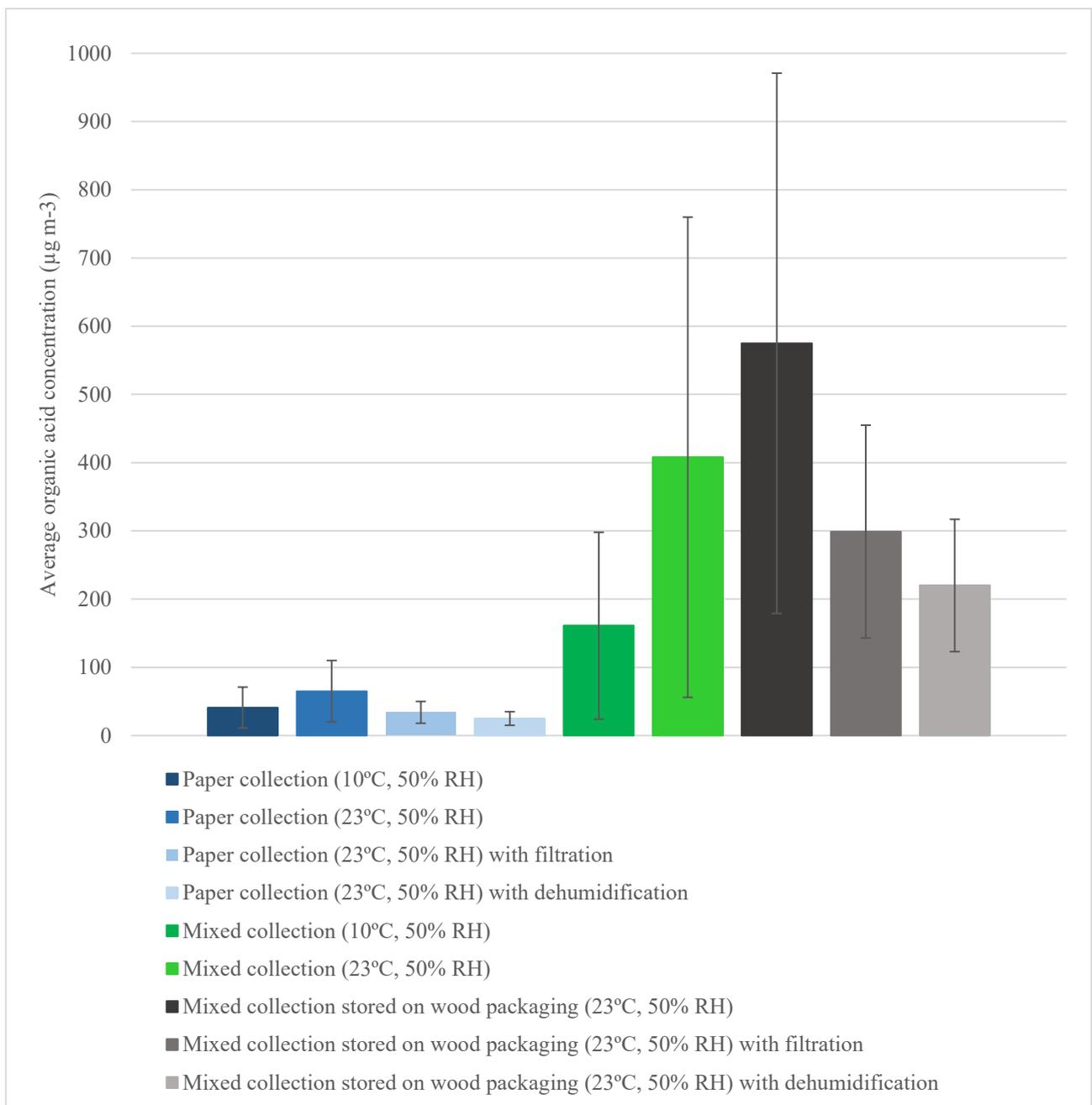


Figure 12. The average organic acid concentration predicted from the Monte Carlo simulations together with the standard deviation.

Active air filtration reduced the average organic acid concentration predicted from the Monte Carlo simulations with 48% in both stores. A larger reduction about 62% in the average organic acid concentration predicted from the Monte Carlo simulations was observed in both stores using a desiccant dehumidifier. The Monte Carlo simulations showed that recirculating air through a desiccant dehumidifier are expected to reduce the organic acid concentration in air more efficiently than active air filtration. A desiccant rotor will only remove organic acids from indoor air when there is a need for dehumidification whereas recirculating air through activated carbon filters can run independently.

The Monte Carlo simulation demonstrated that lowering the temperature from normal indoor room conditions to cool conditions reduced the predicted average organic acid concentration in indoor air in stores with mixed collections more efficiently than recirculating the air through activated carbon filters at 2 h⁻¹.

5.3.2 The fraction of formic acid and acetic acid that deposit onto interior surfaces

The surface removal rate describes the uptake or deposition onto interior surfaces. The nine scenarios simulated result in nine probability density plots showing the expected surface removal rate. Two examples are shown in Figure 13 and 14. Figure 13 shows the probability density plot for the Monte Carlo simulations prediction of the surface removal rate in a store with a mixed collection stored on wood packaging at normal indoor room conditions. Figure 14 shows the probability density plot for the same store with active air filtration.

The surface removal rate probability density plots predicted in the Monte Carlo simulations are highly right skewed and to exclude extremely unlikely values the 95% quartiles were used as the maximum rate. The Monte Carlo simulations also predict scenarios where the source strength is lower than the air exchange rate giving rise to a negative surface removal rate. This is a model error as the surface removal rate can never be below zero. All negative values were therefore set to zero.

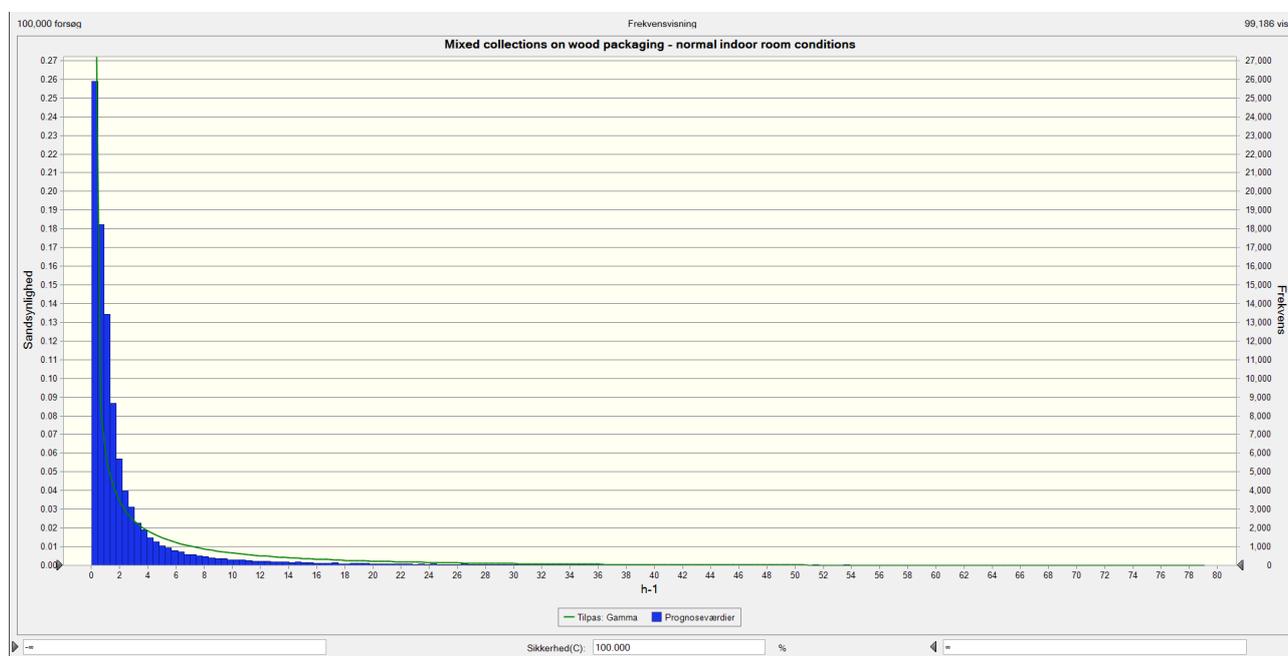


Figure 13. The Monte Carlo simulations prediction of the surface removal rate in a store with a mixed material collection at normal indoor room conditions. The collection is stored on wood packaging.

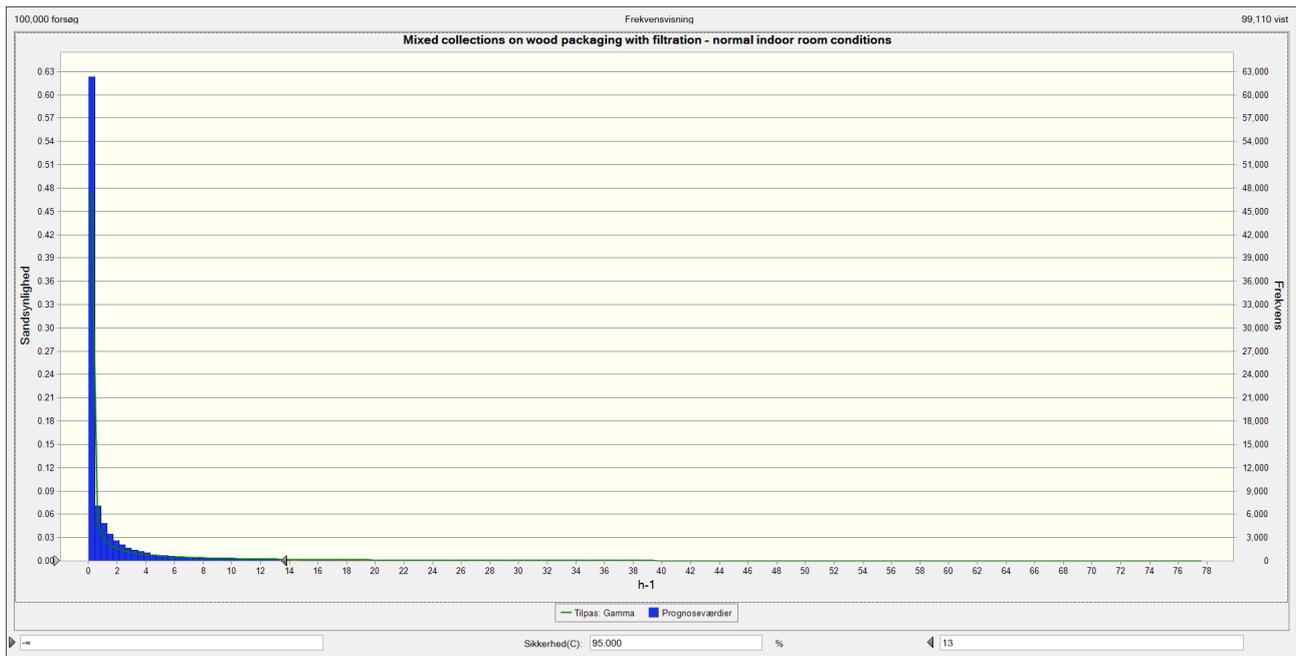


Figure 14. The Monte Carlo simulations prediction of the surface removal rate in a store with a mixed material collection stored on wood packaging at normal indoor room conditions with active air filtration.

Table 5 collects the results from the Monte Carlo simulations with the predicted surface removal rates of formic acid and acetic acid in stores with heritage collections.

Active air filtration might be redundant in stores with paper-based collections due to the small fraction of organic acids that deposit onto interior surfaces predicted in the Monte Carlo simulations. The Monte Carlo simulations showed that the surface removal rates are expected to be below 1 h^{-1} with an average surface removal rate at 0 h^{-1} in a store with paper-based collections under normal and cool conditions. Di Pietro *et al.* (2016) also conclude from a cost-benefit perspective that the use of active air filtration in storage buildings with library and archival collections should be discouraged.

Wood packaging used to transport and store collections led to an increase in the average predicted surface removal rate from 3 h^{-1} for a store with mixed collection to 5 h^{-1} for a store with mixed collection stored on wood packaging at normal indoor room conditions. Non-emissive transport and storage materials could be used to reduce the deposition of formic acid and acetic acid onto interior surfaces potentially causing damage to heritage collections.

Active air filtration led to a small decrease in the average predicted surface removal rate from 5 h^{-1} for a mixed collection stored on wood packaging to 4 h^{-1} for the same store with active air filtration. The same decrease in average surface removal rate was predicted for a store with recirculation through a desiccant silica gel rotor.

The Monte Carlo simulations showed that lowering the temperature from normal indoor room conditions to cool conditions reduced the predicted average surface removal rate in stores with mixed material collections from 3 to 1 h^{-1} . Lowering the temperature thus reduced the predicted fraction of organic acids that deposit onto interior surfaces in stores with mixed collections more efficiently than recirculating the air through activated carbon filters at 2 h^{-1} .

Scenarios	Description	Surface removal rate (h ⁻¹)			
		Min.	95%	Max.	Average
1.	Paper collection (10°C, 50% RH)	0	1	69	0 ±2
2.	Paper collection (23°C, 50% RH)	0	1	131	0 ±3
3.	Paper collection (23°C, 50% RH) with filtration	0	0	120	0 ±3
4.	Paper collection (23°C, 50% RH) with dehumidification	0	0	150	0 ±3
5.	Mixed collection (10°C, 50% RH)	0	4	360	1 ±8
6.	Mixed collection (23°C, 50% RH)	0	10	1009	3 ±20
7.	Mixed collection stored on wood packaging (23°C, 50% RH)	0	14	1055	5 ±27
8.	Mixed collection stored on wood packaging (23°C, 50% RH) with filtration	0	13	973	4 ±25
9.	Mixed collection stored on wood packaging n (23°C, 50% RH) with dehumidification	0	12	937	4 ±25

Table 5. The simulated surface removal rate of formic acid and acetic acid onto interior surfaces in a room with a paper and a mixed collection.

5.4 Uncertainties and limitations

The Monte Carlo simulations contains several uncertainties. The model assumed a well-mixed storage room without pockets with stagnant air. However, the results from the field measurements in storage buildings showed that organic acids can accumulate in concentration in some areas in storage buildings with semi-passive climate control (Smedemark *et al.*, 2019a). The assumption might therefore not always be valid for storage buildings with densely packed collections.

A major limitation was also the small amount of available data. Several parameters in the model were based on estimates while the data on other parameters as the organic acid concentration in indoor air and the air exchange rate with ambient were scarce and cover a large variation in storage facilities etc. The small amount of data furthermore made it difficult to determine the probability distribution for the parameters as it will require more than 30 samples to determine whether a parameter follows for example a normal distribution.

To validate the model it will also be necessary to compare the results from the simulation of the fraction of formic acid and acetic acid that deposit onto interior surfaces with experimental results. Further research is therefor needed to determine the surface removal rate in storage buildings with heritage collections.

5.5 Conclusion on the Monte Carlo simulations

The Monte Carlo simulations revealed that active air filtration only eliminated a fraction of the formic acid and acetic acid from indoor air while a fraction deposit back onto interior surfaces. The average surface removal rate predicted for a store with mixed material collections on wood packaging was 5 h^{-1} while active air filtration reduced the average predicted surface removal rate to 4 h^{-1} .

The predicted surface removal rate of organic acids in a store with paper collections was below 1 h^{-1} under normal and cool conditions. The small organic acid deposition onto interior surfaces potentially causing damage to sensitive materials in heritage collections might make active air filtration redundant in stores with paper collections. Menart *et al.* (2014) and Ligterink and Di Pietro (2018) found a similar result for paper-based library and archival collections based on laboratory measurements and model predictions.

The fraction of organic acids that deposit onto surfaces predicted in the Monte Carlo simulations can be used as a first step to assess the effectiveness of methods to control organic acids in storage buildings. The simulations showed that lowering the room temperature from normal indoor room conditions to cool conditions reduced the predicted average surface removal rate more efficiently from 3 to 1 h^{-1} than active air filtration. Further research is needed to combine the effectiveness of the methods used to control indoor air pollution with their energy use.

6. Discussion and future research

The concentration of organic acids in storage buildings depend as previously mentioned on the strength and amount of emission sources present as well as the removal mechanisms. This chapter discusses some of the methods used to control indoor air pollution in stores with heritage collections.

6.1 Strength and amount of emission sources

The first step to control indoor air pollution is to avoid emissive construction materials and building interior that contribute to its concentration in indoor air (Tétreault, 2003). The wood packaging material used to transport and store collections had the highest organic acid emission rate of all the wood and paper samples tested (Smedemark *et al.*, 2020a). Emission from the wood packaging material will contribute to the organic acid concentration in indoor air. The Monte Carlo simulations predicted that the organic acid concentration on average was 29% higher in stores with collections stored on wood packaging material with a loading between 0.5 to 1 m² m⁻³ than in stores without wood packaging. Alternative transport and storage materials should therefore be examined to reduce the formic acid and acetic acid concentrations in air potentially causing damage to sensitive materials in the collections.

Besides the wood packaging material used to store collections the difference in strength and amount of collections between the two rooms in the store with semi-passive climate control might also have influenced the concentration of organic acids in air. The organic acid concentration was 45 to 134 µg m⁻³ in the room with a mixed material collection stored on wood packaging and 2 to 21 µg m⁻³ in the room with a paper-based archival collection (Smedemark *et al.*, 2019a). The area-specific emission rate of organic acids was up to 26 times higher from naturally aged wood present in the mixed material collection than from paper present in the archival collection at normal indoor room conditions (Smedemark *et al.*, 2020a). The amount of material was also higher in the room with the mixed material collection stored densely packed on shelves while the room with the paper-based archival material was only half-filled (Smedemark *et al.*, 2019a).

Another method to control indoor air pollutants is to separate emissive materials from sensitive materials in the storage building (Tétreault, 2003). This is often done with cellulose acetate films. The Monte Carlo simulations showed that only a minor fraction of formic acid and acetic acid are expected to deposit onto interior surfaces in stores with paper-based collections at normal indoor room conditions. While the average predicted fraction that deposit onto interior surfaces in stores with mixed materials are higher. Sensitive materials could be stored in a separate storage section in storage buildings with emissive wood collections to reduce damage due to organic acids. Many objects are, however, composite and contain both emissive materials and sensitive materials prone to degradation making it difficult to separate the collection into different storage sections.

Heritage collections can also emit other VOCs to the indoor air. Many heritage collections have for example over the years been treated with various biocides and the emission of biocides from the collections could pose a health risk to the staff working in the storage building (Klenz Larsen and Ryhl-Svendsen, 2019). This study focus on the formic acid and acetic acid emissions from heritage collections, however, other indoor air pollutants could also be of interest to the preservation of heritage collections and for staff working in storage buildings with a low air exchange rate with ambient.

6.2 Temperature

Lowering the temperature will reduce the emission rate of VOCs from materials (Wolkoff, 1998). A decrease in temperature from normal indoor room conditions to cool conditions reduced the TVOC emission from all samples tested in the laboratory measurements (Smedemark *et al.*, 2018). The organic acid emission rate from wood and paper present in heritage collections also decreased with a decrease in temperature (Smedemark and Ryhl-Svendsen, 2019; Smedemark *et al.*, 2020a).

A similar behaviour was observed in several storage buildings with heritage collections examined as part of this project where a decrease in room temperature from summer to winter led to a reduction in the concentrations of formic acid and acetic acid in indoor air (Smedemark and Ryhl-Svendsen, 2019; Smedemark *et al.*, 2019b). The same trend have also been observed in studies by Krupinska *et al.* (2013) and Ryhl-Svendsen *et al.* (2014).

The Monte Carlo simulations predicted that lowering the indoor room temperature from comfort conditions to cool conditions will reduce the average concentration of organic acids in indoor air with 61% in a store with mixed materials and 37% in a store with paper-based material. Lowering the temperature will also reduce the predicted average fraction of organic acids that deposit onto interior surfaces with a factor three in a store with mixed collections.

This Ph.D. project established that temperature can be used as an effective control method to lower the emission rate from storage materials and collections as well as the organic acid concentration in indoor air. A decrease in temperature will also reduce the chemical deterioration of cellulose-based materials. Michalski (2002) derived a rule of thumb stating that ‘*for each 5°C drop in temperature the lifetime will double*’ from data on the deterioration of paper, film and magnetic media. A decrease in temperature and RH from summer to winter with the following decrease in organic acid concentration in indoor air also led to a decrease in the indoor atmospheric corrosivity measured as the increase in electrical resistance on a 400 nm lead sensor using the AirCorr™ monitoring system (Smedemark *et al.*, 2019b).

Based on the results from this Ph.D. project it can be recommended to reduce the temperature in storage buildings with heritage collections to reduce the concentrations of formic acid and acetic acid in air and its deposition onto interior surfaces. A decrease in room temperature will furthermore reduce the energy use for heating in temperate climates as in Northern Europe (Smedemark *et al.*, 2020c).

Some materials are, however, sensitive to cool storage temperatures. For example, paints will become brittle at temperatures below its glass transition temperature at about 10 to 7°C (50-45°F) for acrylic paints, 4 to 2°C (40-35°F) for alkyd paints, and 0 to -10 °C (32 to -14°F) for oil paints (Mecklenburg, 2007). Paints are some of the most sensitive materials to cool temperatures and a room temperature above the glass transition temperature for acrylic paints at 10°C could therefore be advisable in stores with general collections. The temperature can be reduced even further if materials sensitive to cool temperatures are stored in a separate section.

6.3 RH

Lowering the RH will also reduce the emission rate of VOCs from materials (Wolkoff, 1998). This project showed that a decrease in RH from 50% to drier conditions reduced the organic acid emission rate from wood and paper present in heritage collections (Smedemark and Ryhl-Svendsen, 2019; Smedemark *et al.*, 2020a). A decrease in RH will also reduce the hydrolysis of organic materials. Michalski (2002) derived a rule of thumb stating that ‘*halving the relative humidity will more than double the lifetime*’ from data on the deterioration of paper, film and magnetic media.

An incorrect RH can however cause damage to materials within heritage collections (see overview in ASHRAE, 2019). A low RH can among other things lead to brittleness and deformation. The RH is therefore often maintained between 40% and 60% RH for general museum collections and cannot be used as a control method to reduce the emission of organic acids from the collections.

6.4 Air exchange rate

An increase in the air exchange rate with ambient is often used to dilute indoor air pollutants (Ryhl-Svendsen *et al.*, 2011). However, this is not a feasible control method in stores with semi-passive climate control and will increase the energy use significantly in stores with a HVAC system (see section 6.5). The air exchange rate as a control method to reduce the concentration of indoor air pollution will therefore not be discussed in further detail in this thesis.

6.5 Recirculation through air filters and other air cleaning devices

Active air filtration in mechanical ventilation systems is commonly used to remove air pollution. Research on the formic acid and acetic acid removal efficiency of active air filtration *in situ* in storage buildings with heritage collections is scarce and the results ambiguous. Ryhl-Svendsen and Clausen (2009) measured opposite what would be expected from model predictions, an increase in the organic acid concentration with an increase in the recirculation rate through mobile stand-alone filter units with activated carbon filters at the National Museum of Denmark. Di Pietro and Mentzel (2012) showed that active air filtration only gave rise to a 20% reduction in the acetic acid concentration measured close to the paper-based library collections stored on shelves and away from the ventilation inlets at the National Library in Bern, Switzerland.

The filter performance measured in this project also varied considerably *in situ* from the values reported from laboratory conditions (Smedemark *et al.*, 2020b). The removal efficiency depended on the airflow through the filter. An increase in the airflow reduced the formic acid and acetic acid removal efficiency from 92% down to 24% for Filter B designed to remove organic acids from indoor air. The large discrepancy between the formic acid and acetic acid removal efficiency reported from standard laboratory tests and its operation *in situ* makes it difficult to predict the effectiveness of active air filtration in storage buildings. The CADR that combines the removal efficiency with the airflow through the filters could therefore be a more useful measure to evaluate the performance of filters *in situ* in heritage institutions.

The ventilation effectiveness is another important parameter that can be used to assess the ventilation systems ability to distribute clean air throughout the building. The organic acid concentration measured close to the

collections during the intervention study in this project didn't stand out from the natural variation (Smedemark *et al.*, 2020b). Natural variation in the concentrations of formic acid and acetic acid in indoor air were expected due to the decrease in the emission rates from interior surfaces with a decrease in temperature from summer to winter (Smedemark and Ryhl-Svendsen, 2019; Smedemark *et al.*, 2019a).

This Ph.D. project also demonstrated that other air-cleaning devices as a desiccant silica gel rotor can remove organic acids from indoor air without additional energy use (Smedemark *et al.*, 2020b). The desiccant rotor will typically be running during the summer where the need for dehumidification is highest. Fortunately this is also where the organic acid concentration is highest.

The Monte Carlo simulations revealed that active air filtration reduced the expected average organic acid concentration with 48% in stores with paper and mixed materials. The desiccant rotor on the other hand reduced the expected average organic acid concentration with 62%. Both scenarios were simulated with a recirculation rate through the filter and the desiccant rotor at 2 h⁻¹.

An increase in the recirculation rate through the air-cleaning device might reduce the concentration even further. An increase in the airflow through activated carbon filters can however also lead to a decrease in their removal efficiency (Smedemark *et al.*, 2020b). Further work is needed in order to examine the CADR *in situ* in stores with heritage collections and the ventilation effectiveness on the organic acid concentration close to the collections stored densely packed on shelves.

The Monte Carlo simulations predicted that the surface removal rate was below 1 h⁻¹ with an average surface removal rate at 0 h⁻¹ in stores with paper-based collections under normal and cool conditions. Active air filtration might therefore be redundant in stores with paper-based collections. Di Pietro and Mentzel (2012) concluded that the only 20% decrease in acetic acid concentration measured close to the paper-based collections at the National Library in Bern, Switzerland was a reason to reconsider the use of active air filtration in storage buildings with library and archival collections. Di Pietro *et al.* (2016) also discourage the use of active air filtration in storage buildings with library and archival collections from a cost-benefit perspective.

The Monte Carlo simulations also revealed that active air filtration only had a minor impact on the predicted fraction of organic acids that deposit onto interior surfaces in stores with mixed collections and active air filtration might therefore also be redundant in stores with mixed material collections.

6.6 Passive adsorption

The Monte Carlo simulations revealed that active air filtration only eliminated a fraction of the formic acid and acetic acid from indoor air while a fraction deposit back onto interior surfaces. Construction materials and building interior can be used as passive adsorbents to reduce the formic acid and acetic acid concentrations in indoor air.

Dry silica gel and unfired clay brick can be used as passive adsorbents to reduce the organic acid concentration in indoor air (Smedemark *et al.*, 2020b). The unfired clay brick wall in the test room reduced the concentration of acetic acid close to the wall with 56% compared to the free room air. A similar trend was observed by Ryhl-Svendsen (2011).

Dry silica gel will also adsorb moisture from the indoor air and can therefore not be used as an adsorbent to passively remove organic acid without also considering its impact on the RH in storage buildings with heritage

collections. Unfired clay brick can also be used to buffer the RH in storage buildings. Padfield and Jensen (2010) found that unfired clay brick had the best buffer capacity with 27 cubic meter per square meter of material surface. Construction materials as unfired clay brick might therefore be a suitable adsorbent to remove organic acids from indoor air and buffer the RH.

Research on the passive adsorption onto construction materials are scarce. The deposition velocities of formic acid and acetic acid onto interior surfaces are only known for a small selection of materials as 0.005 cm s^{-1} for formic acid and acetic acid onto silver (Graedel and McGill, 1986). Sinclair *et al.* (1982, 1984, 1990) proposed to measure the passive adsorption onto materials using a filter paper soaked in water to extract adsorbed pollutants from the materials and determine the compounds with subsequent IC analysis. Further work could have been done in this project to use this method to determine the pollutants adsorbed onto the construction materials in the storage buildings.

Passive adsorbents are however, more effective in small rooms compared to large storage buildings due to a higher surface-area-to-volume ratio in the smaller rooms (Ryhl-Svendsen and Clausen, 2009). Passive adsorbents as construction materials will only account for a small interior surface area compared to the collections. Passive adsorbent might therefore not be an efficient control method in large storage buildings with densely packed collections.

6.7 Energy use

Various energy use have been reported in this Ph.D. project. Even though the field measurements were limited to two storage buildings it is clear that an increase in the air exchange rate with ambient will increase the energy use for outdoor air filtration and climate control. The climate conditions were almost the same in the two storage buildings examined as part of this Ph.D. project. The store with a HVAC system consumed $67 \text{ kWh m}^{-3} \text{ year}^{-1}$ for outdoor air filtration and climate control while the store with semi-passive climate control consumed $1.1 \text{ kWh m}^{-3} \text{ year}^{-1}$ for periodic dehumidification (Smedemark *et al.*, 2019a).

One way to reduce the energy use is to recirculate the air through activated carbon filters inside the store. Recirculation through activated carbon filters consumed $8 \text{ kWh m}^{-3} \text{ year}^{-1}$ in Storage I with a HVAC system (Smedemark *et al.*, 2020b). An increase in the recirculation rate through activated carbon filters with 3.8 h^{-1} in the model storage room increased the energy use with $9 \text{ kWh m}^{-3} \text{ year}^{-1}$ corresponding to about $2.4 \text{ kWh m}^{-3} \text{ year}^{-1}$ per air exchange (Smedemark *et al.*, 2020c).

Lowering the room temperature from comfort conditions to cool conditions reduced the energy use for heating from 161 to $40 \text{ kWh m}^{-3} \text{ year}^{-1}$ in the model storage room in Denmark. This corresponds to a $9 \text{ kWh m}^{-3} \text{ year}^{-1}$ decrease in energy use per 1°C drop in temperature. The results underlined that cold outside winter temperatures in temperate climates as in Northern Europe can be used to improve the air quality in storage buildings and reduce the energy use for comfort heating.

A desiccant rotor and passive adsorbents as construction materials will also contribute to the reduction in the concentrations of formic acid and acetic acid in indoor air. Passive adsorbents as clay brick may require an additional installation cost but will also buffer the RH in the storage building. A desiccant rotor and passive adsorbents will remove air pollution without an additional energy use.

6.8 Organic acid threshold levels in international guidelines

The dogma to use the '*best available technology*' has also been applied to setting threshold limits for outdoor and indoor air pollution (Tétreault, 2018). Minimum threshold limits for air pollution is difficult to establish as the deterioration of heritage collections will depend on the material composition, previous conservation treatments, storage conditions and the synergistic impact of temperature, RH, and air pollution among other things.

Threshold levels for organic acids in heritage institutions have previously been collected in various guidelines as ISO 11799:2003 and BS 5454:2012 for library and archival material as well as PAS 198:2012 for general heritage collections. The threshold levels for formic acid and acetic acid in heritage institutions have been widely discussed. There are currently no consensus on absolute threshold levels within the conservation literature and new guidelines from ASHRAE (2019) for museums, libraries and archives and the European standard on storage buildings for heritage collections (EN 16893:2018) no longer contains target levels.

Brimblecombe and Gibson (1998) proposed the '*operational threshold*' as an approach to set acceptable levels for air pollution in heritage institutions. The operational threshold is the concentration where the deterioration rate due to air pollution becomes less significant than deterioration due to other mechanisms. Fenech *et al.* (2012) used a dose-response function to examine the impact of temperature, RH and the concentration of acetic acid on the deterioration of dyes in colour photographs. The study revealed that a 1°C increase in temperature will cause the same increase in the degradation of dyes in colour photographs as an about 650 ppb (1624 $\mu\text{g m}^{-3}$) increase in the concentration of acetic acid in air. The degradation of dyes in colour photographs due to acetic acid will be less significant than deterioration due other mechanisms as temperature at the organic acid concentrations typically found in heritage institutions (see review Smedemark, 2018).

Ligterink and Di Pietro (2018) used a simple equilibration process instead of the dose-response function to model the acetic acid adsorption onto paper. The model predicted a negligible impact of acetic acid on paper samples with a pH from 3-5 and 9-11 and a limited impact for paper samples with a pH from 6-9. An acetic acid concentration of 150 ppb (368 $\mu\text{g m}^{-3}$) over 100 years only gave rise to a 2% decrease in the degree of polymerization for paper with a pH from 6-9. More research is needed to establish the '*operational threshold*' where the degradation of heritage collections in storage due to organic acids becomes less significant than deterioration due to other mechanisms.

Tétreault (2003) on the other hand introduced a framework with the '*no-observed adverse effect level*' (NOEAL) and the '*lowest-observed adverse effect level*' (LOAEL) for different pollution levels at different exposure times. The definition of NOEAL is the concentration of air pollution that does not produce an observable effect on an object in a specific time period. The concentration level is estimated from quantified adverse effects published in the literature.

Lead is particularly sensitive towards organic acids and will reach its NOEAL value after 100 years at 200 $\mu\text{g m}^{-3}$ formic acid and copper after 1000 years at 8000 $\mu\text{g m}^{-3}$. For acetic acid, lead will reach its NOEAL value after 100 years at 400 $\mu\text{g m}^{-3}$, cotton after 100 years at 4000 $\mu\text{g m}^{-3}$, calcareous materials after 100 years at 10.000 $\mu\text{g m}^{-3}$ and above 1000 years for tarnished lead and zinc at 3000 $\mu\text{g m}^{-3}$ and 20.000 $\mu\text{g m}^{-3}$ respectively (Tétreault, 2003). The highest organic acid concentration measured in the store with semi-passive climate control was 134 $\mu\text{g m}^{-3}$. The concentration was thus below the threshold even for lead that is particularly sensitive towards organic acids with no-observable adverse effect after 100 years.

This Ph.D. project demonstrated that storage buildings with semi-passive climate control can provide an acceptable climate and air quality performance for the preservation of heritage collections at a significantly lower energy use than mechanical ventilation. The study also confirmed that lowering the temperature in unoccupied stores will reduce the formic acid and acetic acid concentrations in indoor air and thereby the need for active air filtration (Smedemark and Ryhl-Svendsen, 2019; Smedemark *et al.*, 2019b).

Storage buildings with semi-passive climate control can provide economic and environmentally sustainable storage solutions for the preservation of heritage collections. Whether to install active air filtration will ultimately depend on the formic acid and acetic acid threshold levels that caretakers are willing to accept. The results from the Monte Carlo simulations questions whether active air filtration can be justified at all.

7. Conclusion

This Ph.D. project examined the route of organic acids in storage buildings from emission sources, such as the collections themselves, to removal through air exchange with ambient, active air filtration and deposition onto interior surfaces.

Altogether, 36 VOCs were identified as emission substances from paper. Organic acids were the most abundant compounds detected in air from all samples. The mass-specific emission rates of formic acid and acetic acid ranged from 12 to 468 ng g⁻¹ h⁻¹ from six paper samples at normal indoor room conditions (22°C, 50% RH). The area-specific emission rates of formic acid and acetic acid ranged from 10 to 259 µg m⁻² h⁻¹ from six naturally aged wood and paper samples while cellulose acetate films emitted above 3000 µg m⁻² h⁻¹ at indoor room conditions (23°C, 50% RH).

The area-specific emission rate of organic acids from the wood packaging material used to transport and store collections was 303 µg m⁻² h⁻¹. The Monte Carlo simulations predicted that using alternative non-emissive transport and storage materials will reduce the organic acid concentration with 29% in indoor air. Alternative storage materials should therefore be explored to diminish its contribution to the concentration in air.

The field measurements demonstrated that both storage buildings with a HVAC system and with semi-passive climate control can provide an acceptable protection from outdoor air pollution. The concentration of ozone and nitrogen dioxide diminished to below 9% from outdoor and the indoor atmospheric corrosivity was very low for zinc and copper in both stores.

The spatial temperature and moisture distribution were almost uniform except for a weak vertical temperature gradient causing a RH gradient opposite to that of temperature. The temperature varied seasonally from about 7°C in winter to 19°C in summer in both stores. The energy use in Storage I with a HVAC system was 67 kWh m⁻³ year⁻¹ while the energy use in Storage II with semi-passive climate control was only 1.1 kWh m⁻³ year⁻¹. Both storage buildings upheld an acceptable climate performance with appropriate temperature and moisture distributions and without air pockets producing problematic microclimates.

The spatial organic acid distribution in Storage I was controlled by the HVAC system. The spatial organic acid distribution showed areas in the storage room with semi-passive climate control and a mixed material collection where incomplete mixing caused a local accumulation of organic acids. The concentration difference between the room with a paper-based archival collection (2 to 21 µg m⁻³) and the room with a mixed material collection (45 to 134 µg m⁻³) in Storage II with semi-passive climate control indicated that other parameters than the ventilation form affected the concentration of organic acids. The indoor atmospheric corrosivity towards lead corresponded to a pure atmosphere in both stores. This study demonstrated that both storage buildings provided an acceptable air quality performance irrespective of the ventilation form.

The removal efficiency was highest for the activated carbon filter specifically designed to remove formic acid and acetic acid in heritage environments. The formic acid and acetic acid removal efficiency depended on the airflow through the filters and varied considerably *in situ* from the removal efficiency obtained at laboratory conditions. An increase in the airflow through the filters from normal ventilation conditions (50% fan power) to full fan power (100%) reduced the organic acid removal efficiency from 77% to 7% for the filter designed to remove outdoor air pollution, and from 92% to 24% for the filter designed to remove organic acids.

The desiccant silica gel rotor used for dehumidification in storage buildings efficiently removed 98-100% acetic acid from the process air. The removal efficiency was independent of the RH in the range between 25% to 70%. The clay brick wall passively reduced the concentration of acetic acid close to the wall with 56%, as compared to the free room air. Furthermore, the use of construction materials as unfired clay brick can be used both to remove organic acids from indoor air and buffer the RH.

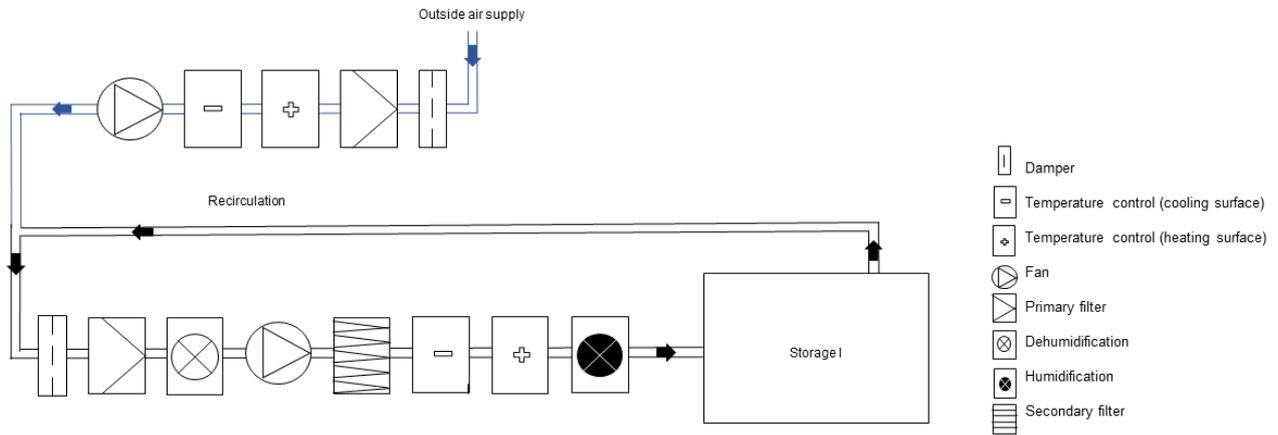
The Monte Carlo simulations predicted that active air filtration only removes a minor fraction of the formic acid and acetic acid from indoor air while a fraction will deposit back onto interior surfaces. The reduction in formic acid and acetic acid concentrations due to active air filtration measured in the middle and in the corner of both storage buildings didn't stand out from the natural variation. A cautious conclusion on the Monte Carlo simulations is that active air filtration is unnecessary in storage buildings with semi-passive climate control. More data is needed to further validate the model.

This Ph.D. project confirmed that temperature is the most efficient control methods to reduce the organic acid emission rate from the collections and its concentration in storage buildings. Lowering the temperature from 23 to 10°C reduced the TVOC emission and led to a 2-16 times reduction in the organic acid emission from wood and paper present in heritage collections. A similar organic acid behaviour was observed in several storage buildings where the decrease in temperature from summer to winter reduced its concentration in indoor air.

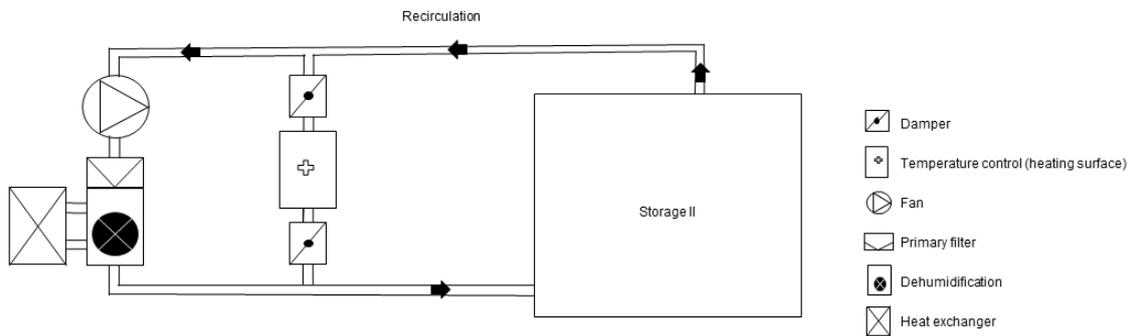
Several heritage institutions will within the years to come invest in new storage buildings or upgrade existing ones to improve the climate and air quality conditions for the preservation of heritage collections. This Ph.D. project confirmed that storage buildings with semi-passive climate control can provide an acceptable climate and air quality performance for the preservation of heritage collections at a significantly lower energy use than mechanical ventilation. Furthermore, the project points to temperature as the most effective control method to reduce the formic acid and acetic acid concentrations in storage buildings and ensure sustainable storage solutions for the preservation of heritage collections for future generations. Storage buildings with semi-passive climate control will require periodic dehumidification in temperate climates as in Northern Europe and choosing a desiccant rotor will remove moisture as well as acetic acid from the indoor air. Whether to install active air filtration will ultimately depend on the organic acid threshold levels that caretakers are willing to accept, but the findings from this Ph.D. project questions whether active air filtration can be justified at all.

Supplementary information 1

Layout of the HVAC system in Storage I with heating, cooling, humidification, dehumidification and air filtration.

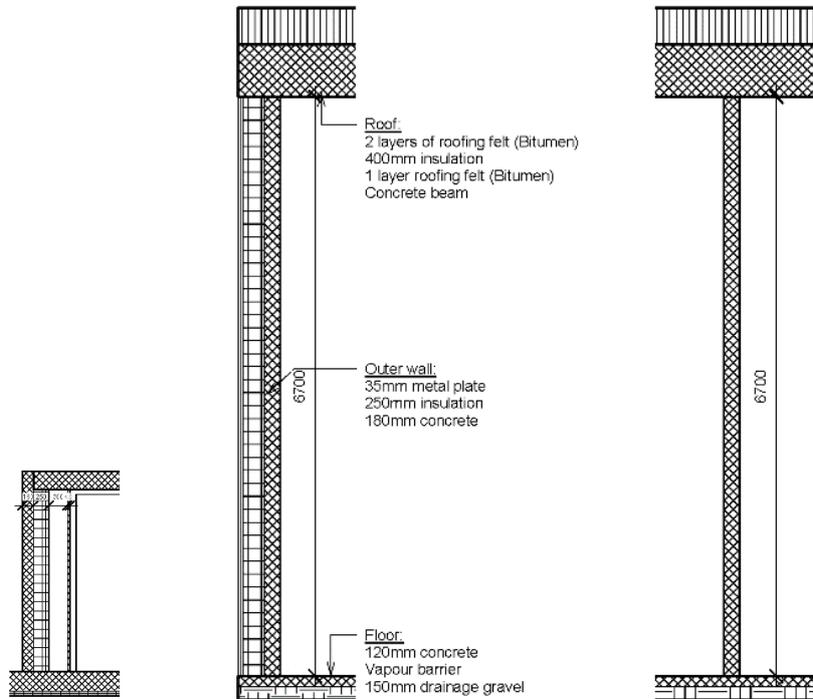


Layout of the ventilation system in Storage II. The system only contains internal dehumidification and a heating surface used only to dry out the building after construction.



Supplementary information 2

A detail showing the construction of the interior and exterior walls in Storage I and II.



All exterior walls in Storage I (left) have a glass facade while the interior walls of the storage area consisted of 180 mm concrete, 200 mm insulation, a vapour barrier, 50 mm insulation, 300 mm air gap and 40 mm concrete.

In Storage II (right) with semi-passive climate control, all exterior walls are made of 35 mm metal plate, 250 mm insulation and 180 mm of concrete. Interior walls are made of 180 mm of concrete. The floor was uninsulated and consisted of 120 mm concrete, a vapour barrier and 150 mm drainage gravel.

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Paper I

Smedemark, S.H.

‘The dynamics and control of indoor air pollution in repositories without mechanical ventilation for cultural heritage collections. A literature review’

ePRESERVATIONScience, 2018, **15**, 17-28.

THE DYNAMICS AND CONTROL OF INDOOR AIR POLLUTION IN REPOSITORIES WITHOUT MECHANICAL VENTILATION FOR CULTURAL HERITAGE COLLECTIONS. A LITERATURE REVIEW

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REVIEW PAPER

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Abstract

Airflow distributes contaminants inside buildings. Infiltration through unintentional openings in the building envelope controls the airflow in unoccupied repositories without heating, ventilation and air-conditioning (HVAC) systems. A restricted airflow may lead to the development of thermal stratification and "dead-spaces" where air pollutants emitted from construction materials or the heritage collection accumulates.

Heritage collections can act as both an emission source and a sink for carboxylic acids. Carboxylic acids can cause irreversible heterogeneous reactions with the surface of materials, e.g. tarnishing metals. It is therefore crucial to establish the dynamics of carboxylic acids inside repositories without HVAC systems, in order to determine and control its impact on the long-term preservation of heritage collections.

This paper presents a literature review on air dynamics and control of carboxylic acids inside unoccupied repositories without HVAC systems. It furthermore reviews reported levels of carboxylic acids found inside heritage institutions and sorbents used to remove them. Further research on air dynamics and whether carboxylic acids is removed primarily by deposition onto collections, or by filtration in HVAC systems inside heritage institutions is, however, necessary in order to establish the benefits of air filtration.

1 Introduction

It is crucial to determine the contribution of carboxylic acids emitted from objects in heritage collections and other indoor sources, as well as their distribution and removal on material surfaces inside heritage institutions, in order to assess air pollution's impact on the preservation of the collections. Carboxylic acids in air causes irreversible heterogeneous reactions with material surfaces, e.g. tarnishing metals¹⁻⁵, particularly lead⁵⁻⁷, formation of white crystalline deposits on glass⁸, efflorescence on seashells², limestone⁹ and ceramic¹⁰ leading to severe pitting and disruption of the surface and hydrolysis of paper leading to loss of physical strength and brittleness¹¹.

A well-documented example of the contribution from heritage collections to the contamination of air by carboxylic acids inside heritage institutions is the "vinegar syndrome", where autocatalytic deterioration of cellulose acetate, especially photographic film introduced in the first half of the 20th century, due to hydrolysis of acetate groups in the polymer structure releases acetic acid and thereby causing deterioration of collection items stored in the vicinity¹².

This paper presents a literature review on air dynamics and control inside unoccupied repositories without heating, ventilation and air-conditioning (HVAC) systems. Section 2 lists the principal building design of unoccupied repositories with semi-passive climate control as found in several Danish storage facilities with heritage collections. Information from a state-of-the-art repository in Vejle, Denmark, with semi-passive climate control is used as an example; however, the data is applicable to other countries as well.

received: 28/06/2018
accepted: 27/11/2018

key words:
carboxylic acid, indoor air quality, cultural heritage, air dynamics, passive climate control

Section 3 describes airflow due to infiltration in repositories without HVAC systems. Section 4 describes outdoor and indoor air contaminants and levels of carboxylic acids previously measured inside heritage institutions. Section 5 list methods to control air contaminants continuing into section 6 with a focus on sorbents used to remove carboxylic acids by passive or active means. The paper draws attention to the lack of research on carboxylic acids dispersion inside unoccupied repositories without mechanical ventilation systems.

2 Unoccupied repositories without mechanical ventilation

A rough estimate predicts that in Europe buildings contribute with 40% of the anthropogenic emission of greenhouse gases and that ventilation including heating and air-conditioning accounts for one third of the energy use in buildings¹³. Controlling climate conditions inside heritage institutions with narrow permissible fluctuations increase the energy consumption in HVAC systems. Research by Mecklenburg and Tumosa¹⁴ based on museum buildings of the Smithsonian Institution show that permitting a fluctuation larger than $\pm 5\%$ in the relative humidity set point values increases energy savings significantly. A case study by Hong *et al.*¹⁵ in a museum exhibition showed a 40% decrease in energy consumption when increasing the allowable fluctuation from $50 \pm 2\%$ RH to $50 \pm 10\%$ RH, and Ascione *et al.*¹⁶ found an energy saving as high as 43% when introducing a seasonal adjustment to the set point of the HVAC system.

Within recent years a growing amount of research, roundtable discussions and conferences in the cultural heritage sector have addressed the need to revise control strategies for a sustainable management of the long-term preservation of collections¹⁵⁻²⁹. This has pushed forward the development of unoccupied repositories without HVAC systems using passive or semi-passive climate control to provide acceptable hydrothermal conditions.

The most widespread principle for passive climate control is to use a well-insulated building envelope with high thermal inertia, to buffer against daily fluctuations in the outside climate, placed on an uninsulated concrete floor acting as a cooling source during summer and heating source during winter³⁰⁻³⁵. In regions with considerable temperature differences between seasons, as in Northern Europe, buildings with a high thermal inertia will have an inside temperature below the outdoor in summer and above in winter. The building envelope will buffer seasonal fluctuations in temperature to a lesser extent than daily fluctuations.

Several repositories with semi-passive climate control have been built in Denmark where one of the earliest is a storage facility at The Centre for Preservation of Cultural Heritage in the region of Vejle³⁶⁻³⁸ (Figure 1).

The first part of the storage facility in Vejle was constructed in 2003 and it has since then been expanded in 2013 and will expand again within the next couple of years. Due to the insulation and the thermal inertia of the construction, the indoor temperature is extremely stable on a daily basis, but varies seasonally between 8 °C in winter and 16 °C in summer³⁷ (Figure 2).



Figure 1: A state-of-the-art storage facility in the region Vejle, Denmark, for general museum collections with semi-passive climate control. What is noticeable is how the facility consists of large storage halls with museum collections stored closely packed on mobile shelving with a large loading of collection materials in a small space. Collections made of diverse materials are stored together.

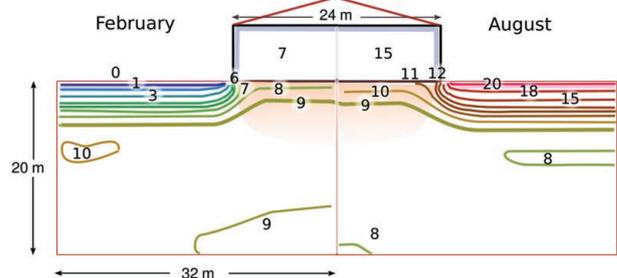


Figure 2: Computer simulation of the temperature in a repository with passive climate control. The building is constructed with a well-insulated building envelope with high thermal inertia placed on an uninsulated concrete floor. Based on outside climate conditions in Denmark the simulation show a winter scenario where the temperature fluctuates from down to 7°C in winter (left side) up to 15°C in summer (right side). (Reproduced with permission by T. Padfield³⁴ based on a simulation by Bøhm and Ryhl-Svendsen³² using the COMSOL Multiphysics® Modelling Software).

The relative humidity inside the repository is kept constant by recirculating the air internally through a dehumidifier, consuming only 1.5 kWh annually per cubic metre of storage space³⁸⁻³⁹. Infiltration through unintentional leaks in the building envelope and opening of doors fitted with two-door airlocks is the only factors which affects the exchange of air with ambient. This result in a low air exchange rate of 0.04 to 0.05 h⁻¹.³⁹

3 Airflow in buildings

Air dynamics inside museum enclosures, e.g. display cases, have been described by Padfield⁴⁰, Thomson⁴¹, Brimblecombe⁴² and Michalski⁴³. In buildings, airflow can be divided in two categories: ventilation and infiltration (see ASHRAE⁴⁴ for general terminology). Ventilation is the intentional process of supplying or removing outside air into a building. The ventilation effectiveness is a measure of the air distribution system's ability to remove contaminants from the indoor environment by replacement with new air. Ventilation is further divided into mechanical ventilation, where fans control the intake, distribution and exhaust of air from outside, and natural ventilation, where air enter the building through intentional openings in the building envelope e.g. windows or ventilation grates.

Infiltration causes an unintentional exchange of air. Kalamees⁴⁵ investigated infiltration in residential houses in Finland and found that infiltration typically were through openings such as cracks around doors and window frames, and in the intersection between walls and floor or ceiling. The opposite airflow, from inside to outside, is referred to as exfiltration.

Pressure differences across the building envelope caused by wind and temperature drives infiltration. Wind induces a high-pressure on the windward areas of a building envelope and a low-pressure on downwind areas⁴⁶. The pressure difference will create an airflow from high-pressure towards low-pressure areas horizontally across the building envelope. The pressure depends on wind direction, wind speed, the surrounding terrain and proximity to other buildings⁴⁷. Wind will lose its force and be redirected due to friction and obstacles in the terrain and exposed buildings can therefore be sheltered from wind driven infiltration by planting trees, etc⁴⁸.

A higher temperature inside a building than outside will cause air to infiltrate through openings at ground level, rise up and escape through openings at the top of the building, and by this generating a vertical airflow. When the inside air temperature is lower than outside the airflow will be reversed. This phenomenon is called the stack-effect and depends on the building height and the temperature difference across the building envelope⁴⁹⁻⁵⁰. Infiltration or the airtightness of a building can be measured using the fan pressurization test⁵¹ or calculated using the European standard 16798-7:2017 (*Calculation Methods for the Determination of Airflow Rates in Buildings Including Infiltration*)⁵².

Disregarding the internal airflow resistance the stack pressure difference per meter building height per temperature difference (°C) between inside and outside is around 0.02 Pa. The outside wind pressure is generally 1-2 Pa at low wind speed (below 2.5 m s⁻¹) and 25 Pa or more at higher wind speed (above 10 m s⁻¹)⁵³. In most situations, a combination of wind and temperature pressure differences persist as the driving force however, as the wind speed decreases, infiltration due to the stack effect starts to dominate⁵⁴. In buildings with a mechanical ventilation system, the unintentional infiltration of outside air can be controlled by enhancing the pressure difference across the building envelope⁵⁵.

A disadvantage of infiltration is that the airflow into and distribution within the building is unstable. This can lead to thermal stratification and the development of "dead-spaces" with static conditions where the airflow is insufficient for the dilution of internally generated air pollutants⁵⁴. The largest temperature gradient measured in the storage facility Vejle was only 2.7 °C between the room air at 5.8 m above the floor (0.5 m below the ceiling) and the floor surface³⁸. Ryhl-Svendsen⁵⁶ showed that inadequate airflow (0.3 h⁻¹) in a room without mechanical ventilation led to a concentration gradient of carboxylic acids across a room with a three times larger concentration close to the emission source compared to an adsorbing clay wall.

3.1 Airflow through large openings

Infiltration will depend on the airflow through doors, as their size, opening time and frequency increases⁵⁰. Single-sided open door airing in historical churches can increase the air exchange rate approximately ten times⁵⁷. European standard 16893:2018 "*Conservation of Cultural Heritage. Specifications for location, construction and modification of buildings or rooms intended for the storage or use of heritage collections*"⁵⁸ recommends using two-door airlocks in repositories with heritage collections in order to reduce infiltration from outside and between varying climate sections. The driving force for airflow through large openings inside a building is a temperature difference between sections⁵⁷. Ryhl-Svendsen *et al.*³⁹ measured the airflow between two sections inside the storage facility in Vejle with semi-passive climate control, and found a two-six times larger internal air exchange rate between one section and the other as compared to the exchange with outside air.

4 Air pollution

Air pollution can originate, from sources outside and inside buildings. Two comprehensive reviews on air pollution in museums are provided by Hatchfield⁵⁹, and Tétreault⁶⁰. Outside contaminants, e.g. ozone, sulfur dioxide, nitrogen dioxide, and hydrogen sulfide, are transported into buildings by airflow. The level of outdoor pollution inside heritage institutions have been extensively measured^{32,61-85}, together with a few studies on air quality in museum exhibitions in connection to human comfort⁸⁶⁻⁸⁷.

Typical indoor contaminants, e.g. volatile organic compounds (VOC) and carboxylic acids are emitted from indoor construction materials and heritage collections. Cellulose acetate¹², paper⁸⁸⁻¹⁰¹ wood¹⁰²⁻¹⁰³ and other materials, e.g. adhesives, paints, varnishes and plastics¹⁰⁴ found in cultural heritage collections release formic and acetic acid as secondary emission products during the material's own deterioration. The presence of acetic acid in indoor air has been identified as a marker of the chemical degradation of paper in library or archival collections⁸⁹. The emission of formic acid from wood is generally an order of magnitude lower than the emission of acetic acid, but still not negligible¹⁰².

The outdoor concentration of formic and acetic acid is approximately 0.75 ppb and 0.5 ppb¹⁰⁵, whereas Zhang *et al.*¹⁰⁶ measured a concentration of 8.77 ± 4.67 ppb for formic acid and 23.97 ± 16.20 ppb for acetic acid inside residential buildings. A concentration of formic acid and acetic acid up to 361 ppb has been measured inside repositories containing heritage collections⁹. Figure 3 collates reported measurements of formic and acetic acid levels inside exhibitions and repositories as well as some studies on display cases and microclimate frames for comparison^{2,8,39,74,76,82,107-120}.

Enclosures, e.g. microclimate frames, display cases and repositories containing a high loading of emissive construction materials and heritage collections can result in an accumulation of airborne contaminants to high concentrations. Thickett⁸⁴ measured a concentration of acetic acid close to 2000 ppb (converted from $\mu\text{g}\cdot\text{m}^{-3}$) in a display case inside The British

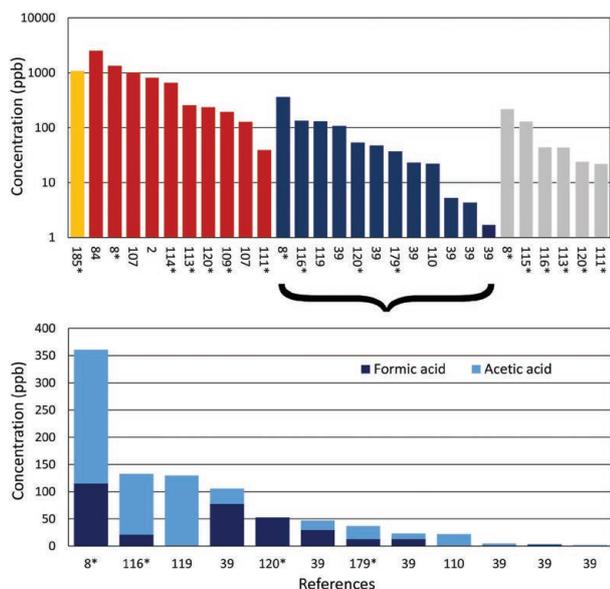


Figure 3: Concentration of carboxylic acids in heritage institutions as reported in literature. At the top diagram and displayed as sum of total carboxylic acids: inside a microclimate frame (yellow), display cases and cupboards (red), repositories (blue), and exhibitions (grey). Please note log scale, which is used due the large span of reported values. The bottom diagram zoom in on the observations from repositories and displays the fractions of formic and acetic acid concentration. Only observations of concentrations above the detection limit are included. In cases where a concentration was given as a range, the highest concentration value is used. Numbers on x-axis gives the literature reference. If (*) the concentration value was given as $\mu\text{g}/\text{m}^3$ in the original reference, but converted to ppb by this author.

Museum in London, Great Britain, whereas Godoi *et al.*¹¹¹ detected a concentration down to around 10 ppb (converted from $\mu\text{g}\cdot\text{m}^{-3}$) in a display case inside The Rubens House Museum in Antwerp, Belgium. Ryhl-Svendsen *et al.* found a concentration of formic and acetic acid down below 2 ppb in repositories with semi-passive climate control, including a concentration of 4 ppb inside the Centre for Preservation of Cultural Heritage in the region of Vejle, Denmark³⁹. Robinet *et al.* detected a concentration of formic and acetic acid up to 361 ppb in the National Museum of Scotland⁸. A reduction in the air exchange rate with the intention of reducing the ingress of outside contaminants and maintaining stable climate conditions can further contribute to the accumulation of indoor air pollutants.

4.1 Emission

Several transport processes control the emission of carboxylic acids from materials. The two main processes are diffusion within a material and surface emission¹²¹. Fick's Second Law describes diffusion through a material over time. The diffusion rate depends on temperature, pressure or concentration gradient and on the molecular weight and size of the compound. The diffusion coefficient for formic and acetic acid at room temperature is $1.53 \times 10^{-5} \pm 0.02 \text{ m}^2 \text{ s}^{-1}$ and $1.24 \times 10^{-5} \pm 0.02 \text{ m}^2 \text{ s}^{-1}$ respectively¹²².

The surface emission rate (evaporation) depend on the concentration gradient across the surface (as described by Fick's First Law) and is influenced by factors such as the surface air velocity¹²³⁻¹²⁴. A number of studies investigate the emission rate from wood¹²⁵⁻¹²⁶ including wood used in display cases^{103,127}. Risholm-

Sundman *et al.*¹²⁵ measured a surface specific emission rate (*mass emitted per surface area per hour, SERa*) of VOC including acetic acid from natural wood ranging from below $10 \mu\text{g m}^{-2} \text{ h}^{-1}$ from birch to $2800 \mu\text{g m}^{-2} \text{ h}^{-1}$ from oak. Ramalho *et al.*⁹⁸ determined the mass-specific emission rate (*mass emitted per gram material per hour, SERm*) of acetic acid from a paper produced from pure cotton ($887 \pm 216 \text{ ng g}^{-1} \text{ h}^{-1}$) and one from ground-wood pulp ($4820 \pm 1120 \text{ ng g}^{-1} \text{ h}^{-1}$) after accelerated ageing. However, the emission rate from heritage collections under climate conditions typically present in unheated repositories are less studied.

4.2 Modelling airflow

Airflow transports contaminants into and around inside buildings. The dynamics of air inside buildings can be predicted and described by mathematical modelling and computational fluid dynamics (CFD) simulations. Nazaroff and Cass developed a general mathematical model to predict the concentration of chemical reactive compounds in indoor air¹²⁸. Evola & Popov¹²⁹ showed that the Renormalization Group (RNG) theory model is useful to assess air exchange rates and the distribution of air inside buildings with natural ventilation. Özgür & Abo-Serie¹³⁰ assessed the natural airflow in a museum using CFD simulations. They showed that within the building, some areas had restricted air movement, and the authors recommend opening windows and doors to increase the ventilation effectiveness. Grau-Bove *et al.*¹³¹ analysed the penetration, dispersion and deposition of particles in a historical house using CFD simulations, and compared the results with field measurements. Their research showed that while the ingress rate of particles was controlled by wind direction and pressure, the amount of particles that reaches a surface ultimately depended on the operation of the ventilation system.

The Innovative Modelling of Museum Pollution and Conservation Thresholds (IMPACT) model was developed during the European research project by the same name, for the use of estimation of concentration and deposition of outdoor pollutants inside museums¹³²⁻¹³⁴. The IMPACT model was based on the indoor to outdoor pollution ratio model by Weschler *et al.*¹³⁵ originally developed for ozone. A corresponding software model is not available for indoor generated air pollution.

5 Control of air pollution

Michalski¹³⁶ and Tétreault⁶⁰ presents a framework of five levels of control: *avoid, block, detect, respond and treat* for the protection of heritage collections against various agents of deterioration: one being contaminants. Within the framework, the preservation of a collection is continuously assessed at the five levels of control. This section discusses the first two levels *avoid* and *block*. The last three levels will not be part of this review.

For outdoor air pollution the first control level is to avoid sources. Placing heritage institutions in areas without exaggerated pollution levels, e.g., away from heavy traffic, industry, etc., will reduce the presence of outside pollutants. The importance of this was exem-

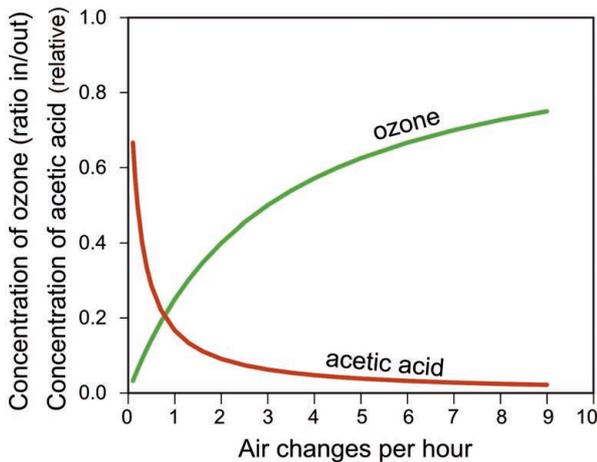


Figure 4. The concentration of outdoor generated ozone and indoor generated acetic acid as a function of the air exchange rate. (Reproduced with permission from Ryhl-Svendsen et al.³³).

plified in the ENVIRONMENT leather project comparing the impact of air contaminants from outside on two identical sets of vegetable tanned leather books, one set stored at the British Library in central London, and another at the National Library of Wales in Aberystwyth¹³⁷⁻¹³⁹. The project illustrated that historically high pollution levels in central London resulted in an increase in the deterioration of book collections compared to the less polluted Aberystwyth.

For indoor pollutants, the first step of control is to avoid construction materials in exhibitions, repositories and display cases, which contribute to the emission of harmful contaminants. However, the contribution of emission products from the collection items cannot be avoided, although emissive and susceptible collection items may be divided into different sections of storage (block action) except for composite items, which at the same time are both emissive and susceptible.

The second step for the control of outdoor contaminants is to block or remove them from the air entering the building, and before it deposit onto the collection. Particle deposition modelling have showed that filtration in mechanical ventilation systems and reducing the air exchange rate are the most effective control strategies to reduce the transport of particles into heritage institutions¹⁴⁰. A study by Ryhl-Svendsen¹⁴¹ showed that installing a mechanical ventilation system in a previously naturally ventilated repository increased the concentration of outdoor air pollution despite the use of filtration. Both studies indicate that reducing the airflow will reduce the transport of contaminants into a building. In occupied exhibitions, however, a supply of "fresh air" is necessary to comply with human comfort requirements¹⁴² and at the same time dilute internally generated air pollutants³³. This is demonstrated in Figure 4, which show how the concentration of an outdoor pollutant such as ozone will increase indoors as the air exchange rate increases (see section 5.1.1). In contrast to this, the concentration of internally generated contaminants, e.g., acetic acid, will decrease with increasing air exchange, and vice-versa other parameters being equal.

5.1 Modelling indoor air pollution

The concentration of indoor generated air pollution can be calculated from the following mass balance, assuming no contribution of pollutants from outside:

$$C_i = G/V (n + v_d A/V) \quad (5.1)$$

where C_i is the indoor concentration of air pollutant at steady-state ($\mu\text{g m}^{-3}$), G is the generation rate of pollutant ($\mu\text{g h}^{-1}$), V is the air volume (m^3), n is the air exchange rate (h^{-1}), v_d is the deposition velocity (m h^{-1}) (see section 5.1.2.1) and A is the surface area of the enclosure (m^2)¹⁴¹.

Air contaminants are mainly removed by ventilation, sorption onto surfaces inside the building, and chemical reactions in air¹⁴³. Air pollution measurements performed in cultural heritage institutions have additionally shown a decrease in the concentration of formic and acetic acid from higher summer to lower winter temperatures^{39,115} stressing the use of temperature as a mean to control carboxylic acid emission from materials.

5.1.1 Air exchange rate

The air exchange rate is a measure of the air volume in an enclosure (e.g., building, display case) which is replaced with outside air per unit of time:

$$n = Q/V \quad (5.2)$$

where n is the air exchange rate (h^{-1}), Q is the airflow ($\text{m}^3 \text{h}^{-1}$) and V the volume of air (m^3). The ASTM¹⁴⁴ "Standard Test Method for Determining Air Change in a Single Zone by Means of a Tracer Gas Dilution" describes three methods to measure the air exchange rate across a building envelope by using a tracer gas: the concentration decay method (based on the measured rate of which a finite amount of tracer gas injected into a room will decrease in concentration over time), the constant injection method (based on the measured steady-state concentration of a tracer gas injected into the room at a constant rate), and the constant concentration method (based on the measured amount of constantly dosed tracer gas necessary to maintain a constant concentration in the air). The latter is especially useful for measuring short-time variations of the air exchange rate.

In residential buildings uncontrolled infiltration of outside air result in an air exchange rate of approximately $1-4 \text{ h}^{-1}$ for new and $4-10 \text{ h}^{-1}$ for old buildings⁴⁶. Inside repositories containing heritage collections, the air exchange rate can be significantly lower. Thickett et al.⁸³ measured an air exchange rate between 0.28 h^{-1} to 0.93 h^{-1} inside library and archival collection storage facilities in the United Kingdom. Ryhl-Svendsen et al.³⁹ measured an air exchange rate down to 0.03 h^{-1} in repositories with passive and semi-passive climate control. Christoffersen¹⁴⁵ recommended keeping the air exchange rate below 0.1 h^{-1} in order to provide stable climate conditions in repositories with passive climate control.

5.1.2 Sorption

5.1.2.1 Deposition velocity

As outside air infiltrates through the building envelope the concentration of pollution in that air will constantly decrease as contaminants deposit onto surfaces inside the building. The rate of pollutant uptake by surfaces (the sink-effect) is commonly expressed by the deposition velocity (v_d). The deposition velocity depends firstly on the mechanisms that control the flow of pollutant towards the surface, and secondly on the physical or chemical interaction between the pollutant and surface¹⁴⁶. Nazaroff *et al.*¹⁴⁷ provides a detailed discussion of the deposition velocity concept; in brief the definition is the flux of a pollutant to a surface (F) divided by its concentration in air, and holds the unit of velocity (m h^{-1} or cm s^{-1}).

The deposition velocity of carboxylic acids is only known for a few materials, e.g., 0.005 cm s^{-1} of formic and acetic acid onto silver¹⁴⁸, 0.007 cm s^{-1} and 0.014 cm s^{-1} respectively onto copper¹⁴⁹, and between $0.00089 \text{ cm s}^{-1}$ and 0.0095 cm s^{-1} (converted from m s^{-1}) for acetic acid onto canvas¹⁵⁰. The deposition velocity of carboxylic acids to general interior surfaces has never been described, however, Grøntoft¹⁵¹ estimated a deposition velocity of 0.0016 cm s^{-1} (converted from m s^{-1}) of acetic acid inside museum display cases based on measurements and modelling. Ryhl-Svendsen¹⁵² suggested a deposition velocity of 0.002 cm s^{-1} formic and acetic acid inside heritage repositories using mass-balance modelling.

5.1.2.2 Surface removal rate

A useful factor used to describe sorption of air contaminants to a surface is the surface removal rate (S), defined as the deposition velocity multiplied by the surface-to-volume ratio of the enclosure:

$$S = v_d A/V \quad (5.3)$$

where v_d is the deposition velocity (m h^{-1}), A the surface area of the material (m^2) and V the volume (m^3). The surface removal rate has the unit reciprocal time (h^{-1}) and is therefore directly comparable to the air exchange rate.

Several surface mechanisms control the removal of air contaminants by sorption¹³. Air pollution can be adsorbed by two mechanisms: physical or chemical adsorption. Physical adsorption involves a comparatively weak bond between the pollutant and sorbent surface. This process is reversible and desorption can occur due to changes in the concentration gradient between the sorbent and the airflow, or by an increase in temperature. Chemical adsorption involves an irreversible chemical reaction between the pollutant and sorbent.

Thickett⁸⁴ found a surface removal rate for organic acids inside display cases made of glass and powder coated metal of approximately 0.0042 h^{-1} to 0.0063 h^{-1} (converted from per day) whereas Ryhl-Svendsen¹⁴¹ calculated a surface removal rate of 0.26 h^{-1} for organic acids in repositories with brick walls and filled with heritage collection items.

5.1.3 Chemical reactions in air

In cases where chemical reactions in air are fast enough to dominate over the rate of removal by the air exchange or surface reactions they will cause a sink-effect¹⁵³⁻¹⁵⁴. However, no chemical reaction with carboxylic acids will occur at the air exchange rates typically found inside buildings¹⁵⁵.

5.1.4 Temperature

The primary emission of VOC from building products, paints, varnishes, etc., depend on temperature^{121,156-157}. For the same reason the level of carboxylic acids inside display cases^{151,158} and heritage repositories^{39,115} depend on temperature (as well as other environmental parameters). Krupinska *et al.*¹¹⁵ found a five to six times increase in the concentration of carboxylic acid in The Plantin-Moretus Museum/Print Room Antwerp, Belgium, and Ryhl-Svendsen *et al.*³⁹ found an up to six times concentration increase in unheated storage buildings in Denmark from winter to summer.

Brimblecombe and Grossi¹⁵⁹ predicted that the in the future increasing temperature due to global warming will lead to a greater impact from carbonyl compounds such as formic and acetic acid. Krupinska *et al.*¹¹⁵ and Ryhl-Svendsen *et al.*³⁹ both recommend reducing the temperature in repositories to improve the preservation of cultural heritage collections.

6 Sorbents

Sorbent media are used to remove contaminants actively by passing air through filters in ventilation systems, or passively as reactive interior surfaces inside buildings. Blades *et al.*¹⁶⁰ propose to reduce the air exchange rate and recirculate air through filters inside buildings in order to reduce the ingress of contaminants from outside and the cost of air-conditioning. Ryhl-Svendsen & Clausen¹⁶¹ showed that recirculating internal air through activated charcoal filters impregnated with potassium permanganate inside a storage room was generally the most effective method to reduce contaminants from outside, as compared to mechanical ventilation with filtration, or passive sorption on active wall materials. Ryhl-Svendsen⁵⁶ showed that installing a wall of unfired clay bricks inside a room passively reduced the concentration of organic acids by 71%, due to the sorption of acid onto the clay. The loading of the clay bricks was rather high with a surface-to-volume ratio of $0.46 \text{ m}^2 \text{ m}^{-3}$. Passive sorption performs better in small repositories compared to larger ones due to a higher ratio of surface-area to volume¹⁶¹.

Several studies points to activated charcoal as the most efficient sorbent for carboxylic acid removal in heritage institutions^{150,162-164}. Carbonaceous materials, such as wood, nutshells, peat, hard coal or lignite is used to produce activated charcoal. A sorbent's removal capacity depends on its surface area, with one gram of activated charcoal having a surface area (depending on the type) of above 1000 m^2 .⁴⁶ Activated charcoal can furthermore be impregnated, often by an alkali such as KOH, to enhance its removal efficiency towards specific contaminants, i.e. acids. The advantage of impregnated activated charcoal filters is that

the contaminants adsorb irreversibly whereas concern about saturation and re-release (desorption) of previously adsorbed contaminants from non-impregnated activated charcoal have been raised¹⁶⁵. However, research by Thickett and Short-Traxler show no desorption of acetic acid from activated charcoal used to control the concentration of carboxylic acid passively in display cases¹⁶⁶.

According to Brokenhof¹⁶⁵ sorbents impregnated with potassium hydroxide will remove acetic acid more efficiently than sorbents containing calcium carbonate. Schieweck¹⁶⁴ showed that out of 39 sorbents zeolites, activated charcoal, and activated charcoal impregnated with an alkaline substance were the most efficient to remove formic and acetic acid. However, Schieweck¹⁶⁴ recommended using activated charcoal without impregnation due to its lower cost and good adsorption capacity.

European standard EN 16893¹⁶⁷ "Conservation of cultural heritage – New sites and buildings intended for the storage and use of collections" recommends using internal recirculation through activated carbon filters to remove air contaminants generated inside repositories with heritage collections, while ASHRAE¹⁶⁸ recommends the application of permanganate impregnated aluminium or activated carbon filters to remove acetic acid from air.

6.1 Justification of the use of air filtration

The increase in energy consumption of a HVAC system necessary to overcome the airflow resistance through filters have traditionally been assumed to account for the largest pressure drop of such installations¹⁶⁹. In residential and light-commercial buildings, filtration have been shown to account for 21-100% of the total pressure drop¹⁷⁰. However, new and more energy efficient filters are constantly being developed. Irrespective of the energy use for air filtration in HVAC systems there is a consensus on the benefits associated with filtration in connection to human comfort and productivity with several studies examining energy consumption and efficiency of air filtration¹⁷¹⁻¹⁷⁶.

Within heritage institutions, there is, however, an ongoing debate on the justification of air filtration for the removal of carboxylic acids inside buildings. Menart *et al.*¹⁷⁷ stated that the effect of acetic acid on the deterioration of paper collections is insignificant and therefore questions whether chemical air filtration in library and archival collections can be justified. Di Pietro *et al.*¹⁷⁸ additionally examined the use of air filtration from a cost-benefit perspective stating that carboxylic acids are expected to cause insignificant deterioration to library and archival collections, and in comparison with the associated expenses air filtration should be discouraged. Mašková *et al.*¹⁷⁹, on the other hand, concluded from outdoor and indoor air pollution measurements in five archives in Czech Republic, that only repositories with air filtration were suitable for long-term storage of archive and library collections.

Further research on air dynamics, and whether carboxylic acids are removed primarily by deposition onto the collections, on interior surfaces, or by filtration in HVAC systems, is however necessary to determine the

conservation benefits of filtration for heritage institutions.

7 Conclusion / Summary

Airflow transports and distributes contaminants inside buildings. Infiltration through unintentional openings in the building envelope controls the airflow in unoccupied repositories without HVAC systems. Ryhl-Svendsen *et al.*³⁹ measured an air exchange rate down to 0.03 h⁻¹ in repositories with passive climate control. A restricted airflow can lead to the development of thermal stratification and "dead-spaces" where air pollutants emitted from construction materials or the heritage collection accumulates. As shown by Ryhl-Svendsen⁵⁶ a low air exchange rate (0.3 h⁻¹) led to a concentration gradient of carboxylic acids across a room with a three times larger concentration close to the emission source compared to an adsorbing clay wall.

Carboxylic acids can cause irreversible heterogeneous reactions with the surface of materials e.g. tarnishing of metals. It is therefore crucial to establish the route and fate of air pollutants, including the fraction removed by deposition onto heritage collections inside repositories, compared to the fraction removed by recirculation through filters. Thickett⁸⁴ estimated a surface removal rate for carboxylic acids inside display cases from 0.0042 h⁻¹ to 0.0063 h⁻¹ and Ryhl-Svendsen¹⁵² 0.26 h⁻¹ in repositories.

The level of carboxylic acids inside repositories can be controlled by using non-emissive construction materials (avoiding the source) and by decreasing the temperature (reducing the emission rate). The use of active and passive sorbents will remove carboxylic acids from air (blocking the pollutant). Several studies points to activated charcoal as the most efficient sorbent for carboxylic acid filtration in heritage institutions^{150,162-164}. Passive sorption performs better in small repositories compared to larger ones due to a larger surface-area relative to the air volume¹⁶¹. Therefore, passive sorption is probably not efficient at removing carboxylic acids with a high loading of heritage collections stored in a small volume inside repositories with passive climate control only.

No studies on air dynamics inside repositories without mechanical ventilation systems used for the storage of cultural heritage collections were encountered during this literature review. Further research on air dynamics and whether carboxylic acids are removed primarily by deposition onto collections or by filtration in HVAC systems inside collection storage rooms is however necessary to determine the cost and benefits of air filtration.

8 Acknowledgement

The Independent Research Fund Denmark is acknowledged for supporting this work. The author thank Morten Ryhl-Svendsen for comments and advice, and Tim Padfield for the permission to reproduce Figure 2.

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Paper II

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‘The contributions of formic acid and acetic acid from paper to indoor air pollution in archives and its dependence on temperature’

Journal of Paper Conservation (accepted 18.09.2019, version for proof ahead of print).

Indoor air pollution in archives

Temperature dependent emission of formic acid and acetic acid from paper

Signe Hjerrild Smedemark* and Morten Ryhl-Svendsen

The overwhelming majority of library and archival collections are kept in storage. Paper collections themselves are a source of formic acid and acetic acid within the storage room. This paper investigates the concentrations of formic acid and acetic acid in three storage facilities during summer and winter as well as the temperature-related off-gassing of formic acid and acetic acid from six paper samples in a laboratory set-up. The study reveals a basic pattern in the formation of formic acid and acetic acid which was notably higher in summer than in winter at all three storage sites. The temperature-dependent changes of formic acid and acetic acid level during the seasons corresponds to the changes in off-gassing from the six paper samples measured in a laboratory set-up. The study indicates that reducing the temperature in storage facilities with libraries and archival collections will reduce the off-gassing of organic acids from paper and by this its concentration in air.

KEYWORDS: cellulose degradation, storage temperature, volatile organic compounds, formic acid, acetic acid, mass-specific emission rate, ion chromatography

Introduction

Libraries and archives are charged with the responsibility to collect, disseminate and preserve our written cultural heritage. The overwhelming majority of library and archival collections are almost constantly kept in storage facilities. Only few selected records may be requested for study at reading rooms elsewhere. The typical storage room holds as many records on as little space as possible, sometimes densely packed in movable compact-shelves. Following this, the so-called loading (amount of material per cubic meter of space) of paper in archives can be extremely high.

The long-term preservation of paper collections is largely determined by the environmental conditions; primarily the temperature and relative humidity (RH) (Strlič and Kolar 2005). In addition, the composition of the paper influences its rate of decay, depending on the chemical stability of the different components. Generally, the rate of chemical degradation of organic materials follows an Arrhenius style function, in which a 5°C temperature increase roughly halves the life span of a stored object (Michalski 2002). As one of the main decay mechanisms of cellulose is acid hydrolysis, the reaction rate is also influenced by the RH. If the indoor climate is warm and humid, the chemical reaction rate is fast, whereas if conditions are cool and dry then the reaction rate diminishes. By combining temperature- and humidity-dependent life-time functions, equal permanence can be drawn in a so-called isoperm matrix (Figure 1) (Sebera 1994).

The emission of several volatile organic compounds (VOC), including formic acid and acetic acid, have been identified from paper (Lattuati-Derieux et al. 2004, 2006; Gaspar et al. 2010; Clark et al. 2011; Bembibre and Strlič 2017). Other sources of VOCs in an indoor environment include construction materials, e.g. wood (Risholm-Sundman et al. 1998). Formic acid and acetic acid are believed to contribute to the degradation of paper (Tétreault et al. 2013), although the extent of the deteriorative effect of these compounds, as compared to other environmental risks, is debated (Ligterink and Pietro 2018).

It has, however, been pointed out, that the presence of these acids in the air serves as a marker of the rate of chemical processes within decaying paper (Dupont et al. 2007). The rate of which a material releases decay products (the emission rate) is proportional to the production rate within it. Typically, for characterizing e.g. building materials, emission rates are expressed as mass release per unit surface area per unit time (area-specific emission rate). However, for stacks of paper sheets it is difficult to determine the true surface area, and inspired by Ramalho et al. (2009), in this study we use instead 'mass-specific emission rate' (expressed as amount/mass (ng) of emitted acid per gram of paper, per hour).

The high loading of paper-based objects in a storage room may result in high concentrations of pollutants in the air. This is especially the case if, at the same time, the storage room has a low ventilation rate. This is not an unusual scenario in cultural heritage storage buildings, due to energy savings, and a little demand for comfort ventilation.

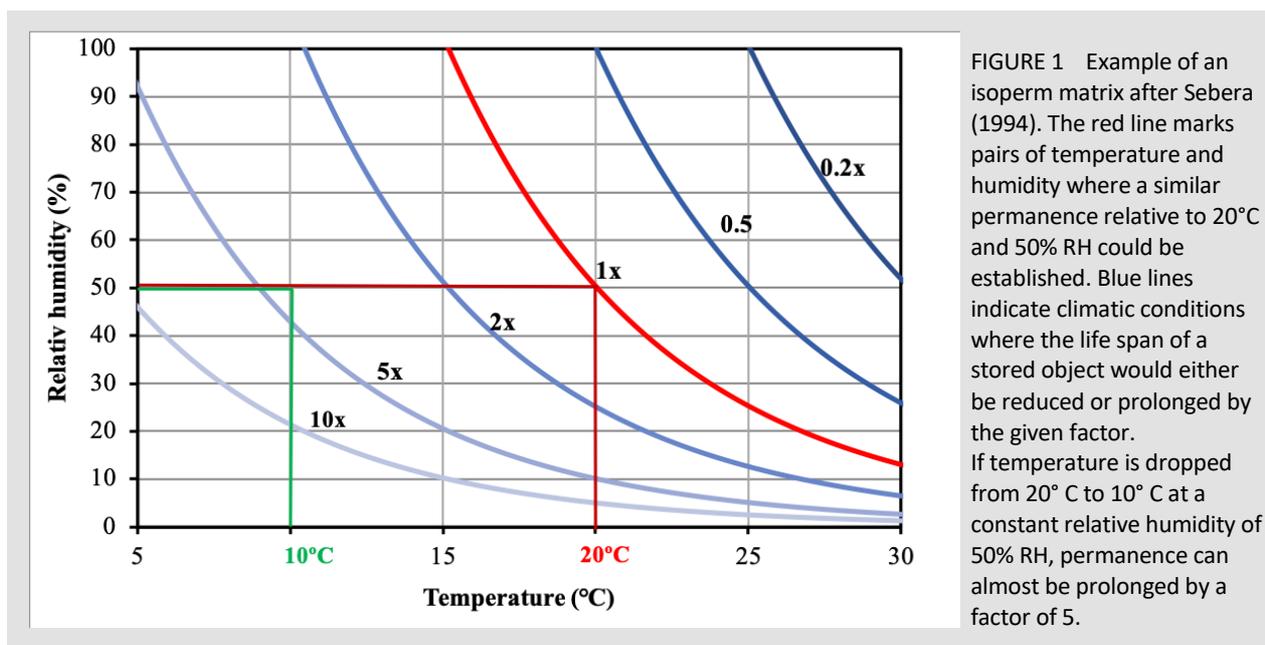


FIGURE 1 Example of an isoperm matrix after Sebera (1994). The red line marks pairs of temperature and humidity where a similar permanence relative to 20°C and 50% RH could be established. Blue lines indicate climatic conditions where the life span of a stored object would either be reduced or prolonged by the given factor. If temperature is dropped from 20° C to 10° C at a constant relative humidity of 50% RH, permanence can almost be prolonged by a factor of 5.

Likewise; for energy saving reasons, for institutions in temperate climate zones, the temperature within storage areas is often allowed to decrease in winter; the indoor climate in a typical Scandinavian archive could vary between 25°C in summer and 10°C during winter (Ryhl-Svendsen et al. 2012). It has been observed for museum storage rooms that the concentration of indoor air pollutants vary with seasonal change in temperature, while other influencing factors remain unchanged. For example, Ryhl-Svendsen et al. (2014) reported on museum storage rooms where the organic acid concentration in air decreased by more than 80% from summer to winter.

Experimental

In this paper, we report on observations from three different archival and library storage buildings, in which we have investigated the summer and winter conditions. Although the locations had differences in collection types, material loading, and building design, we observed a similar pollution behaviour.

The pollution levels observed in an archive reflect the absolute amount of VOCs emitted by the paper records, balanced against the amount that is removed through ventilation or resorbed back by adsorbing materials. Since numerous influencing factors are unknown (the ventilation rate, the total mass of paper, etc.) the estimation of the paper's emission rate is somewhat uncertain.

This led us to quantify the mass-specific emission rates from a selection of typical papers (historic and modern) in order to establish the fraction of indoor air

pollution in archives, which directly can be attributed to the collection itself. This was performed under laboratory conditions, at which the environmental conditions were controlled to mimic winter and summer indoor climate scenarios (10°C and 22°C).

Field test on three Storage Sites

Two storage sites of the Danish Royal Library were investigated: Vestindisk Pakhus is a historic former warehouse of Copenhagen Port (built in 1781), which now serves as a remote storage facility of the library. The storage rooms house mainly newspaper collections, with the bound newspapers stored on free-standing metal shelves, with an average room loading of about 61 kg paper per cubic meter of space.

The Slotsholmen storage area is part of the main library complex, in a building from 1906. This storage area contains mainly paper records kept in cardboard folding covers, stored on free-standing wooden shelves, at an average room loading of about 42 kg paper per cubic meter.

The third location was one floor of the storage facility of the Regional State Archive for Zealand (capital island of Denmark) in Copenhagen. The 'Koppel Wing' was a functional building, made of concrete and built as an archival store in 1966 [1]. The storage room contained paper records in boxes, on compact metal shelves, at an average room loading of about 69 kg paper per cubic meter of space.

The two Royal Library buildings were only climate controlled by heating in winter, and were without mechanical ventilation. The exchange rate with

ambient air was not measured, but based on previous measurements in other, comparable buildings, we estimate a passive air exchange of 2-3 room volumes per day (about 0.1 room volume per hour) (Ryhl-Svendsen et al. 2012). The Regional State Archive building was climate controlled by winter heating, and had forced mechanical ventilation at a rate of about 0.6 room volumes per hour. All three sites are located in central Copenhagen, Denmark.

Passive diffusion samplers

At all three sites the concentrations of formic acid and acetic acids were measured in the indoor air. The concentration of both acidic compounds was determined using a diffusion sampler for acid gases, mounted on an aluminium rack with metal spring clips, with sufficient distance from walls and other large, sorptive surfaces (Figure 2). Samplers were ring-shaped, with a highly porous membrane in front of a carbonate-impregnated filter, on which the gases were collected in “passive mode” by diffusion.

After about one month, the concentration of acid gases was analysed through aqueous extraction and ion chromatographic analysis, carried out by the Swedish Environmental Research Institute, IVL (Gothenburg, Sweden). The results expresses the average concentration during the sampling period (Ferm et al. 2002). The uncertainty of the method is expected to be about $\pm 20\%$.

Set-Up of laboratory measurements

Test papers

Six paper types were selected to represent the variation of paper types found in a typical library collection.



FIGURE 2 A passive diffusion sampler for formic and acetic acid mounted on an aluminum rack with a metal spring clip.

Two papers are modern standard test papers produced by Klug Conservation (Immenstadt, Germany): Novo Test Paper 1 contains mechanical wood pulp including 17% lignin, and Novo Test Paper 2 is a wood-free paper made from 100% bleached cellulose pulp. The four other samples are naturally aged historic papers, covering a period of almost 70 years of the 19th and 20th century. They originate from a test sample collection of the Royal Library in Denmark. The exact composition of the historic papers was not established, except for the presence of lignin, which was identified by the phloroglucinol spot test (TAPPI T401, 1992). The aqueous cold extract pH of the samples was

Paper Sample	Type	Year	pH	Lignin
#1	Novo Test Paper 1 (Klug art.-no. 007090)	2009	4.5 *	Yes
#2	Novo Test Paper 2 (Klug art.-no. 007091)	2009	4.6 *	No
#3	Book	1864	4.9	Yes
#4	Book	1930	4.6	No
#5	Newspaper	1895-96	6.1	No
#6	Newspaper	1946	3.5	Yes

Table 1 The characteristics of the six paper samples. pH values with an asterisk were determined with own measuring according to TAPPI T509 and differed slightly from the manufacturer's specifications.

determined according to TAPPI T509, 1992 and ranged between 3.5 and 6.1 (measured with a pH C2001-8 combination electrode attached to a MeterLab® PHM240 (both by Hach, Radiometer Analytical); see Table 1.

All paper samples were cut out from the middle of the book block or paper stack. They were cut in a small stack of 200 ± 1 g (weighed at 50% RH). All samples had roughly the same dimensions (and by this a uniform projected surface area) of about 9.0 x 9.0 x 5.0 cm.

Laboratory set-up

The emission of formic acid and acetic acid from the papers were collected in a 2.9 L glass test chamber (desiccator jar), which was ventilated continuously with clean air at a rate of 8 chamber volumes per hour.

The air was purified with activated charcoal, and conditioned to 50% RH by splitting the air stream in two, and bubbling one part of it through water (see Figure 3).

The tests were carried out at two temperatures; 10°C and 22°C, with the relative humidity maintained at 50% RH. The lower 10°C was obtained by placing the test chamber in a cooled water bath, insulated on top using polystyrene foam. The higher 22°C was controlled via the room temperature.

The paper samples were pre-conditioned to the climate inside the test chamber for at least 10 hours before sampling was initiated. The emitted organic acids were collected over a 24-hour period, by venting the chamber's exhaust air through two impingers which were connected in series, each containing 20 mL of 0.1 M NaOH.

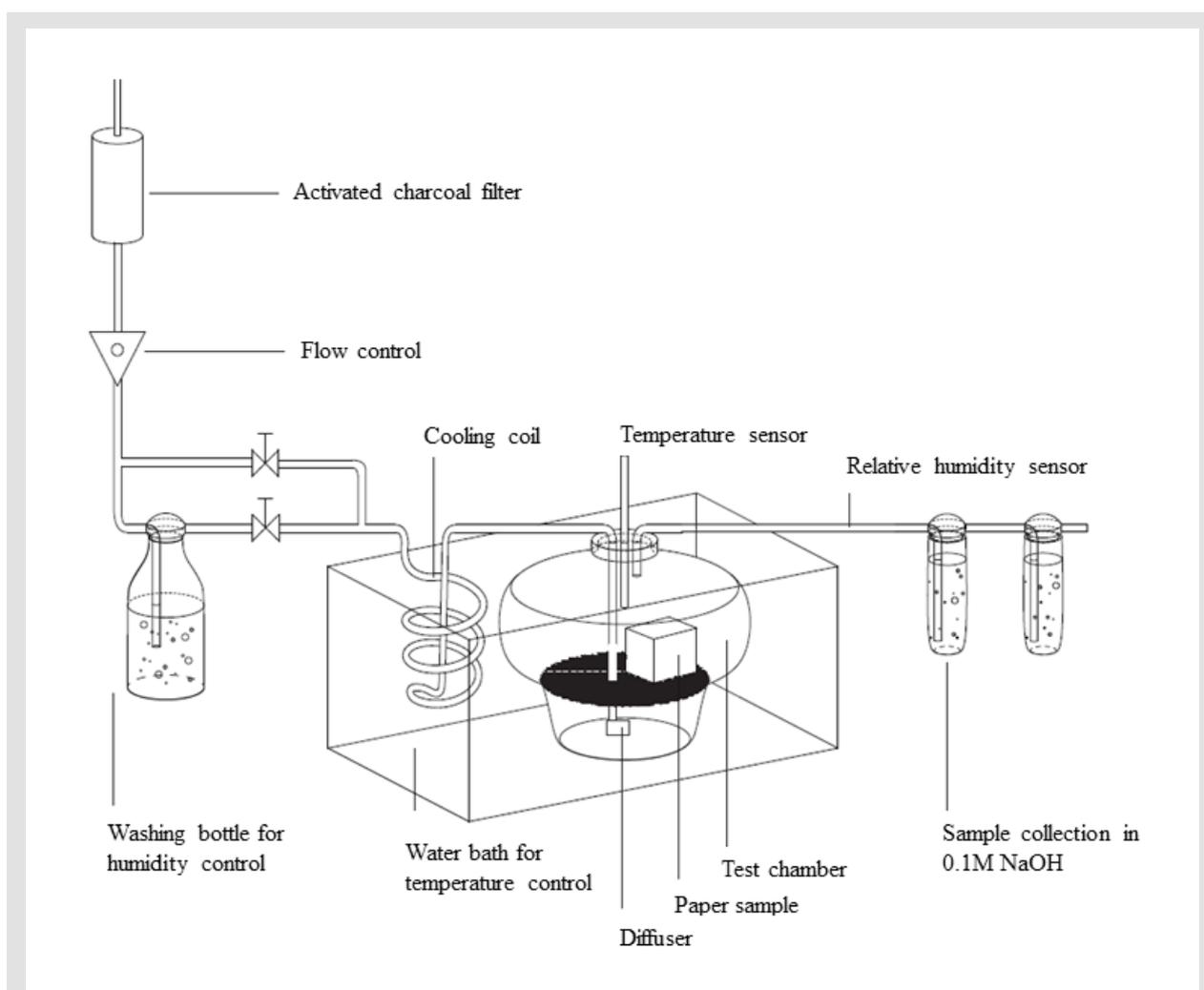


FIGURE 3 The test chamber set-up. Clean air was conditioned by splitting the air stream in two, and bubbling one part of it through a washing bottle with water. The conditioned air was then supplied to the temperature controlled test chamber. The chamber's exhaust air was passed through two impingers with an alkaline solution to collect formic acid and acetic acid from air.

Between each emission test, a background measurement was taken from the exhaust of air of the empty chamber.

The amount of collected organic acid was quantified by ion chromatography on an 881 Compact IC pro instrument with an 863 Compact Auto sampler, using an anionic precolumn (art.-no. 6.1005.250) and a column (art.-no. 6.1005.200) for determination of organic acids; all from Metrohm (Herisau, Switzerland). An acceptable baseline separation between formic acid and acetic acid was achieved with 0.33 mmol L⁻¹ H₂SO₄ as eluent, 0.1 mol L⁻¹ LiCl as suppressor, a flow rate of 0.4 mL min⁻¹ and a column temperature of 30°C.

Results and Discussion

Field test

As expected, the emissions of formic and acetic acid were significantly lower in winter compared to the summer period, which could be observed at all locations.

An overview of the results is given in Table 2.

In the Koppel store the concentration of formic acid and acetic acid together decreased from 95.6 ppb during the summer to 11.9 ppb during the winter season. Assuming a steady ventilation rate in summer and winter, the change in climate conditions resulted in an 88% decrease in the emission rate of the archival materials. The concentrations of formic acid and acetic acid in the Slotsholmen facility decreased from 150.9 ppb during the summer to 34.4 ppb during the winter, corresponding to a 77% decrease in the emission rate.

In the Vestindisk Pakhus store the passive diffusion samplers became exhausted during the midsummer measurement. The concentrations of formic acid and acetic acid together rose beyond 489 ppb which exceeded the capacity of the samplers. The test series was therefore repeated in late summer, where a concentration of 220.8 ppb was reached. During the winter season the concentration declined to 84.0 ppb. The change in climatic conditions resulted in a decreasing emission of organic acids of more than 83% from midsummer to winter, and a 62% decrease from late summer to winter, assuming a constant air exchange in both cases.

At all sites, the organic acid concentration was significantly higher in summer than in winter. Although the Koppel store had the highest loading of

Site	Season	climatic conditions, average		Formic acid (ppb)	Acetic acid (ppb)	Formic and Acetic acid (total ppb)
Koppel	Winter	19°C	31% RH	9.3 ±1.9	2.6 ±0.2	11.9
	Summer	25°C	48% RH	64.9 ±8.1	30.7 ±0.5	95.6
Vestindisk Pakhus	Winter	12°C	40% RH	39.0 ±1.4	45.0 ±1.4	84.0
	Summer	25°C	50% RH	> 317 *	> 172 *	> 489 *
	late Summer	20°C	45% RH	123.0 ±12.7	97.8 ±4.1	220.8
Slotsholmen	Winter	15°C	40% RH	31.0 ±6.2	3.4 ±0.7	34.4
	Summer	25°C	50% RH	100.0 ±20.0	50.9 ±11.0	150.9

* Samplers were exhausted, level might be higher

Table 2 The concentrations of formic and acetic acid as well as temperature and relative humidity during measurements in summer and winter at the three archives. The concentration values given are the average of duplicate sampling (standard deviations are named next to the average values).

paper, the ventilation rate was also the highest (0.6 room volume per hour), which retarded the accumulation of volatile organic compounds. Still, the relative difference between summer and winter concentrations was comparable to that of the other two sites.

Comparing the two storage sites with a natural ventilation, Slotsholmen and Vestindisk Pakhus, the latter produced significantly higher concentrations of organic acids, due to its higher paper loading. The emission of organic acids was even higher during the late summer period (at a lower average temperature and relative humidity) compared to the midsummer emissions at Slotsholmen.

Although other interior materials may have contributed to the indoor pollution (e.g., wooden shelves), the high loading of paper and the emission here-from was assumed to dominate the indoor air quality completely.

Not only the temperature decreased from summer to winter; there was also an average decline in relative humidity of about 10% RH at the natural ventilated sites, and 17% RH at the mechanically ventilated Koppel store. Relative humidity must also be considered to have a certain effect on the emission rate

(Steckel et al. 2013) and on the observed seasonal variations.

The observations are in line with those of Ryhl-Svendsen et al. (2014), who, in several museum storage facilities, observed the exact same pattern of a drastic decrease in organic acid concentration when the indoor temperature dropped, other things being equal. [2]

Laboratory measurements

Formic acid and acetic acid were identified both in the field tests and in the laboratory setup, where the gas-phase emission of all the paper samples was studied (Table 3). Within the laboratory tests it was possible to look at potential influencing factors separately.

Influence of Paper Quality

The mass-specific emission rates (mass of emitted acid per gram of paper, per hour) of formic and acetic acid at normal room conditions (22°C; 50% RH) were generally higher for the four historic paper samples (# 3-6) compared to the two standard test papers (#1-2) (Figure 4; Table 3). The historic newspaper #6 produced the highest emission rates of formic acid and

	Paper Sample	Formic acid (ng g ⁻¹ hour ⁻¹)	Acetic acid (ng g ⁻¹ hour ⁻¹)	Total acids (ng g ⁻¹ hour ⁻¹)
Room conditions <u>22°C</u> , 50% RH	#1	9.2 ±4.8	19.6 ±4.5	28.8 ±9.3
	#2	1.6 ±2.3	9.9 ±3.8	11.5 ±6.1
	#3	25.3 ±1.8	19.4 ±0.9	44.6 ±2.7
	#4	31.0 ±4.9	27.8 ±3.6	58.7 ±8.5
	#5	76.3 ±24.2	74.7 ±19.3	151.0 ±43.5
	#6	189.0 ±1.4	279.0 ±3.5	468.0 ±2.1
Cool conditions <u>10°C</u> , 50% RH	#3	3.9 ±2.7	4.5 ±0.8	8.4 ±3.5
	#4	16.8 ±3.4	10.4 ±0.5	27.2 ±2.9
	#6	1.3 ±2.3	27.3 ±5.2	28.6 ±7.2
Dry conditions <u>21°C</u> , 0% RH	#6	7.80 ±3.8	2.90 ±1.0	10.8 ±4.1

Table 3. Mass-specific emission rate of paper samples from climate chamber measurements, in ng acid emitted per gram of paper, per hour, at normal room temperature, cool, and at dry conditions. The values given are the average of two measurements, plus-minus one standard deviation.

acetic acid at room conditions, with a mass-specific emission rate of $468 \text{ ng g}^{-1} \text{ h}^{-1}$, corresponding to forty-times the emission rate measured for the modern Novo Test Paper #1.

The mass-specific emission rates of formic acid and acetic acid from the standard paper containing wood pulp with a lignin content (Novo Test Paper #2) was more than twice the rate of the standard paper produced from sulphate pulp (Novo Test Paper #1).

In a similar experiment Ramalho et al. (2009: Table 3) determined the emission rate of acetic acid from two standard papers at room conditions after accelerated ageing. Similar to our study he found the mass-specific emission rate from a paper sample with lignin content to be significantly higher than a paper sample without lignin.

Influence of pH value

The results of the laboratory experiments did not confirm a direct link between the pH-value of a paper sample and the emission of volatile organic acids. However, the pH value may play a decisive role, if the volatility of an acidic component depends on its degree of dissociation. In this case the acid dissociation constant pK_a serves as a relevant marker.

Sample #6 had a pH clearly below the pK_a value of acetate (4.8), under which the volatile acid form dominates. Above a pH of 4.8 the acetate form predominates. The acetate form preferably remains in

the paper while acetic acid is mainly released into the air (Ramalho et al. 2009). Strlič et al. (2007) observed a similar pattern, with no variation in the emission of acetic acid from paper samples within pH values ranging between about 5 to 9. Likewise, a study by Gibson and Watts (2010) on the emission of organic acid from wood samples indicated that the emission rate of acetic acid was independent of the pH of the wood samples.

Influence of Temperature

Temperature's influence on the emission rate was tested for paper samples #3, #4 and #6 by lowering the test chamber temperature to 10°C , while maintaining 50% RH (Table 3). This reduced the emission rates of formic acid and acetic acid from the paper samples up to 54 to 94%, which is on the same level as the concentration decreases observed in the field measurements between summer and winter conditions. Comparably, at study by Steckel et al. (2013) demonstrated how a temperature drop from 23°C to 15°C (at 50% RH) decreased the acetic acid emission from beech wood by 50%.

Influence of Relative Humidity

Although the focus of this study was on temperature dependency, one test chamber measurement demonstrated humidity's influence as well. With a decrease in relative humidity from 50% to 0% RH, maintaining temperature, the emission rates of formic acid and acetic acid from Sample #6 were reduced by 98%. Decreasing the relative humidity will reduce the amount of water available for the hydrolytic degradation of paper and thereby the production of degradation products such as formic acid and acetic acid. As discussed previously a lower relative humidity may also have contributed to the winter concentration decrease in the archives.

The emission of formic acid and acetic acid from paper into the air is a marker of the reaction rate of the chemical deterioration within the paper. The chemical reaction rate and the general mechanisms controlling the emission rate depend strongly on the temperature. According to Sebera's isoperm model for the climate depending deterioration rate of paper (Sebera 1994), paper permanence will be about 5 times higher at 10°C than at 22°C (maintaining 50% RH), or, in other words; the climate induced deterioration rate will be 5 times lower at 10°C than at 22°C (Figure 1). This is in line with the observed changes in emission rate for the individual paper samples, and reflected in the concentration levels at the archives winter and summer.

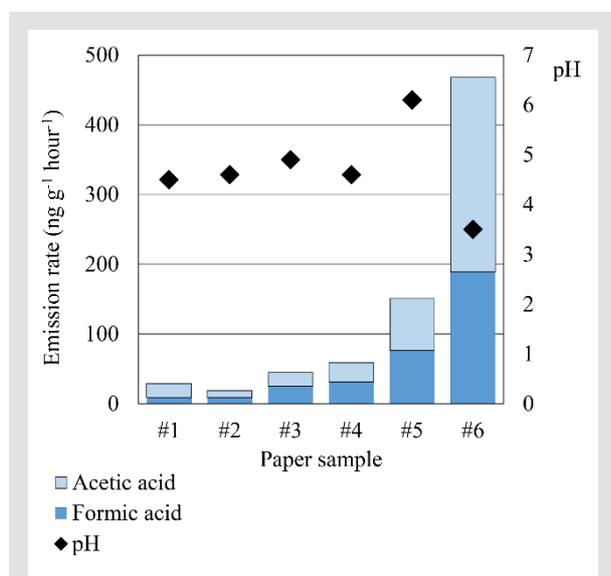


FIGURE 4 Mass-specific emission rate at 22°C and 50% RH, and the pH (aqueous cold extract) of each paper sample. Each data point represents the mean value of two replicate tests.

Calculating concentration or emission rate from archival collections

Typically, the concentration of a pollutant in air is the measure of choice when investigating air quality in an archive or storage room, for example, by passive diffusion samplers. However, the expected level of air pollution can also be estimated from knowing or presumption of a few other factors. The steady state concentration of air pollutants inside a storage room will depend on the amount of emissive materials in the collection and their removal by exchange with outdoor air and adsorption onto interior surfaces. The mass-balance given in Equation 1 (Ryhl-Svendsen, 2006; Ryhl-Svendsen and Clausen, 2009) can be used to estimate the concentration of organic acid from emission from the paper collection, if the rates of emission and removal (through ventilation and surface deposition) are known:

Equation 1:

$$C = \frac{G}{n + S}$$

Definition of variables:

- C steady state concentration of pollutant in air [$\mu\text{g m}^{-3}$]
- G generation rate of pollutant [g hour^{-1}]
- V volume of the room [m^3]
- n air exchange rate of the room [room volumes hour^{-1}]
- S surface removal rate, reduction of air pollutants by surface adsorption [room volumes hour^{-1}]

This type of calculation can serve as an aid to visualize which counter measures are most effective (e.g., change in ventilation rate) if an improvement to the air quality is desired.

Conversely, if the concentration in air is known (by measurement) the same mass-balance can be used for estimating the amount of acids generated by the collection. By re-arranging Equation 1, considering one average cubic meter of space, and dividing by the mass of paper in it, we get the average mass-specific emission rate for the archival records in the room:

Equation 2:

$$ER = \frac{C (n+S)}{m}$$

Definition of variables:

- ER mass-specific emission rate [$\text{g}_{\text{pol}} \text{g}_{\text{pap}}^{-1} \text{hour}^{-1}$]
where g_{pol} is mass of pollution and g_{pap} is mass of paper in gram
- m mass of paper [g m^{-3}]

In order to carry out this calculation for an actual archive or storage room the rates of pollutant's loss by ventilation and surface uptake must be known. In the Koppel building the air exchange rate was controlled by the ventilation system, which replaced air at a rate of 0.6 room volumes per hour. For the other two buildings there were no mechanical ventilation systems, so the air exchange was entirely driven by natural ventilation. Although the air exchange rates were not known for these sites, we know from experience in other, similar buildings that an exchange rate of 0.1 room volume per hour is a fair estimate (Ryhl-Svendsen et al. 2012).

For organic acids, there is only little data available on the deposition velocity to interior surfaces, hence the surface removal rate. Based on concentration measurements, Ryhl-Svendsen and Clausen (2009) estimated, for a number of museum storage rooms, surface removal rates ranging between about 0.2 to 2 room volumes per hour. For a test room with a highly reactive interior (clay brick) Ryhl-Svendsen (2011) calculated a surface removal rate of 1-2 room volumes per hour. As a comparison, for the much more reactive compound ozone, typical surface removal rates for museum interiors are in the order of 3-4 per hour, and for rooms with large fleecy surfaces even higher than 7 per hour (Ryhl-Svendsen 2006; Weschler 2000). Based on this we estimate that for organic acids a surface removal rate of about 2 room volumes per hour is realistic for a heavily loaded archive room. Based on those estimates, using Equation 2, the mass-specific emission rates of the paper records were in the summer time (at 25°C for all locations) between 7 $\text{ng g}^{-1} \text{h}^{-1}$ for the Koppel archive to more than 22 $\text{ng g}^{-1} \text{h}^{-1}$ for Vestindisk Pakhus. Assuming all other things equal; for all locations the emission rate decreased more than 70% from summer to winter conditions, see Figure 5.

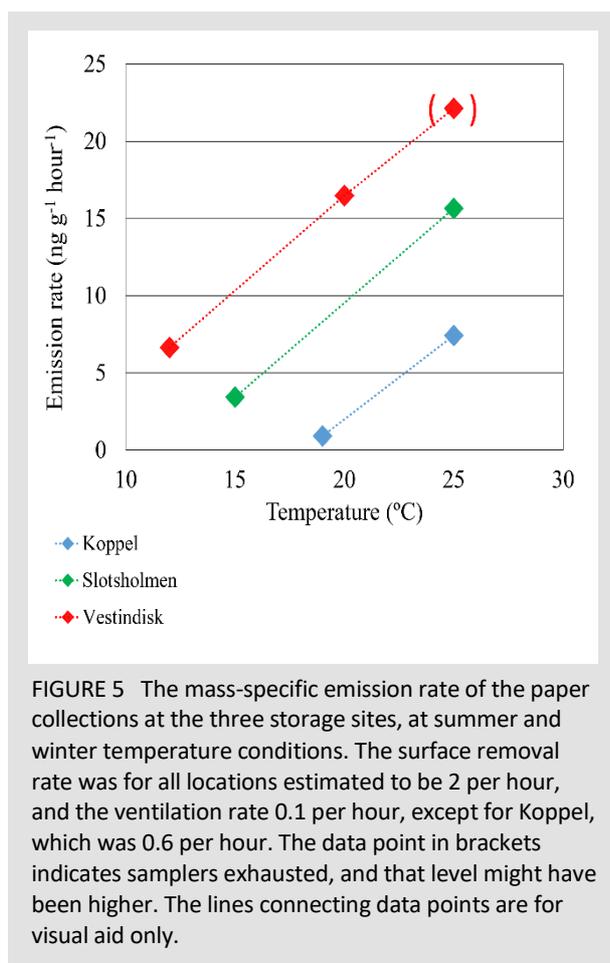


FIGURE 5 The mass-specific emission rate of the paper collections at the three storage sites, at summer and winter temperature conditions. The surface removal rate was for all locations estimated to be 2 per hour, and the ventilation rate 0.1 per hour, except for Koppel, which was 0.6 per hour. The data point in brackets indicates samplers exhausted, and that level might have been higher. The lines connecting data points are for visual aid only.

The observed difference in the temperature - emission rate relation between rooms could be due to differences in collection material content. Vestindisk Pakhus contains a newspaper collection, which can be assumed to be among the highly emissive paper types. For the two other sites, we could not establish the exact combination of content, however, at both places it were paper records other than newspaper, and at the Koppel building (least emissive collection) the records were stored in card board boxes.

Conclusion and Perspective

The chemical decay of paper and its dependence on temperature reported by Sebera (1994) is in line with the observed changes in emission rates of formic acid and acetic acid from the paper samples, and reflected in the concentration levels at the three storage sites from summer to winter. The results from the field measurements at the three storage sites show a decrease in the concentrations of formic acid and acetic acid from summer to winter. The decrease in temperature, and to some degree relative humidity, assuming steady state ventilation, reduces the level of organic acid in air with up to above 83%. Ryhl-

Svendsen et al. (2014) observed the exact same pattern in several storage facilities where a drop in temperature led to a drastic decrease in organic acid concentration, other things being equal. The laboratory tests show a similar behaviour. Reducing the temperature from 22°C to 10°C reduces the off-gassing of formic acid and acetic acid from the six paper samples with 54 to 94%.

The removal of formic acid and acetic acid from storage areas with a high loading of paper by ventilation and air filtration will lead to an increase in energy use. This study show that reducing the temperature in storage facilities with library and archival collections will reduce the off-gassing of organic acids from paper and by this it's concentration in air. Furthermore, a reduction in temperature will decrease the chemical decay of paper thereby offering a better solution from a sustainable energy use and preservation of our written cultural heritage perspective.

Further research is needed to investigate the composition of emission products from paper as well as other heritage materials and its dependence on typical climate conditions in storage facilities, especially with regard to relative humidity.

Notes

- [1] This building no longer serves as an archive, and the collection removed to the main State Archive facility.
- [2] For example, a decline in organic acid concentration of 88% was measured for a storage room of the Danish Music Museum filled with wooden objects, when the temperature decreased from about 25°C in summer to 8°C in winter.

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Paper III

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

Heritage Science (submitted 21.01.2020).

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 $\mu\text{g m}^{-2} \text{h}^{-1}$. 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.

Key words indoor air pollution, volatile organic compounds, emission rate, relative humidity, temperature, active sampling, passive sampling, wood, paper degradation.

1. 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 VOCs emitted directly from books. Risholm-Sundman *et al.* [2] and Ramalho *et al.* [3] pointed to acetic acid as one of the most abundant emission substances 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 the formation of crystalline corrosion products on historic glass surfaces, causing efflorescence on limestone and ceramics [8-12] and corrosion on copper alloys, cadmium, zinc, magnesium and in particular lead [12-14]. Robinet *et al.* [15] measured a concentration of 614 $\mu\text{g m}^{-3}$ acetic acid and 220 $\mu\text{g m}^{-3}$ formic acid in 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.

2. Laboratory measurements

2.1 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).

Sample no.	Material	Description	Year
1	Paper	Handmade cotton rag paper	1795-1809*
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**	Viking Age (10 th century)
6	Wood	Hardwood from the handle of a shoemakers tool	19 th century
7	Wood	New softwood packaging	New
8	Cellulose acetate	Photographic negative	Mid-20 th century

Table 1. Description of the eight samples. *Sample no. 1 was dated based on watermark identification. **The archaeological wood was treated with PEG from October 2013 to July 2016 and then freeze-dried from August 2016 to January 2017.

2.2 Method

2.2.1 Experimental set-up

Formic acid and acetic acid emissions from the four paper and three wood samples (sample no. 1-7) were measured in a climate controlled 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. The emission of acetic acid from cellulose acetate negatives (sample no. 8) was 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 hours before sampling. After sampling the test sample was removed and the test chamber heated up for several hours before another sampling interval started.

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 2. Surface area, mass and loading factor of sample 1-8.

2.2.2 Active air sampling and analysis

Active air sampling was performed on silica gel tubes or an alkaline liquid absorber to trap formic acid and acetic acid, as well as on Tenax TA® sorbent tubes to detect VOCs.

Formic acid and acetic acid were trapped on silica gel tubes at standard conditions (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 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 (0.1 M sodium hydroxide). The concentration from both sampling media were quantified by ion chromatography (IC) analysis. The method has a limit of quantitation (LOQ) of 5 µg m⁻³ for formic acid and acetic acid, respectively.

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:

$$SER_a = C_i * n/L \quad (1)$$

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 (m² m⁻³) [16].

Air sampling to detect VOCs was done on Tenax TA® sorbent tubes with an air flow rate of 125 mL min⁻¹. The sampling volume was 4 L. The tubes were analysed thermally desorbed (TD) into a coupled gas chromatography (GC)-mass spectrometry (MS)-system. The described method has a LOQ of approximately 1 µg m⁻³ and was performed in accordance with DIN ISO 16000-6 [17].

3. Field measurements

3.1 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 m³) and contained a 15th to 17th century book collection. The building was from 2008 and used mechanical ventilation with air filtration. Storage II was part of the shared storage facility at the Centre for Preservation of Cultural Heritage in Vejle, Denmark. The building was from 2013 and contained one room with a paper-based archival collection (room volume: 3200 m³) and another with museum objects made of mixed materials (room volume: 4800 m³). Storage II used semi-passive climate control with no heating and periodic dehumidification.

3.2 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 museums environments to measure the concentrations of formic acid and acetic acid in air [18-19]. 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 [18]. Measurements were conducted over three weeks in February and again three weeks in August 2018. From previous years, these two 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 temperature and RH were measured using TinyTag View 2 sensors (Gemini Dataloggers, UK), having an accuracy of ±0.4°C and ±3% RH.

4. Results and discussion

4.1 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 Figure 1 (the exact values are also tabulated as supplementary information). The area-specific emission rate 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 VOC 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 $887 \text{ ng g}^{-1} \text{ h}^{-1}$ from a cotton rag paper and $4820 \text{ ng g}^{-1} \text{ h}^{-1}$ from a paper made of ground-wood pulp. Smedemark and Ryhl-Svendsten [20] measured the mass-specific emission rate 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 $45 \text{ ng g}^{-1} \text{ h}^{-1}$ from a book printed in 1864 up to $468 \text{ ng g}^{-1} \text{ h}^{-1}$ from a newspaper printed in 1946. The mass-specific emission rate from the four paper samples in our study are within the same range. The mass-specific emission rate of formic acid and acetic acid ranged from $262 \text{ ng g}^{-1} \text{ h}^{-1}$ from the book printed in 1993 (sample no. 3) up to $1692 \text{ ng g}^{-1} \text{ h}^{-1}$ from the newspaper printed in 2017 (sample no. 4).

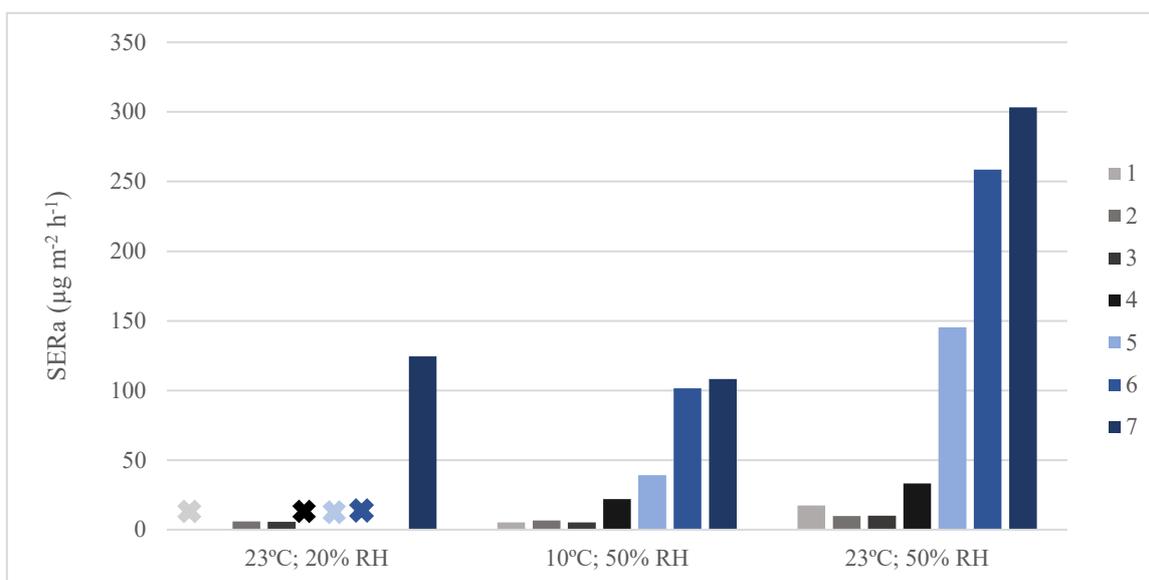


Figure 1. Area-specific emission rates of formic acid and acetic acid from sample 1-7 at 20% RH and constant temperature ($23 \pm 2^\circ\text{C}$) as well as at 10 and 23°C with constant RH ($50 \pm 5\%$ RH). The cross indicates measurements that are below the LOQ of $5 \mu\text{g m}^{-3}$.

Avoiding emissive construction materials and building interiors are used as an air pollution control strategy in order to reduce the concentration of formic acid and acetic acid in storage buildings with heritage collections [21, 22 Chapter 4]. The high emission rate 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 concentration 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 from the cellulose acetate negative (sample no. 8) was $3185 \mu\text{g m}^{-2} \text{ h}^{-1}$ 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.

4.2 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 [23-26]. 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 $\mu\text{g m}^{-2} \text{h}^{-1}$ and the emission rates from the three wood samples from 39 to 108 $\mu\text{g m}^{-2} \text{h}^{-1}$ 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 rate 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 [20] 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 [23-25]. Reducing the RH from 50% to 20% reduced the emission rate to below 6 $\mu\text{g m}^{-2} \text{h}^{-1}$ from all samples, except the softwood packaging. The emission rate from the softwood packaging was 124 $\mu\text{g m}^{-2} \text{h}^{-1}$ 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.

4.3 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 concentration of formic acid and acetic acid were larger inside the storage buildings than outdoor. It is assumed that internal sources as the heritage collections themselves 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 the concentrations of formic acid and acetic acid.

Concentration ($\mu\text{g m}^{-3}$)				
Season	Storage I	Storage II – archival collections	Storage II – mixed materials	Outdoor
Winter	7	3	28	< LOQ
Summer	15	9	97	< LOQ

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. The measurements were conducted in winter and summer.

Table 4 shows the increase in temperature from winter to summer within each storage room. 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 concentration increased by a factor of

3 in both rooms. Within the same period the temperature increased 7-8°C whereas RH variations remained within the uncertainty of the sensor ($\pm 3\%$ RH). A study by Krupinska *et al.* [19] showed a similar trend where the concentration of formic acid and acetic acid increased 5-6 times from winter to summer, and Smedemark and Ryhl-Svendsen [20] showed a 3-8 times increase in the concentration 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 the concentration in air inside real storage buildings with heritage collections depend on the temperature.

Temperature (°C)			
Season	Storage I	Storage II – archival collections	Storage II – mixed materials
Winter	6	9	9
Summer	14	17	15

Table 4. Temperature (monthly average) in all three storage rooms in winter and summer.

4.4 VOC emissions from paper

Table 5 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 were measured in trace concentrations below $10 \mu\text{g m}^{-3}$ (shown in light blue in Table 5). 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, 27-31]. 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.

Sample no.	1	2	3	4	Reference
C13 (Tridecane)					[7, 27-28, 31]
C14 (Tetradecane)					[6, 31]
C15 (Pentadecane)					[7, 27-28, 31]
C16 (Hexadecane)					[7, 27-28, 31]
C17 (Heptadecane)					[31]
C18 (Octadecane)					[7, 27-28, 31]
Benzaldehyde					[1, 6-7, 27-28, 32]

Pentanal					[6, 29]
n-Hexanal					[6, 29-32]
n-Heptanal					[6-7, 27-28, 31-32]
Octanal					[6-7, 27-28]
n-Nonanal					[1, 6-7, 27-28, 31-32]
n-Decanal					[1, 6-7, 27-28]
Furfural					[1, 3, 6-7, 27-29, 31-33]
Acetophenone					
2-ethyl-1-hexanol					[1, 6-7, 27-28, 30-31]
n-propanol					
1,2-Propanediol					
n-Butanol					[6, 31]
n-Pentanol					
Toluene					[1, 6-7, 27-29, 31-32]
Phenol					[6-7, 27-28, 31]
Formic acid					[5, 34]
Acetic acid					[1, 3, 5-7, 27-34]
Propanoic acid					[3, 6, 32]

Butanoic acid					[3, 6-7, 27-28]
Pentanoic acid					[3, 6-7, 27-28]
Hexanoic acid					[3, 6-7, 27-28]
Acetone					[3, 6-7, 27-29]
2,6-Diisopropyl-naphthalene					
2,6-Di(tert-butyl)-1,4-benzoquinone					
Benzothiazole					
N,N-Dibutylformamide					
Vanillin					[3, 5-7, 27-28]
Hexamethylcyclotrisiloxane					

Table 5. VOCs detected in chamber air from the four paper samples at 23°C and 50% RH. The blue colour indicates the presence of the specific compound (light blue indicates trace concentrations and dark blue concentrations above 10 µg m⁻³). 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, 27-30, 32-33]. 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 [35-37]. 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.

5. 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, paper and cellulose acetate 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 concentration of formic acid and acetic acid in a model storage room with heritage collections [38].

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Paper IV

Smedemark, S.H. and Ryhl-Svendsen, M.

‘Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions – Part II: a model study’

Journal of Cultural Heritage (submitted 27.01.2020).

Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions – Part II: a model study

Smedemark, S.H. and Ryhl-Svendsen, M.

Abstract

Formic acid and acetic acid are among the possibly most critical indoor air pollutants causing damage to heritage collections. Construction materials, building interior and the collections themselves can be a source of formic acid and acetic acid in unoccupied storage buildings. The area-specific emission rates of formic acid and acetic acid from wood and paper were determined in '*Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions – Part I: laboratory and field measurements*'. In the current study we used a mass-balance model to simulate the concentrations of formic acid and acetic acid in a model storage room under normal indoor room conditions. The impact of changes in the room temperature, the air exchange rate with ambient and the surface removal rate were furthermore modelled as three separate cases. The results were compared with the energy use. A decrease in temperature from normal indoor room conditions to cool conditions reduced the concentrations of formic acid and acetic acid from 508 to 204 $\mu\text{g m}^{-3}$ in the room with a wood collection. A decrease in temperature will also reduce the energy use for heating in temperate climates as in Northern Europe. To achieve the same reduction in the concentrations of formic acid and acetic acid at normal indoor room conditions it would be necessary to increase the air exchange rate with 3.8 h^{-1} in the room with a wood collection. An increase in the air exchange rate with ambient will, however, also increase the energy use for outdoor air filtration and climate control. The current model study demonstrated that the area-specific emission rates of formic acid and acetic acid from heritage collections can be used to simulate the concentration of acids in indoor air at different scenarios and to priorities air pollution control methods in storage buildings with heritage collections.

Key words mass-balance, temperature, air exchange rate, surface removal rate, air filtration, energy use.

Research aim

The area-specific emission rates of formic acid and acetic acid from heritage collections were determined in '*Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions – Part I: laboratory and field measurements*' [1]. The current study used the area-specific emission rates to calculate the concentrations of formic acid and acetic acid in a model storage room with heritage collections. The impact of changes in the model storage room temperature, the air exchange rate with ambient and the surface removal rate were furthermore modelled as three separate cases and the results compared with the energy use. The aim was to determine the best control method to reduce the concentrations of formic acid and acetic acid in indoor air.

1. Introduction

Organic acids are among the possibly most critical indoor air pollutants causing damage to heritage collections [2]. Chiavari *et al.* [3] found that the corrosion of historical organ pipes in churches is interrelated with the concentrations of gaseous formic acid and acetic acid in the organ. Organic acids have also been reported to

damage varnish, tarnish metals and form white crystalline deposits on glass, ceramics, shells etc. [4-8]. The concentrations of formic acid and acetic acid within storage buildings with heritage collections have been measured in several previous studies. For example, Krupinska *et al.* [9] measured an organic acid concentration of 307 $\mu\text{g m}^{-3}$ in the Plantin-Moretus Museum with manuscript and book collections in Antwerp, Belgium.

The concentrations of formic acid and acetic acid in storage buildings depend on the strength and amount of emission sources present as well as removal mechanisms. The mass-balance model (Equation 1) describes the concentration of indoor air pollution in a storage room under steady-state conditions assuming a negligible contribution from outside [10]:

$$C_i = (G/V) / (n + S) \quad (1)$$

where C_i is the steady-state concentration of air pollution within the storage ($\mu\text{g m}^{-3}$), G is the generation rate of the pollutant ($\mu\text{g h}^{-1}$), V is the air volume (m^3), n is the air exchange rate (h^{-1}) and S is the surface removal rate (h^{-1}). The air exchange rate describes the rate at which air in a room is being replaced with outside air while the surface removal rate describes the passive uptake of air pollution on interior surfaces.

The generation rate of the pollutant can be calculated from the area-specific emission rate [11]:

$$G = \text{SER}_a * V * L \quad (2)$$

where, SER_a is the area-specific emission rate ($\mu\text{g m}^{-2} \text{h}^{-1}$), V is the air volume (m^3) and L is the loading factor of the material in the room ($\text{m}^2 \text{m}^{-3}$).

The mass-balance model (Equation 1) show that an increase in the emission rate (source strength) and the loading (amount) of emissive materials will increase the concentration of indoor air pollution. On the other hand, will an increase in the air exchange rate with ambient or the surface removal rate reduce the concentration of indoor air pollution.

Storage buildings with heritage collections are mostly unoccupied and emission sources of formic acid and acetic acid inside the buildings therefore mainly include construction materials, building interior and the collections themselves. The use of non-emissive construction materials and building interior can reduce the concentrations of formic acid and acetic acid inside unoccupied storage buildings [12] however; the contribution from the collections will remain.

The emission rates of formic acid and acetic acid from heritage collections under normal indoor room conditions were determined in '*Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions – Part I: laboratory and field measurements*' [1]. The formic acid and acetic acid emission rates from naturally aged wood and paper in heritage collections ranged from 10 to 300 $\mu\text{g m}^{-2} \text{h}^{-1}$ under normal indoor room conditions [1].

This study used the area-specific emission rates of formic acid and acetic acid from heritage collections, measured under normal indoor room conditions, to calculate the concentration of organic acids in a model storage room (Case 1). The concentration was modelled for a storage room with either a wood or a paper collection separately. The impact of changes in the model storage room temperature (Case 2), the air exchange

rate with ambient (Case 3), or the surface removal rate (Case 4) on the concentrations of formic acid and acetic acid were also modelled (Figure 1). The results are compared with the resulting energy use of each case.

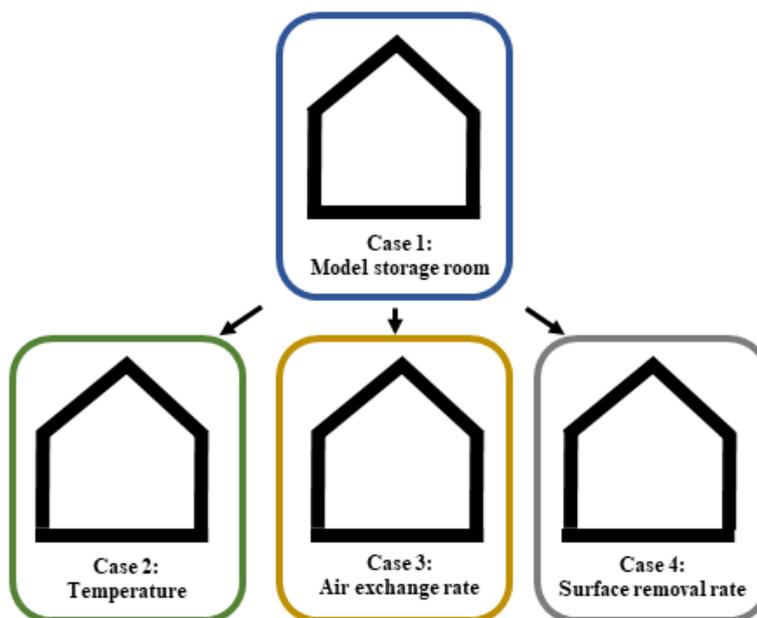


Figure 1. Overview of the four simulations. Case 1 is the model storage room. Case 2-4 modelled the impact of changes in the temperature, the air exchange rate with ambient and the surface removal rate on the concentrations of formic acid and acetic acid in indoor air.

2. Method

The mass-balance model (Equation 1) was used to calculate the concentrations of formic acid and acetic acid in a model storage room under normal indoor room conditions (Case 1). The concentration was modelled for a wood and a paper collection separately. One parameter was changed at a time to model the impact of temperature (Case 2), the air exchange rate with ambient (Case 3) and the surface removal rate (Case 4) on the concentrations of formic acid and acetic acid in indoor air.

2.1 The generation rate

The volume of the model storage room was set to 1000 m³. The model ignores the contribution of formic acid and acetic acid from outdoor as well as emission from construction materials and building interior. The model only accounts for the emission of organic acids from the heritage collections. The generation rates (source strength) of formic acid and acetic acid were calculated from the area-specific emission rates (Equation 2) [1]. The amount of emissive wood and paper was set to 5 m² m⁻³ to imitate a densely packed storage room [13]. All input data are shown in Table 1.

Material	Emission rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)		Volume (m^3)	Loading ($\text{m}^2 \text{m}^{-3}$)
	23°C	10°C		
Wood	145 – 303	39 – 108	1000	5
Paper	10 – 33	5 – 22		

Table 1. Input data to calculate the generation rates of formic acid and acetic acid from wood and paper.

2.2 The removal mechanisms

Case 1 modelled the concentrations of formic acid and acetic acid in the model storage room at 23°C and 50% RH. The air exchange rate with ambient was set to 0.03 h^{-1} to imitate a storage building with semi-passive climate control [14]. The surface removal rate in the model storage room was set to 2 h^{-1} to imitate a densely packed room with a large area of interior surfaces [13].

For Case 2 the temperature was reduced from normal indoor room conditions to cool conditions (10°C, 50% RH) in order to model the decrease in organic acid concentration following a decrease in the emission rate from the collections.

In Case 3 the air exchange rate was increased from 0.03 to 1 h^{-1} to simulate the impact of an increase in the exchange of air with ambient on the concentrations of formic acid and acetic acid in the model storage room [14-15].

For Case 4 the surface removal rate was reduced from 2 to 0.2 h^{-1} to simulate the impact of a decrease in the surface removal rate on the concentrations of formic acid and acetic acid in the model storage room [13]. All input data are shown in Table 2.

Control parameter	Case 1: Indoor room conditions	Case 2: Temperature	Case 3: Air exchange rate	Case 4: Surface removal rate
Temperature (°C)	23	10	23	23
Air exchange rate (h^{-1})	0.03	0.03	1	0.03
Surface removal rate (h^{-1})	2	2	2	0.2

Table 2. Overview of the input data used to calculate the concentrations of formic acid and acetic acid in the model storage room (Case 1), and the impact of the temperature (Case 2), the air exchange rate (Case 3) and the surface removal rate (Case 4) on the concentration of organic acids in indoor air. The input data for the air exchange rate in Case 3 was taken from [14] and [15], and for the surface removal rate in Case 4 from [13].

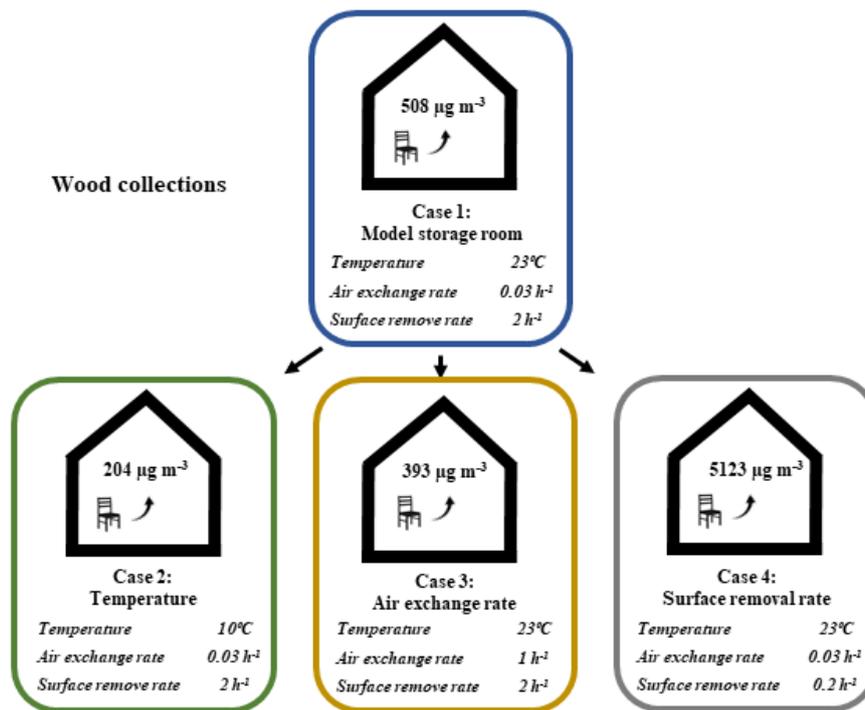
2.3 Calculation of the energy use

The energy use needed to maintain normal indoor room conditions (23°C) was calculated from the heat loss Q (kWh) through the building envelope and the air exchange rate with ambient [16]. The input data has been collected in Supplementary information A. The average monthly indoor and outdoor temperature used were real data from an unheated storage building with semi-passive climate control in Denmark [1]. The thermal transmittance (U-value) through all exterior walls and the ceiling in the model room with semi-passive climate control was set to 0.1 W m⁻² K⁻¹ [16] and the airflow was calculated from the air exchange rate at 0.03 h⁻¹.

Fisk *et al.* [17] presented an equation to calculate the energy use E (kWh) needed to recirculate air through filters inside a building. A typical filter designed to remove formic acid and acetic acid in heritage institutions has a removal efficiency about 90% [18]. The pressure drop in the ventilation system was 400 Pa [19] while the pressure drop across the filter was 222 Pa [20]. The motor efficiency was set to 0.9 and the fan efficiency to 0.75 to represent the performance of motors and fans used in larger commercial building with mechanical ventilation systems [17]. All input data has been collected in Supplementary information B.

3. Results and discussion

The results from Case 1-4 are shown in Figure 2.



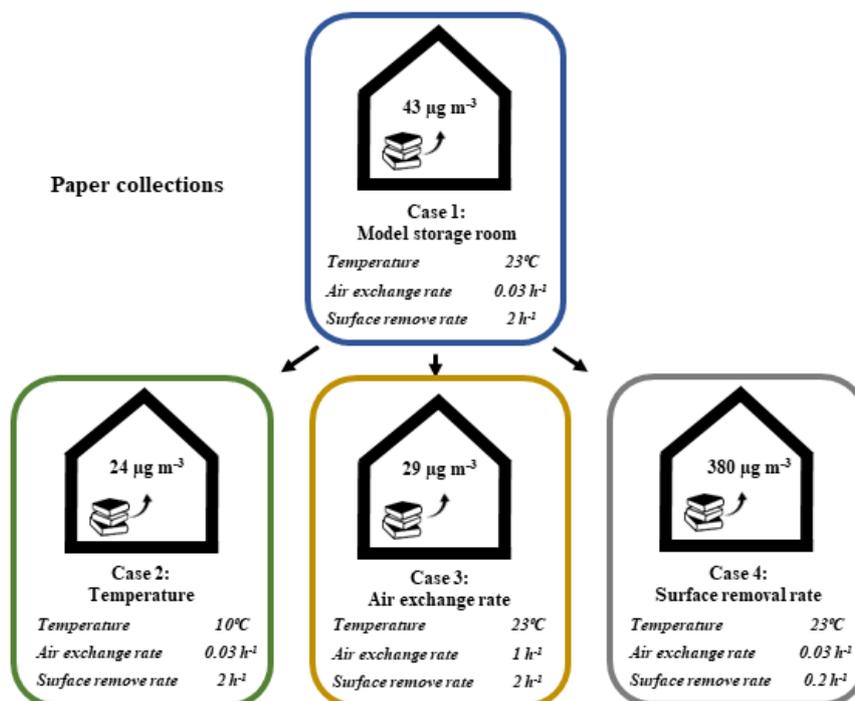


Figure 2. Concentrations of formic acid and acetic acid together in the modelled Case 1-4. Results are given in bold and input data in italic below.

The energy use for each case is collected in Table 3.

Case	Energy use (kWh m ⁻³ year ⁻¹)	Comment
1	161	Normal indoor room conditions
2	40	Cool conditions
3	9	Recirculation with air filtration at 3.8 h ⁻¹
3	4	Recirculation with air filtration at 1.6 h ⁻¹
4	0	Passive surface removal

Table 3. The energy use (kWh m⁻³ year⁻¹) for Case 1-4.

3.1 Case 1: model storage room

In Case 1 the concentrations of formic acid and acetic acid were modelled under normal indoor room conditions in a densely packed room with semi-passive climate control. The air exchange rate was 0.03 h⁻¹ and the surface removal rate at 2 h⁻¹. The organic acid concentration in the model storage room with a wood collection was 508 $\mu\text{g m}^{-3}$ while the concentration was 43 $\mu\text{g m}^{-3}$ in the model storage room with a paper collection. The results are within the same range as measurements conducted in real storage buildings with heritage collections e.g. Robinet *et al.* [7] measured an organic acid concentration of 428 $\mu\text{g m}^{-3}$ in a storage building at the Royal

Museum of Scotland and Smedemark *et al.* [1] measured an organic acid concentration of $97 \mu\text{g m}^{-3}$ in a storage building with semi-passive climate control in Denmark.

The total energy use to maintain normal indoor room conditions was $161 \text{ kWh m}^{-3} \text{ year}^{-1}$. The energy use for heating to normal indoor room conditions was considerably higher than the energy use in unheated storage buildings with semi-passive climate control. For comparison; the energy use in the shared storage facility at the Centre for Preservation of Cultural Heritage in Vejle, Denmark with semi-passive climate control was only $1.1 \text{ kWh m}^{-3} \text{ year}^{-1}$ [21].

3.2 Case 2: temperature

Case 2 modelled the impact of room temperature on the concentrations of formic acid and acetic acid in indoor air. Lowering the temperature from normal indoor room conditions to cool conditions reduced the organic acid concentration to $204 \mu\text{g m}^{-3}$ in the room with a wood collection and $24 \mu\text{g m}^{-3}$ in the room with a paper collection. A reduction in the concentrations of formic acid and acetic acid following a decrease in temperature have also been observed in several field measurements. Krupinska *et al.* [9] measured a decrease in the concentration of organic acids from $307 \mu\text{g m}^{-3}$ in summer to $54 \mu\text{g m}^{-3}$ in winter in the Plantin-Moretus Museum in Antwerp, Belgium. Smedemark *et al.* [1] measured a decrease in the concentration of organic acids from $97 \mu\text{g m}^{-3}$ in summer to $28 \mu\text{g m}^{-3}$ in winter in a storage building with semi-passive climate control in Denmark.

One way to reduce the temperature in a storage building in temperate climates as in Northern Europe without increasing the energy use is to take advantage of cold winter temperatures. The energy use in the model storage room will decrease from $161 \text{ kWh m}^{-3} \text{ year}^{-1}$ at normal indoor room conditions to only $40 \text{ kWh m}^{-3} \text{ year}^{-1}$ for cool conditions. Several previous studies have examined the decrease in energy use as a result of relaxing set point condition for temperature and RH in heritage institutions. For example, Hong *et al.* [22] simulated the energy use in the National Archives storage building in Kew, UK using the modelling software *EnergyPlus*. The simulation showed that allowing a seasonal adjustment in the HVAC system with an annually change in set point conditions from winter (16°C , 35% RH) to summer (20°C , 55% RH) resulted in energy savings as high as 43%. Kramer *et al.* [23] assessed the impact of relaxing specification for allowable fluctuations in temperature and RH on the energy use over one year within a museum in Amsterdam, Netherlands. The measurements of outside as well as inside temperature and RH showed that changing from no permissible fluctuations to ASHRAE Class AA (precision control with seasonal change in temperature) reduced the energy use with 49% whereas changing from no permissible fluctuations to ASHRAE Class A (precision control with seasonal change in temperature and RH) reduced the energy use with 63% from 1053 to $385 \text{ kWh m}^{-3} \text{ year}^{-1}$.

This model study demonstrated that lowering the temperature from normal indoor room conditions to cool conditions would reduce the organic acid concentration in the storage rooms. A decrease in temperature will also reduce the energy use for heating in temperate climates as in Northern Europe. Lowering the temperature will however not always be feasible depending on the construction of the building envelope etc. [24].

3.3 Case 3: air exchange rate

Case 3 modelled the impact of the air exchange rate on the concentrations of formic acid and acetic acid in indoor air. Ryhl-Svendsen *et al.* [14] measured an air exchange rate down to 0.03 h^{-1} in storage buildings with

semi-passive climate control in Denmark while Thickett *et al.* [15] measured an air exchange rate up to 0.93 h⁻¹ in stores with archival and library collections in England. An increase in the air exchange rate with ambient from 0.03 to 1 h⁻¹ would dilute the concentrations of formic acid and acetic acid from 508 to 393 µg m⁻³ in the model storage room with a wood collection, and from 43 to 29 µg m⁻³ in the model storage room with a paper collection.

Figure 3 show how the concentration of organic acids would vary in the model storage room with a paper collection as a function of the air exchange rate for normal indoor room conditions (Case 1) as well as cooler conditions (Case 2). The air exchange rate would need to be increased with 1.6 h⁻¹ in order to achieve the same reduction in concentration of organic acids as could be achieved by lowering the temperature from normal indoor room conditions to cool conditions. Likewise, the air exchange rate would need to be increased with 3.8 h⁻¹ to achieve the same reduction in concentration of organic acids as could be achieved by lowering the temperature in the model storage room with a wood collection.

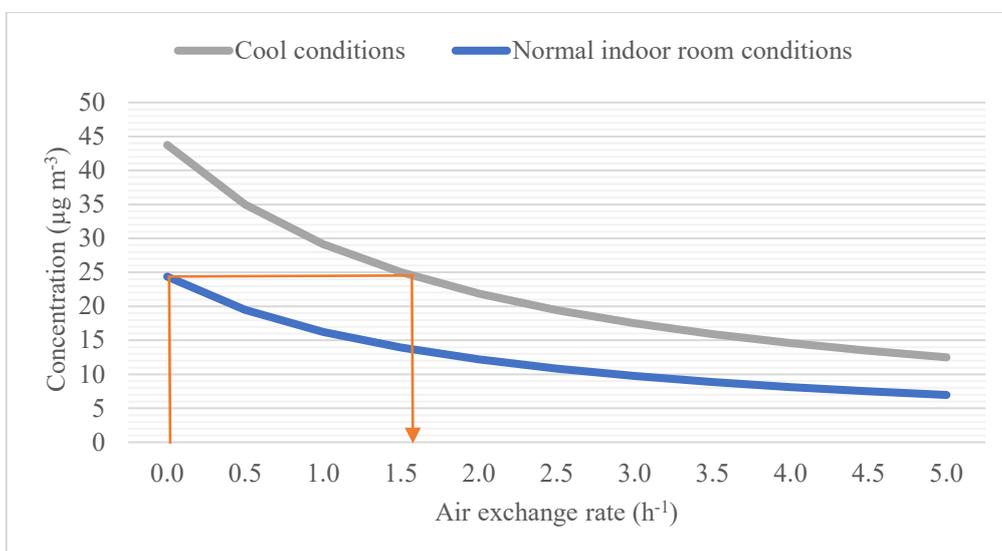


Figure 3. Concentration of organic acids in the model room with a paper collection at normal indoor room conditions, and cool conditions, as a function of the air exchange rate. The trace of the orange arrow shows that the air exchange rate must be increased from 0.03 to 1.6 h⁻¹ for reaching the same reduction in organic acid level as could be achieved by lowering the temperature from 23 to 10°C.

An increase in the air exchange rate with ambient would however, also increase the energy use needed to remove outdoor air pollution and maintain stable climate conditions inside the storage building. Smedemark *et al.* [21] examined the climate and air quality performance in one storage building with semi-passive climate control and one with a HVAC system. Despite the different ventilation forms, both stores maintained an acceptable indoor environment for the preservation of collections with almost the same annual change in temperature from 7°C in winter up to 19°C in summer. The energy use in the storage building with semi-passive climate control and periodic dehumidification was 1.1 kWh m⁻³ year⁻¹ whereas the energy use in the storage building with a HVAC system was significantly larger at 67 kWh m⁻³ year⁻¹ for air quality and climate control.

Another solution to reduce the concentration of formic acid and acetic acid is to recirculate air through adsorbent filters within the unoccupied storage building. This will increase the cost due to regular replacement

of air-filters as well as the energy use to overcome the pressure drop across the filter. The energy use needed to increase the recirculation rate through adsorbent filters up to 3.8 h^{-1} in the model storage room with a wood collection was $9 \text{ kWh m}^{-3} \text{ year}^{-1}$, while the energy use needed to increase the recirculation rate with 1.6 h^{-1} in the model storage room with a paper collection was $4 \text{ kWh m}^{-3} \text{ year}^{-1}$.

The model demonstrated that an increase in the air exchange rate would reduce the concentration of formic acid and acetic acid in indoor air. One solution to reduce the energy use in unoccupied stores is to reduce the air exchange rate with ambient and to increase the internal recirculation rate through adsorbent filters.

3.4 Case 4: surface removal rate

Case 4 modelled the impact of reducing the surface removal rate from 2 to 0.2 h^{-1} on the concentrations of formic acid and acetic acid in indoor air. A decrease in the surface removal rate increased the concentrations of formic acid and acetic acid from 508 to $5123 \mu\text{g m}^{-3}$ in the model storage room with a wood collection and from 43 to $380 \mu\text{g m}^{-3}$ in the model storage room with a paper collection.

The model study demonstrated how the concentrations of formic acid and acetic acid in indoor air depend on the passive removal rate onto interior surfaces. The surface removal rates of formic acid and acetic acid on interior surfaces are largely unknown. Only a few studies reports a surface removal rate of organic acids; from about 0.0042 and 0.0063 h^{-1} (converted from per day) in display cases made of inert glass and powder coated metal [25], to between 0.2 and 2 h^{-1} in storage buildings with heritage collections [13]. Adsorbent materials such as textile wall coverings impregnated with silica gel or activated carbon can be used to passively reduce the organic acid concentration in indoor air [13]. Passive adsorbents will reduce the concentrations of formic acid and acetic acid in indoor air without consuming energy, but will come with a cost of installation.

3.5 Final remarks

The emission rates of formic acid and acetic acid from heritage collections were determined in '*Quantification of formic acid and acetic acid emissions from heritage collections under indoor room conditions – Part I: laboratory and field measurements*' [1]. The study showed that the emission rates of formic acid and acetic acid from wood and paper depend on temperature. As temperature is also one of the primary factors affecting cellulose degradation [26], a decrease in temperature will reduce the chemical decay of cellulose-based materials. Michalski [27] derived a rule of thumb from data on the decay of paper, film and magnetic media stating that '*for each 5°C drop in temperature the lifetime will double*' and '*halving the relative humidity will more than double the lifetime*'. In the present model study, we demonstrated that temperature can be used as a control method to reduce the decay of cellulose-based materials as well as the concentrations of formic acid and acetic acid in indoor air. This is in line with the recommendations by Krupinska *et al.* [9] and Ryhls-Svendsen *et al.* [14]. Furthermore, we show that by knowing the area-specific emission rate from collection materials such as wood and paper it is possible to model the concentrations of formic acid and acetic acid in indoor air at different conditions, and by this the impact of removal mechanisms such as the air exchange rate and the air pollution removal onto interior surfaces.

4. Conclusion

The study showed that a decrease in temperature from normal indoor room conditions to cool conditions reduced the concentrations of formic acid and acetic acid in indoor air. The concentration decreased from 508 to 204 $\mu\text{g m}^{-3}$ in the room with a wood collection and from 43 to 24 $\mu\text{g m}^{-3}$ in the room with a paper collection. This is in line with the recommendations by Krupinska *et al.* [9] and Ryhl-Svendensen *et al.* [14]. A decrease in temperature will also reduce the chemical decay of cellulose-based materials, and the energy use needed in temperate climates to maintain climate conditions in storage buildings for heritage collections.

The air exchange rate must be increased from 0.03 to 3.8 h^{-1} to achieve the same reduction in organic acid level as could be achieved by lowering the temperature from normal indoor room conditions to cool conditions in our model storage room with a wood collection. The increase in air exchange rate needed will of course depend on the conditions within the storage building. Overall, the simulations showed however, that the air exchange rate should be increased significantly to achieve the same reduction in the concentrations of formic acid and acetic acid in indoor air as can be achieved by lowering the temperature from normal room conditions.

Overall, the model study demonstrated that the area-specific emission rates of formic acid and acetic acid from heritage collections can be used to model the concentration of acids in indoor air and to prioritize air pollution control methods in storage buildings with heritage collections.

Supplementary information A – input data heat loss calculations

The input data to calculate the heat loss through the building envelope and air exchange with ambient was taken from [16].

Volume (m^3)	Thermal transmittance ($\text{W m}^{-2} \text{K}^{-1}$)	Surface area (m^2)	Air exchange rate (h^{-1})
1000	0.1	1000	0.03

Average monthly outdoor and indoor temperature and RH from a storage building with semi-passive climate control in Denmark [1].

	Outdoor		Indoor	
Month	T (°C)	RH (%)	T (°C)	RH (%)
January	1.4	92	10.1	46
February	-1.2	87	8.9	45
Marts	0.2	87	8.4	45
April	8.8	80	9.5	46
May	15.1	71	11.6	48
June	16.3	74	13.5	49
July	19.2	68	14.7	49
August	16.9	82	15.2	49
September	13.2	90	14.4	48
October	9.7	91	14.1	46
November	5.7	94	12.8	46
December	4.1	95	10.9	46

Supplementary information B – input data energy use air filtration

The input data for pressure drop in the ventilation system [19], pressure drop due to air filtration [20], motor and fan efficiency [17] used to calculate the energy use for internal recirculation with filtration.

Volume (m ³)	Air exchange rate (h ⁻¹)	Pressure drop ventilation (Pa)	Pressure drop air filtration (Pa)	Motor efficiency	Fan efficiency
1000	0.03	400	222	0.9	0.75

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Paper V

Smedemark, S.H., Ryhl-Svendsen, M. and Schieweck, A.

‘The effect of temperature on emissions of carboxylic acids in passive climate controlled repositories with cultural heritage collections’

In Proceedings from the *15th Conference of the International Society of Indoor Air Quality & Climate (Indoor Air 2018)*, 22-27 July 2018, Philadelphia, USA.

The effect of temperature on emissions of carboxylic acids in passive climate controlled repositories with cultural heritage collections

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SUMMARY

This study investigates the effect of reducing temperature on the emission of carboxylic acids and other volatile organic compounds (VOCs) released from museum objects. Volatile carboxylic acids cause deterioration of cultural heritage collections, e.g. tarnishing of metals, salt efflorescence on calcareous structures, and acid hydrolysis of organic materials. The concentrations of VOCs and carboxylic acids in air were determined in a test chamber set-up. Active sampling of VOCs was performed on Tenax TA[®] with subsequent thermal desorption and coupled gas chromatography/mass spectrometry (TDS-GC/MS) analysis. Carboxylic acids were trapped on silica gel tubes and analyzed by ion chromatography (IC). The results show that reducing the temperature from 23°C to 10°C will reduce the emission of carboxylic acids from selected cultural heritage materials to 27-68%. It has to be clarified if reducing temperature can have a beneficial effect on air filtration requirements in repositories with passive climate control in Northern Europe.

KEYWORDS

Conservation; cultural heritage; emissions; air filtration; VOCs.

1 INTRODUCTION

The increasing awareness of human contribution to global climate changes and the demand to increase energy efficiency has led to several initiatives to revise climate standards for cultural heritage collections and a fundamentally different principle for their climate control (ICOM-CC, 2014). Temperature affects the chemical deterioration of organic materials and lowering the temperature will increase longevity of collections.

In Northern Europe with a considerable temperature difference between seasons, a well-insulated building envelope placed on an uninsulated concrete floor can be used to passively control the climate in unoccupied cultural heritage repositories. The building envelope will buffer against daily fluctuations in temperature while the uninsulated concrete floor will act as a cooling source during summer and heating source during winter resulting in a temperature fluctuation from around 13°C in summer to 7°C in winter (Bøhm and Ryhl-Svendsen, 2011).

The request to increase energy efficiency has led to an increase in the airtightness of buildings generating an air exchange rate between 0.03-0.05h⁻¹ in low-energy repositories (Ryhl-Svendsen et al., 2014). While the emission of VOCs in unoccupied repositories can be largely avoided by selecting appropriate construction materials, the emission of contaminants from chemical decay processes within the cultural heritage collection themselves cannot be eradicated. The emission of carboxylic acids can cause deterioration of cultural heritage collections e.g. tarnishing metals, or salt efflorescence on calcareous structures. The question is if the emission rate from museum objects at temperatures found in repositories with passive climate control is significant enough to cause deterioration and whether air filtration can be justified or not.

2 MATERIALS AND METHODS

The effect of temperature on emissions from cultural heritage collections was investigated in a spherical 48L test chamber. Four samples were investigated: (i) polyethylene glycol (PEG) treated archeological wood, (ii) historical wood sample, (iii) a newspaper made from ground-wood pulp printed in 1914 and (iv) recent EUR-pallet used to transport and store collections. The chamber was supplied with purified air conditioned to 50% relative humidity. Active air sampling was performed at 10°C, 23°C and 30°C, respectively. The air exchange rate was adjusted to 1h⁻¹. Active air sampling on volatile organic compounds (VOCs) was performed on Tenax TA[®] tubes with subsequent analysis by TDS-GC/MS. Sampling on low-molecular weight carboxylic acids (formic acid, acetic acid) was done separately by using silica gel tubes with analysis by IC.

3 RESULTS

As shown in Figure 1, the emission rate of carboxylic acids depends on temperature. A decrease in temperature from 23°C to 10°C reduces the emission of formic and acetic acid from the tested samples to 27-68%. In addition, a decrease in temperature led to a reduction in the total VOC emission.

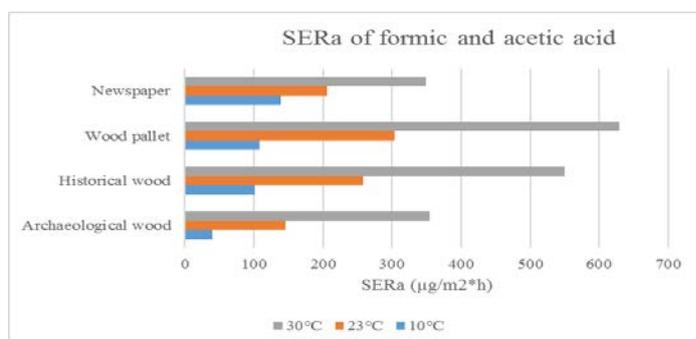


Figure 1. Surface specific emission rates (SER_A) calculated from the summarized value of formic and acetic acid released from four historical paper and wood samples at 10°C, 23°C and 30°C.

5 CONCLUSIONS

The concentration of carboxylic acids and other VOCs from all the tested museum objects reduced when temperature decreased. Although the surface specific emission rates were low, the loading of collections in repositories is usually very dense, so the total impact of the emission from the collection items on the air quality may be high. With a lower temperature inside repositories, the chemical deterioration rate of cultural heritage collections will decrease, and following this, the emission of harmful pollutants must also decrease. A forthcoming field test in a Danish museum storage building will investigate this further.

ACKNOWLEDGEMENT

The authors acknowledge the Independent Research Fund Denmark for supported this work. S. H. Smedemark also thanks Fraunhofer WKI, department of material analysis and indoor chemistry, Germany, for hosting a research visit.

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Paper VI

Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J.

'Distribution of indoor air pollution in storage facilities with heritage collections'

Building and Environment (submitted 12.12.2019).

Distribution of temperature, moisture and organic acids in storage facilities with heritage collections

Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J.

Abstract

The preservation of heritage collections in storage largely depends on the climate and air quality conditions. Uncontrolled airflow transports unconditioned air into the building. Lowering the air exchange rate in unoccupied storage facilities is therefore essential to ensure acceptable climate conditions for the preservation of collections, while at the same time reducing the energy use for climate control. The concern is, however, that a restricted airflow can create uneven microclimates within a room, with thermal stratification as well as accumulation of indoor generated pollutants, which may accelerate the deterioration of the collections. This paper examines the air distribution within one storage building with a heating, ventilation and air-conditioning (HVAC) system, and in two rooms in another storage with semi-passive climate control. A sensor grid was established in each room in order to map the distribution of temperature, relative humidity (RH) and volatile organic acids determined as the sum of acetic acid and formic acid concentration. This study demonstrated that both tested ventilation forms upheld an acceptable climate performance with appropriate temperature and moisture distributions and without air pockets producing problematic microclimates. However, organic acids accumulated in concentrations up to $134 \mu\text{g m}^{-3}$ in parts of one storage room with semi-passive climate control. Whether to install a HVAC system with gaseous air filtration to remove organic acids will ultimately depend on the threshold level that caretakers are willing to accept.

Keywords semi-passive climate control, air distribution, temperature, relative humidity, organic acids, microclimate, constant dosing tracer gas.

1. Introduction

The main part of the world's heritage collections are kept in storage buildings. For a typical museum, more than 90% of the collection objects are packed away in storage facilities, leaving less than 10% on display. The long-term preservation of collections largely depends on climatic factors such as temperature, RH and air pollution level within the storage¹. Temperature can accelerate the chemical deterioration of organic materials as valuable leather bound books and magnetic media present in heritage collections. A change in temperature will also result in a change in RH. An incorrect RH can among other things tarnish metals, produce salt efflorescence on porous materials as stone and ceramics as well as accelerate mould growth. Fluctuations in RH can also cause damage to composite materials due to differences in expansion and contraction between materials. The American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) provide a good overview in their chapter on museums, galleries, archives and libraries². Organic acids are among the possibly most critical indoor air pollutants causing damage to heritage collections³. Organic acids can among other things cause damage to varnish, tarnish metal, produce white crystalline deposits on the surface of glass and efflorescence on seashells, limestone and ceramic that can lead to pitting and disruption of the surface and a loss in value⁴⁻⁵.

Until recently, the dogma has been to use the '*best available technology*' to maintain constant climate conditions. The development of HVAC systems made it possible to set increasingly strict specifications for allowable fluctuations in temperature and RH leading to an accompanying increase in energy use⁶. The recent

shift from ‘*best available technology*’ towards more sustainable collection management of keeping the storage climate within a wider, but still acceptable temperature and RH range, includes the development of unoccupied storage facilities with semi-passive climate control⁷.

One concept of semi-passive climate control is to construct an almost airtight but thermally highly insulated building envelope laid on an uninsulated heavy floor acting as a heat buffer⁷. The temperature within the storage follows a seasonal cycle, whereas the RH is kept constant through periodic mechanical dehumidification. A storage with semi-passive climate control consumes only 2% of the energy use of a storage with a full HVAC system⁸.

Increasing the airtightness of the building envelope will diminish the moisture load from ambient air and improve the building’s energy performance. Nevertheless, the higher the airflow, the better will indoor generated pollutants be diluted and removed. In storage facilities with semi-passive climate control, infiltration through the building envelope defines the air exchange rate (see review by Smedemark⁹). Uncontrolled ventilation or infiltration is the transport of ambient air through unintentional openings such as cracks in the building envelope¹⁰. Pressure differences across the building envelope due to wind and temperature drive infiltration and can lead to variable air exchange rates¹¹. Ventilation, on the other hand, is the intentional transport of outdoor air into a building; one example being mechanical ventilation using a HVAC system¹⁰. Ventilation performance quantifies the ability of a ventilation system to distribute air within a building. One method to assess the ventilation performance is to measure the spatial distribution of air pollution in a room. Another method is to measure the time air spends in a room, also called the age of air¹².

A widespread concern in connection with the application of semi-passive climate control is that a restricted airflow can give rise to temperature, moisture and concentration stratification with development of problematic microclimates, or stagnant zones with little air movement. A microclimate is a local set of temperature and RH conditions that deviate from the surrounding atmosphere¹³. A uniform temperature distribution throughout the storage area is essential to ensure a uniform RH. Concentration gradients are believed to result from accumulation of internal air pollution off-gassing from construction materials or the collections themselves, caught in pockets of stagnant air. A study by Ryhl-Svendsen¹⁴ showed that inadequate air distribution in a test room without mechanical ventilation led to three times higher concentration of acetic acid close to the emission source (wood-fibre wall boards) compared to close to an adsorbing clay brick wall. Several studies have measured the temperature and RH in one or a handful of locations within heritage institutions¹⁵⁻¹⁷. To the knowledge of the authors however, no other studies have measured the spatial distribution in temperature, moisture and organic acids in unoccupied storage facilities with heritage collections on a room scale.

This study examined the local mean age of air together with the temperature, RH and organic acid distribution in one storage facility with a HVAC system and in one with semi-passive climate control. The spatial distribution in temperature and RH was measured in a grid of sensors laid out to map the possible formation of microclimates, as well as the concentration of organic acid, to assess the ventilation performance and possible formation of stagnant zones. The study serves as a baseline to understand air distribution in unoccupied storage facilities holding heritage collections.

2. Field measurements

2.1 The storage facilities

The objects of this study were two storage facilities. Storage I (HVAC system) contained a 15th to 17th century book collection from the Royal Library in Denmark. Books are stored on movable compact shelves on each side of a central passage (Figure 1). The facility was built in 2008. The storage room has no external walls. All walls are without windows and connect to services areas or other storage rooms. Light sensors turn the light on when people enter the store. The entrance has a double door airlock. One HVAC system with heating, cooling, humidification, dehumidification and air filtration serviced the storage room (596 m³). A building management system (BMS) controlled the intake of outdoor air as well as the internal recirculation rate. Air was supplied to the storage room to maintain a constant overpressure and control the RH. The RH was kept constant throughout the year while the set-point conditions for temperature was changed gradually from 6°C in winter up to 19°C in summer to reduce the energy use for climate control. There were no ventilation to comply with human comfort requirements. The energy use for Storage I was 67 kWh per cubic meter of storage space, per year, corresponding with 210 kWh m⁻² year⁻¹ (3 m height).¹⁸



Figure 1. Storage I with a 15th to 17th century book collection stored on movable shelves on each side of a central passage.

Storage II (semi-passive climate control) was part of a shared storage facility at the Centre for Preservation of Cultural Heritage in Vejle, Denmark. Storage II contained one room with a paper-based archival collection (3242 m³) and one with a mixed materials collection (4831 m³). All heritage objects are stored on movable shelves (Figure 2). The two rooms are part of an extension from 2013 to the existing facility. The storage room with a paper-based archival collection has two external walls as well as one wall facing a central hall and one facing another storage room. The storage room with a mixed materials collection has one external, one wall facing a central hall and two facing other storage rooms. Storage II contained no windows in order to reduce the infiltration of air from outside as well as heat gain. The entrance has a double door airlock. Uncontrolled infiltration through cracks in the building envelope controlled the airflow. The rooms are unheated with periodic mechanical dehumidification. Light sensors are activated when the storage rooms are in use. The energy use was 1.1 kWh per cubic meter per year corresponding with 7.4 kWh m⁻² year⁻¹ (6.7 m height).¹⁹

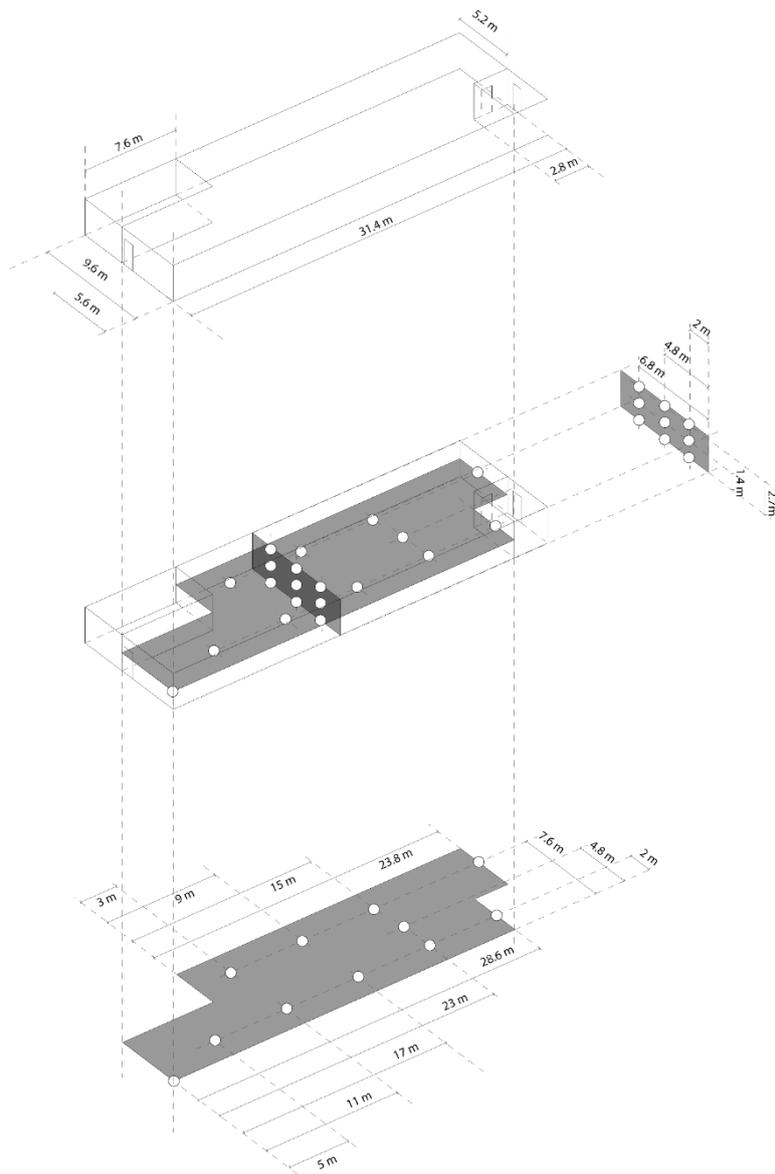


Figure 2. Storage II with a mixed material collection densely packed on wooden pallets, placed on movable shelves.

2.2 Method

The mean age of air was measured in order to assess the average time the air spends in the rooms. Measurements were performed using constant dosing with perfluorocarbon tracer gas (PFT) and sampling on duplicate passive samplers with a sorbent material^{12,20}. The PFT was released at a known emission rate from 94 capillary tubes evenly distributed throughout the three storage rooms as well as neighbouring halls and storage areas in Storage II. The mean age of air and the air exchange rate were determined from the known PFT emission rate from the capillary tubes and the concentration of tracer gas measured as an average over 16 days within each storage room. Samplers were supplied and analysed by PentIAQ, Sweden (www.pentiaq.se). The internal airflow between the room with archival collections and the room with mixed collections in Storage II was additionally determined using the same method.

The spatial temperature and RH distribution was measured using 74 battery-driven climate sensors with data loggers (Onset HOBO and Gemini TinyTag View 2, $\pm 0.4^{\circ}\text{C}$ and $\pm 3\%$ RH). The sensors were distributed in a horizontal and vertical grid (Figure 3). The horizontal grid in Storage I contained eleven sensors mounted 1.4 m above the floor (middle height) on the movable shelves. A vertical grid with six sensors was placed 0 m and 2.7 m above the floor as an extension from the horizontal grid. The horizontal grid in Storage II contained 16 sensors in the room with archival collections, and 23 sensors in the room with mixed collections. The sensors were mounted 2.5 m above the floor (middle height) on the movable shelves. A vertical grid with six sensors in the room with archival collections and twelve sensors in the rooms with mixed collections extended from the horizontal grid at 0 m and 5 m above the floor. The distance between the sensors was 3 to 6 m in Storage I and 5 to 7 m in Storage II. The distance between the measurement locations varied over time due to use of the movable compact shelves, but never more than ± 2 m.



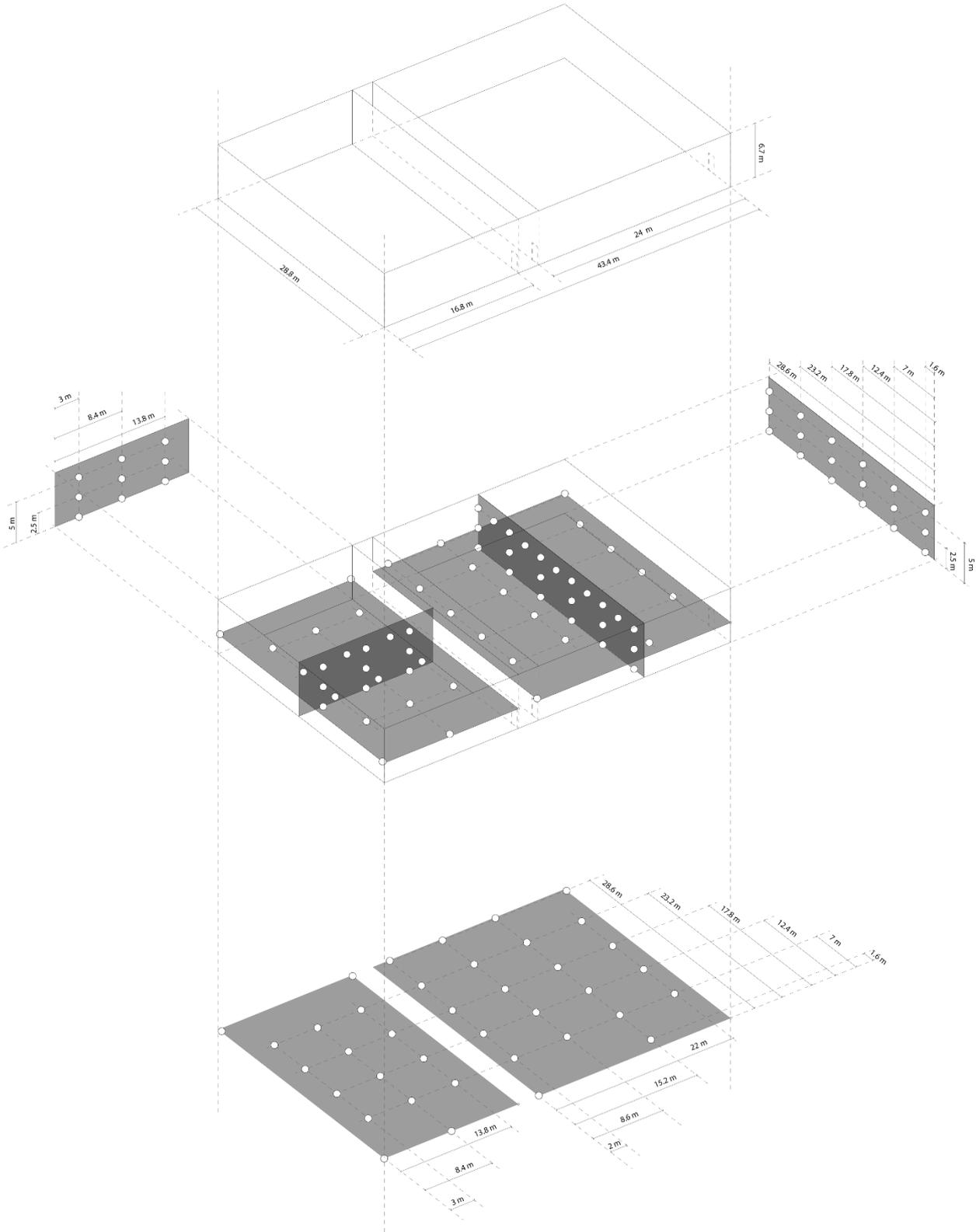


Figure 3. The distribution of measurement locations in Storage I and II.

All sensors were calibrated against a pre-calibrated reference sensor (Brüel & Kjær Indoor Climate Analyzer Type 1213) in a climate chamber (accuracy $\pm 1^\circ\text{C}$). Measurements were taken every 30 minutes over one year from February 2018 to January 2019.

The temperature and RH outside the storage facilities were measured with external climate sensors (Onset HOBO H08-Pro with an accuracy of $\pm 0.2^\circ\text{C}$ and $\pm 3\%$ RH) mounted in weather stations near the buildings.

The concentration of organic acids was measured as the average concentration over three weeks in August 2018 (summer period) using passive diffusion samplers supplied and analysed by The Swedish Environmental Research Institute IVL (www.ivl.se). The passive diffusion samplers have a detection limit of $1.4 \mu\text{g m}^{-3}$ for acetic acid and $1.0 \mu\text{g m}^{-3}$ for formic acid. The results were corrected using ambient temperature, and standard pressure. One sampler was placed in each grid point in Storage I and II, as well as outside at the weather stations. An additional measurement (winter period) was made over three weeks in February 2019 in the centre of each storage room and outdoors. The measurements at the room centres and outdoors were conducted with duplicate samplers (total of 100 samplers).

The air speed was measured in each grid point with a Brüel & Kjær Indoor Climate Analyzer Type 1213 with an air velocity transducer Type MM0038 (measurement range $0.05 - 1 \text{ m s}^{-1}$, accuracy $\pm 0.05 \text{ m s}^{-1}$)²¹. The air velocity transducer was placed in a rack and the air speed measured as an average over three minutes with one person in the room standing away from the measurement location.

3. Results

The average mean age of air was four hours in Storage I with a HVAC system, 82 hours in the room with archival collections and 151 hours in the larger room with mixed collections (Storage II, with semi-passive climate control). This corresponds to an air exchange rate of 0.25 hour^{-1} in Storage I and 0.01 hour^{-1} in Storage II.

3.1 Climate performance

From February 2018 to January 2019, the outdoor temperature fluctuated from -9°C in winter up to 33°C in summer, and with large daily variations up to about 15°C . The temperature in Storage I was allowed by the HVAC system to fluctuate seasonally from 6°C in winter up to 19°C in summer. The average temperature throughout the one-year measurement period was 12°C . The building design of Storage II controlled the seasonal temperature fluctuation from 7°C in winter up to around 19°C in summer. The one-year average temperature in Storage II was 13°C . On a daily basis, the temperature fluctuations were rather modest (below $\pm 0.5^\circ\text{C}$) (Supporting information I).

The average temperature during the three weeks' measurement of air pollution in August 2018 is shown for each location in Figure 4. The temperature distribution throughout the horizontal measurement grids within Storage I and II was uniform. However, there was a weak vertical temperature gradient with a decrease in temperature from the floor towards the ceiling in Storage I, and oppositely an increase in temperature from the floor to the ceiling in Storage II. The maximum vertical temperature gradient was -2.7°C in Storage I (floor to 2.7 m height) and up to 3.8°C in Storage II (floor to 5 m height).

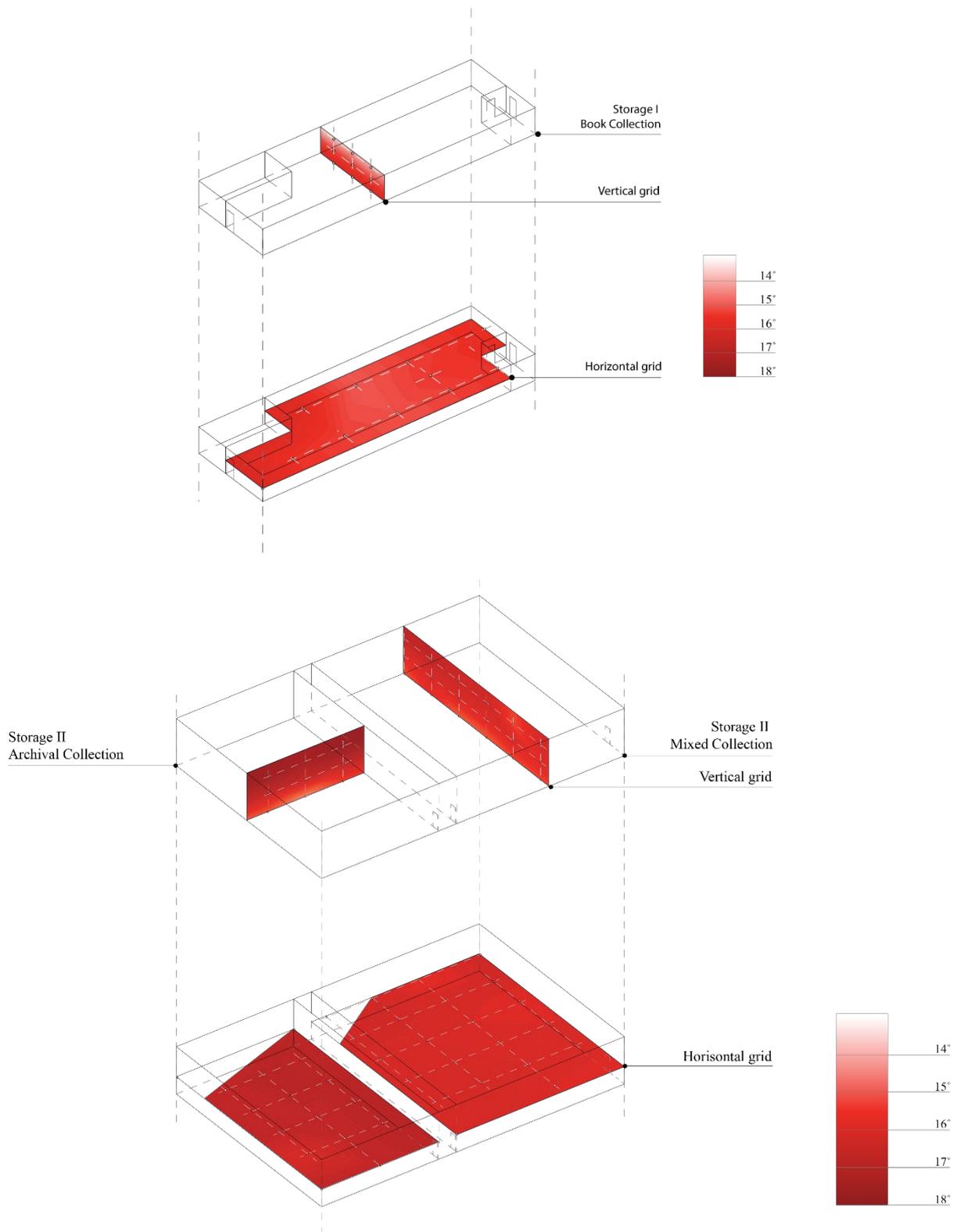


Figure 4. The average temperature over three weeks in August 2018 in each measurement location in the horizontal and vertical grid in Storage I and II. Low temperatures are shown in light red and high temperatures in dark red.

Figure 5 shows the temperature variation between January 2018 and February 2019 in the vertical grid in the archival collection in Storage II. The weak vertical temperature stratification is visible from late spring and increase through the summer. The largest temperature difference was 3.8°C between the floor and 5 m height. The same temperature stratification was observed within the room with mixed collections in Storage II.

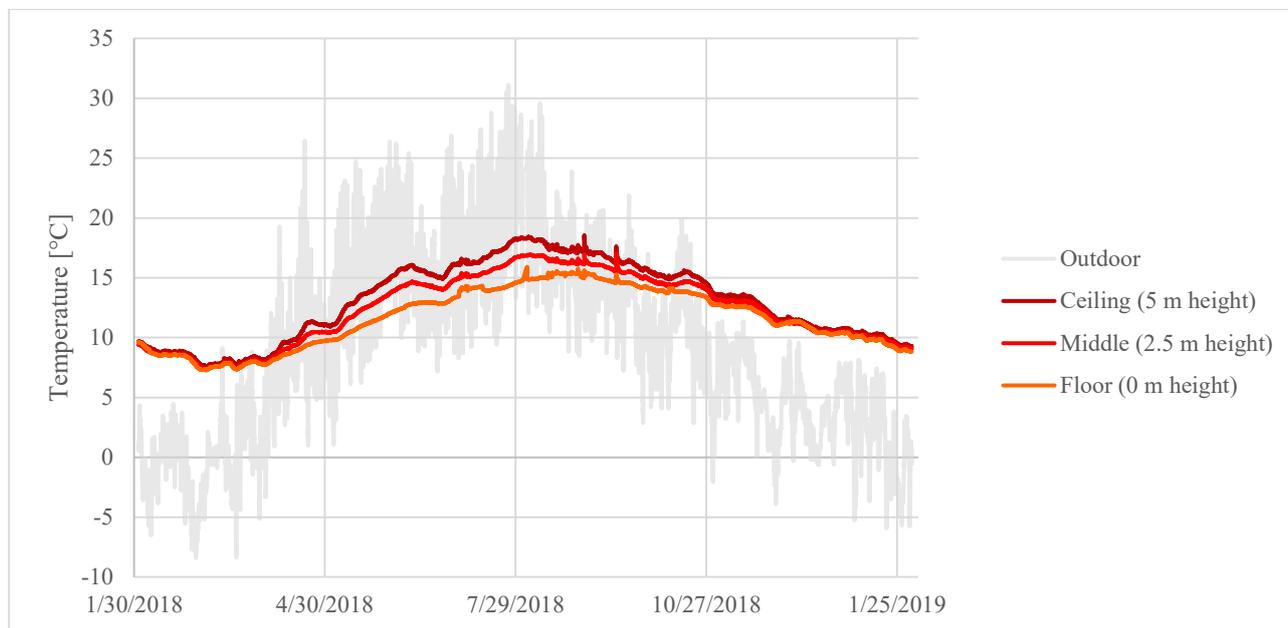
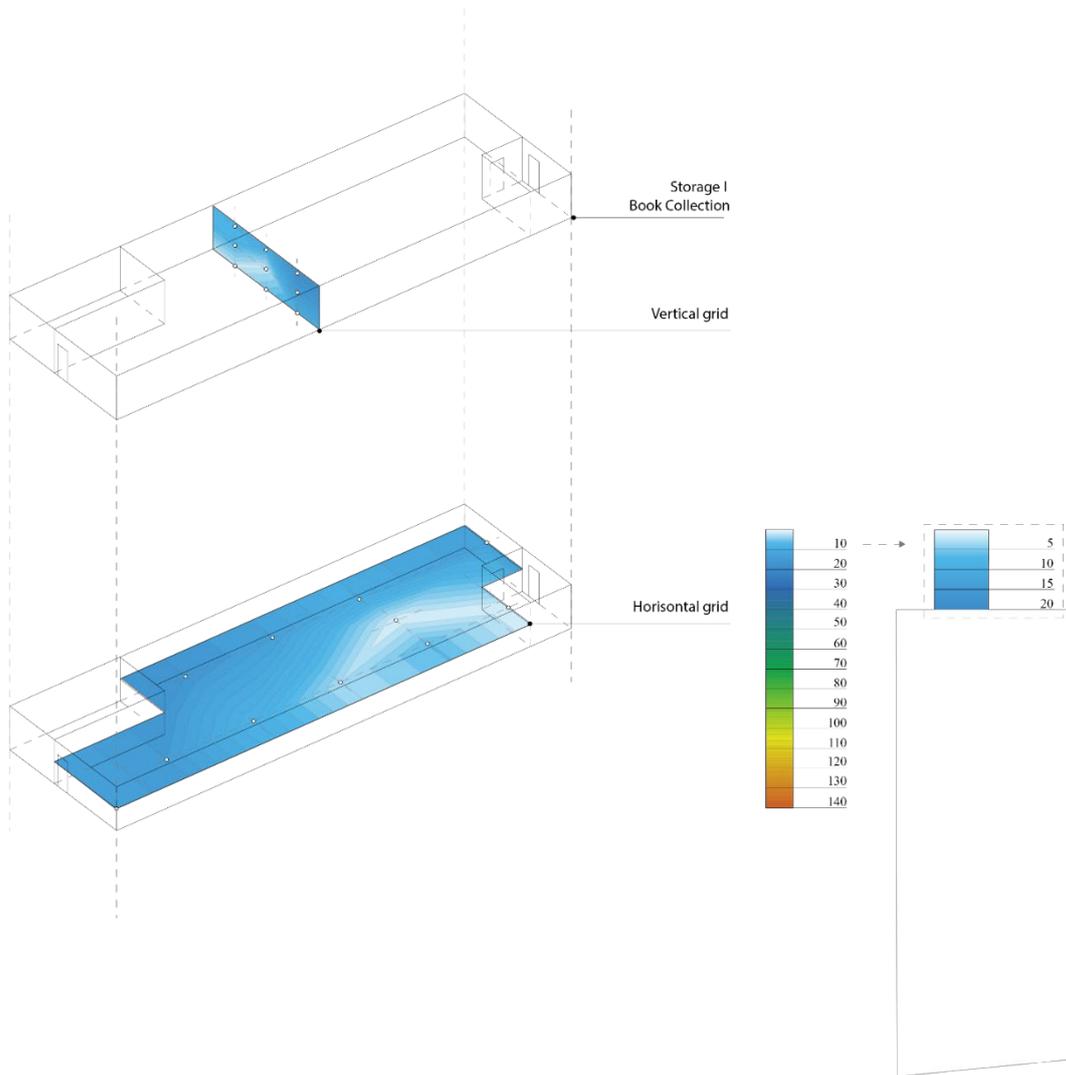


Figure 5. Temporal plot of the temperature in the vertical grid in the room with archival collections (Storage II) from January 2018 to February 2019. (The two peaks in temperature in late autumn in the middle and close to the ceiling could be due to human activities such as heritage objects being handled close to the measurement location).

The outdoor RH fluctuated with large daily variation from 17% RH to 100% RH, where condensation will occur. Indoors the absolute humidity (air concentration of water vapour, g m^{-3}) was uniform within the entire storage area. The vertical temperature gradient, however, caused a RH gradient opposite to that of temperature. Storage I maintained an average RH of 46% (range 29-58% RH) aided by the HVAC system. Storage II maintained a moderate RH of 37% on average in the archival room (range 25-48% RH). In the mixed collection's room the average RH was 43% (range 33-57% RH).

3.2 Air quality performance

The average concentration of organic acids, as measured over three weeks in August 2018, ranged from 2 to $19 \mu\text{g m}^{-3}$ in the room with library collections within Storage I, from 2 to $21 \mu\text{g m}^{-3}$ in the room with paper-based archival collections, and 45 to $134 \mu\text{g m}^{-3}$ in the room with mixed collections within Storage II (Figure 6 and Supporting information 2).



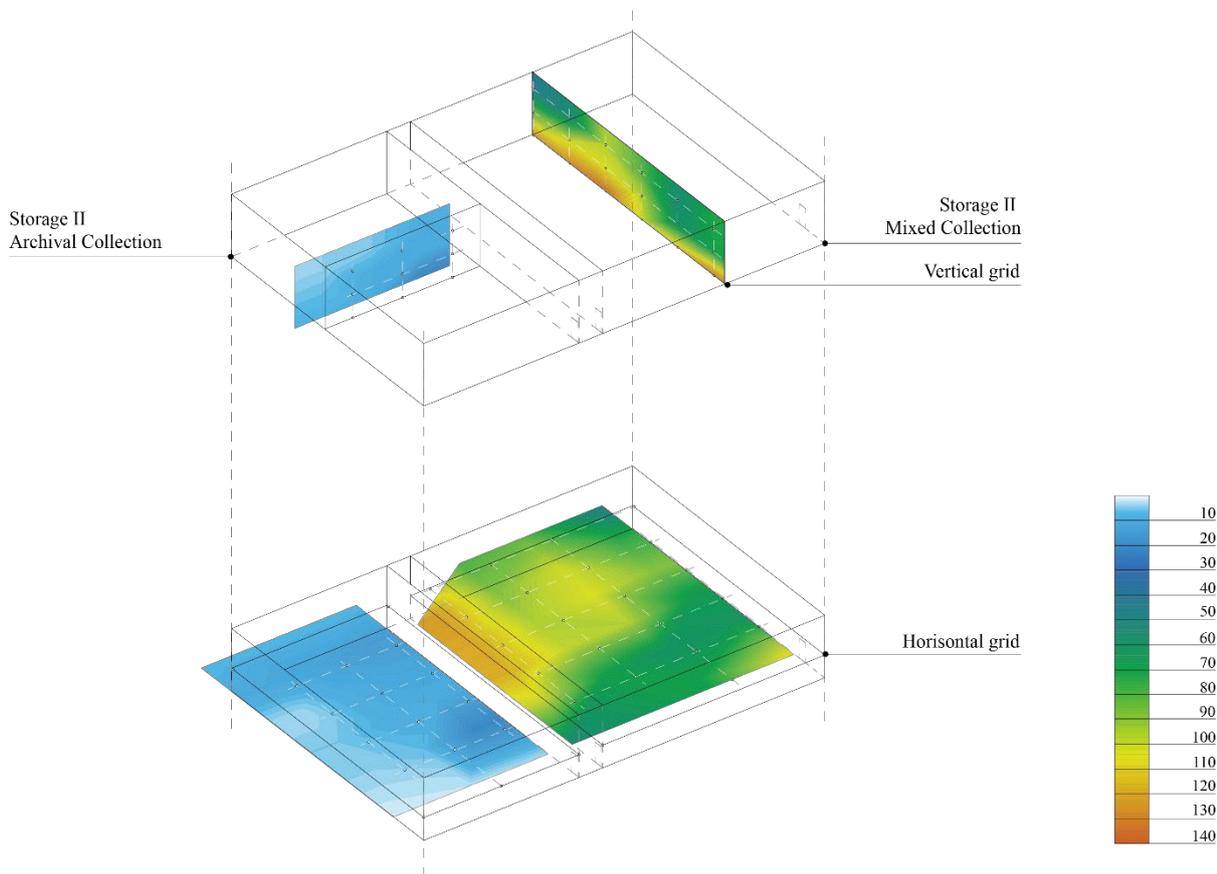


Figure 6. The vertical and horizontal grid within Storage I and II showing the air concentration of organic acid ($\mu\text{g m}^{-3}$). The colour scale shows the sum of organic acid from blue (lowest concentration) to orange (highest concentration). One measurement location in the corner of the room with mixed collections in Storage II was left out due to a large object.

Outdoors the concentration of organic acids was below detection limit ($< 1 \mu\text{g m}^{-3}$) in winter and $4 \mu\text{g m}^{-3}$ in summer. Inside at the centre of Storage I the concentration increased from $6 \mu\text{g m}^{-3}$ in winter to $15 \mu\text{g m}^{-3}$ in summer. At the centre of the room with archival collections in Storage II the concentration increased from $3 \mu\text{g m}^{-3}$ in winter to $9 \mu\text{g m}^{-3}$ in summer, and in the room with mixed collections organic acids increased from $28 \mu\text{g m}^{-3}$ in winter to $97 \mu\text{g m}^{-3}$ in summer.

In Storage I, the air speed was $0.10\text{-}0.09\text{ m s}^{-1}$ in measurement locations close to the air supply units, whereas the air speed at all other locations were below the measurement range of the instrument (0.05 m s^{-1}). The air speed was below the instrument range in all measurement locations in the horizontal plan in Storage II except at the entrance to the room with a mixed material collection (0.06 m s^{-1}). The air speed decreased from the ceiling towards the floor in the vertical plan from 0.11 m s^{-1} to below instrument range in the archival room and from up to 0.15 m s^{-1} to below instrument range in the mixed collections room.

Figure 7 shows the internal airflow between the rooms with archival and mixed collections, and the exchange with other rooms of Storage II. The airflow rate ($\text{m}^3\text{ h}^{-1}$) was ten times higher from the room with mixed collections into the rooms with archival collections than in the opposite direction. The room with mixed collections received $1 \pm 0.1\text{ m}^3\text{ h}^{-1}$ air from the room with archival collections and $44 \pm 5.1\text{ m}^3\text{ h}^{-1}$ from other parts of Storage II, whereas the room with archival collections received $11 \pm 1.2\text{ m}^3\text{ h}^{-1}$ air from the room with mixed collections and $43 \pm 6.2\text{ m}^3\text{ h}^{-1}$ from other parts of Storage II.

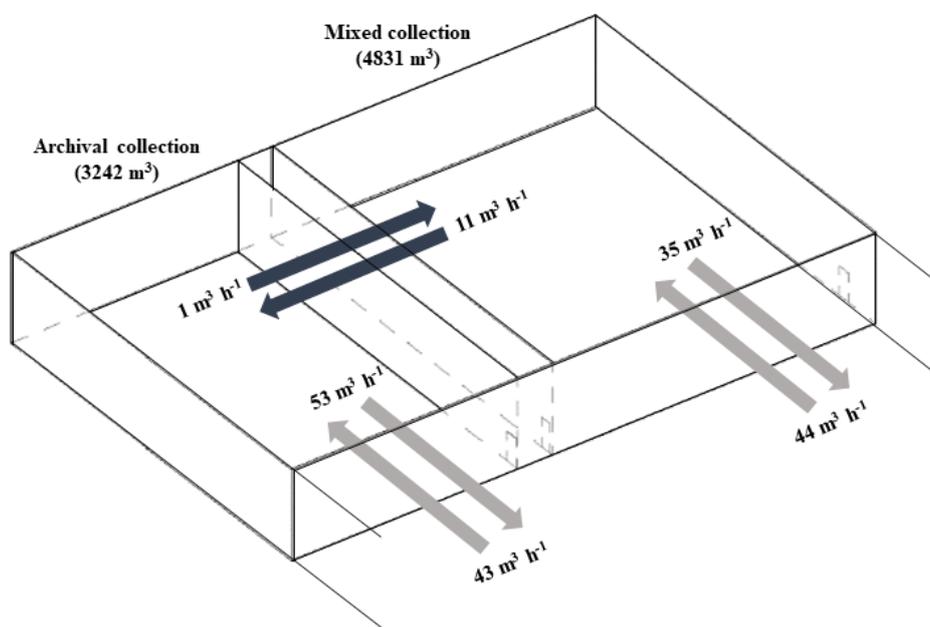


Figure 7. Internal airflow between the room with archival and mixed collections in Storage II and adjacent rooms.

4. Discussion

The different ventilation forms significantly influenced the average time the air spends within the two storage facilities. On average, the air spent nearly 40 times longer in the room with mixed collections in Storage II with semi-passive climate control than in Storage I with a HVAC system. Constant dosing with PFT assumes an even distribution in tracer gas throughout the storage room and uncertainties about 20-25% can be expected under optimal measurement conditions²². The restricted airflow in Storage II with semi-passive climate control can increase the uncertainty. The measurements still confirmed, however, that the air exchange rate was low in Storage II. The higher energy use for climate control in Storage I clearly demonstrated that increasing airtightness increases the time the air will spend in the storage and at the same time eliminates the demand for energy to condition and clean the supplied outdoor air.

The temperature distribution was uniform in the horizontal plane within both storages but it varied in the vertical plan. A vertical temperature stratification is not uncommon in large rooms²³. In Storage II with semi-

passive climate control, the temperature decreased from the ceiling towards the floor. The results are in accordance with a study by Ryhl-Svendsen *et al.*²⁴ who measured a vertical temperature gradient as high as 2.7°C between the floor and 5.8 m height in a storage with semi-passive climate control. The uninsulated heavy floor in Storage II cools down the storage area as the outdoor temperature increase in summer, possibly giving rise to thermal stratification with a weak temperature decrease from the ceiling towards the floor. Additionally, the mechanical dehumidification system was running in summer when the temperature in the storage was below the outdoor temperature. Reactivation of the silica gel dehumidification system can generate heat that was supplied with the air close to the ceiling probably contributing to the temperature stratification.

Generally, the distribution of absolute humidity was rather uniform within both storage buildings. The vertically increasing temperature led to a RH gradient in the opposite direction; decreasing from the ceiling towards the floor in Storage I and from the floor to the ceiling in Storage II. In Storage I, the HVAC system controlled the moisture content in the air and the relatively high air exchange rate lead to a uniform moisture distribution. In Storage II, on the other hand, the buffer capacity of the building interior and the collections upheld a uniform moisture distribution due to the low air exchange rate.

This is to the knowledge of the authors the first study measuring the spatial distribution of temperature, moisture and organic acids on a room scale in special storage facilities with heritage collections. The results clearly demonstrate that both ventilation forms can uphold an acceptable climate performance with appropriate temperature and moisture distributions and without air pockets producing problematic microclimates. The temperature and RH are, except for a low winter temperature and occasional short-term peaks in the RH, within the specifications set for Class A1 (precision control with seasonal adjustment from the annual average) ASHRAE for museums, libraries and archives².

The different ventilation forms also influenced the distribution of organic acids in different ways. In Storage I, the HVAC system supplied air along one wall and the concentration increased as the air passed through the room to the exhaust on the opposite wall producing a vertical concentration stratification. In addition, the concentration of organic acids increased in two corners in the horizontal plan within Storage I next to the entrance and service areas (left uncoloured in Figure 6). A possible explanation to this could be the lack of exhaust openings in the entrance and service areas, which may give rise to a local increase in the concentration of organic acids.

There were areas in the room with mixed collections in Storage II where incomplete mixing caused a local accumulation of organic acids in stagnant zones. The concentration particularly increased in one measurement location in the corner, in larger areas in the middle of the room and along the wall facing the corridor to the room with archival collections. The larger areas with accumulation of organic acids spanned three measurement locations with an area of about 11 m x 7 m. The stagnant zones could indicate an uneven distribution of emissive heritage objects within the storage room. The collection seemed however evenly distributed and the stagnant zones therefore more likely indicated areas in the corner and in the middle of the compact movable shelves where there was poor mixing of the air.

The vertical organic acid stratification, which was up to three times from the ceiling towards the floor in both rooms in Storage II, could be due to the low air exchange rate producing stagnant zones with little air movement. The air speed was below 0.05 m s⁻¹ in all measurement locations except for one location next to the entrance in the room with mixed collections and all measurement locations close to the ceiling in the vertical grid (5 m height). The mechanical dehumidification system supplied air close to the ceiling in Storage

II increasing the air speed in this area. In addition to air humidity control, the desiccant silica gel rotor type dehumidifier is known to also remove volatile organic compounds from air²⁵ and could maybe contribute to the local decrease in organic acid concentration and the vertical concentration stratification. Further research is needed to determine the organic acid removal efficiency of desiccant silica gel rotors.

The concentration of organic acid in Storage II increased with up to four times across the room with paper-based archival collections. The concentration increased from the outside wall towards the entrance to the room with mixed collections. This could be due to a combination of an empty section of the room and the internal airflow. The room with archival collections was only partly in use and the section facing the outside wall was entirely empty. Ryhl-Svendensen¹⁴ showed that inadequate airflow in a test room without mechanical ventilation caused a similar concentration gradient with a three times larger concentration of acetic acid close to the emission source compared to an adsorbing clay wall. In addition, the room with archival collections received more air from the room with mixed collections, and therefore had a higher concentration of organic acid than other parts (Figure 7). The internal airflow measurements are specific for Storage II however; the results demonstrate how internal airflow between rooms can influence the distribution of air pollution inside a building.

There was a clear difference in the magnitude of the organic acid concentrations measured in the mixed collections room and the archival collections room in storage II. This difference indicated that, besides the ventilation form, other parameters also affected the concentration level. One such parameter was the type of collection in the storage. The mixed collections room contained archaeological wood, wooden furniture etc. stored on new wood packaging, whereas the archival collection room contained paper. The area-specific emission of organic acid from wood and especially wood packaging materials used to transport and store collections may be five to 30 times larger than the emission from paper²⁶.

In addition, temperature and RH may affect the rate of emission of organic acids from heritage collections. Smedemark *et al.*²⁶ measured a decrease in organic acid emission by up to a factor four from naturally aged wood and paper in test chamber experiments when lowering the temperature from 23°C to 10°C and a factor two or more when lowering the RH from 50% to 20% RH. The concentration of organic acids in air within all three rooms decreased with 60% to 71% from summer to winter. Krupinska *et al.*¹⁶ found a similar decrease in organic acid concentration with a decrease in temperature from summer to winter. This stresses that emission of organic acids from internal sources depend on temperature and that temperature can be used as a control measure. The difference between the average RH in the room with archival collections (37% RH) and the room with mixed collections (43% RH) was only 6%-points and other factors might therefore have been more significant.

The concentration of organic acids in Storage I and II were within the thresholds specified in PAS198:2012²⁷. The standard proposes about 2500 µg m⁻³ (1000 ppb) for general collections as limestone, ceramics, fossils, pottery, egg shells and copper, whereas sensitive materials as lead should be stored in environments with a concentration below about 250 µg m⁻³ (100 ppb). The threshold level for organic acid in storage buildings with heritage collections has however been widely discussed and there are no consensus on absolute threshold levels for organic acids within the conservation literature. This study demonstrated that both storages provided an acceptable indoor climate and air quality performance irrespective of the ventilation form.

5. Conclusion

This study demonstrated that both the tested ventilation forms upheld an acceptable climate performance with appropriate temperature and moisture distributions and without air pockets producing problematic microclimates. The study thereby confirmed that semi-passive climate control may provide an acceptable climate performance for the preservation of collections at a significantly lower energy use than mechanical ventilation.

In addition, the study showed that the organic acid concentration was within the recommendations for sensitive materials as set by PAS198:2012. In Storage I, the HVAC system controlled the organic acid distribution. The concentration of organic acid increased with up to five times from the air supply across the room to the exhaust. Stagnant zones with a local accumulation of organic acids were only present in the horizontal grid in the mixed collections room within Storage II with semi-passive climate control. The concentration difference was up to $44\mu\text{g m}^{-3}$ between adjacent measurement locations. Furthermore, a vertical concentration stratification existed in Storage II with an up to three times increase in concentration from the ceiling to the floor. The vertical concentration stratification may be due to organic acid removal by the desiccant silica gel dehumidifier.

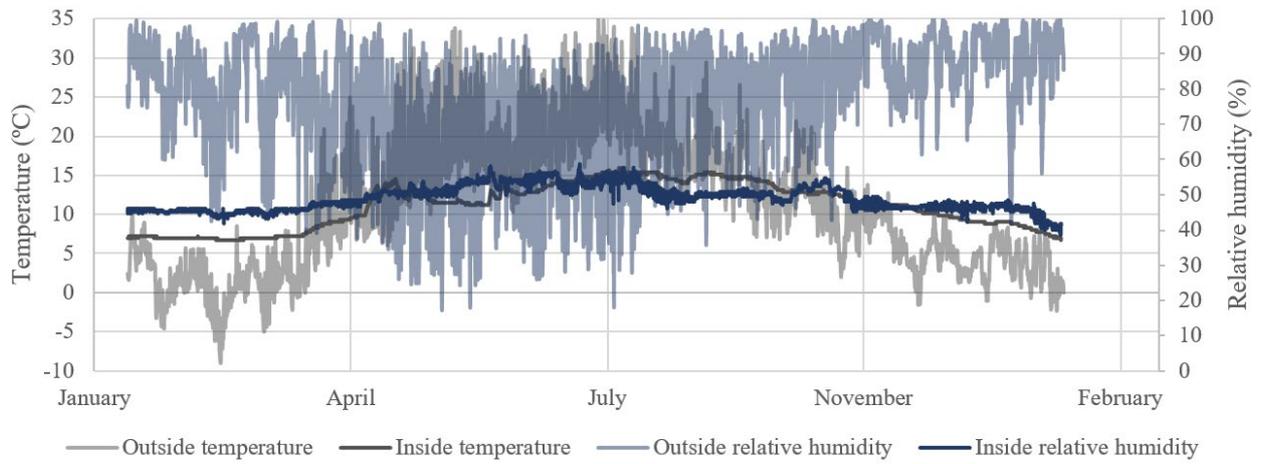
The difference in the concentration of organic acids between the archival collection room ($2\text{-}21\mu\text{g m}^{-3}$) and the mixed collections room ($45\text{-}134\mu\text{g m}^{-3}$) in Storage II however, stresses that other parameters than the ventilation form may impact the concentration of air pollution off-gassing from indoor sources. Parameters that can affect the concentration of organic acid include the loading and type of materials as well as the temperature and RH within the storage.

This study demonstrated that both storages provided an acceptable indoor climate and air quality performance irrespective of the ventilation form. Although the study was limited to two storage facilities only, the general differences in the two ventilation forms are clearly shown. The decision to install a ventilation system with air filtration will ultimately depend on the organic acid concentration that caretakers are willing to accept as well as the removal efficiency and energy use of air filtration. Further research is needed to expand our understanding of the air distribution in storage facilities with heritage collections and ensure sustainable storage solutions that preserve heritage collections for future generations without excessive energy use.

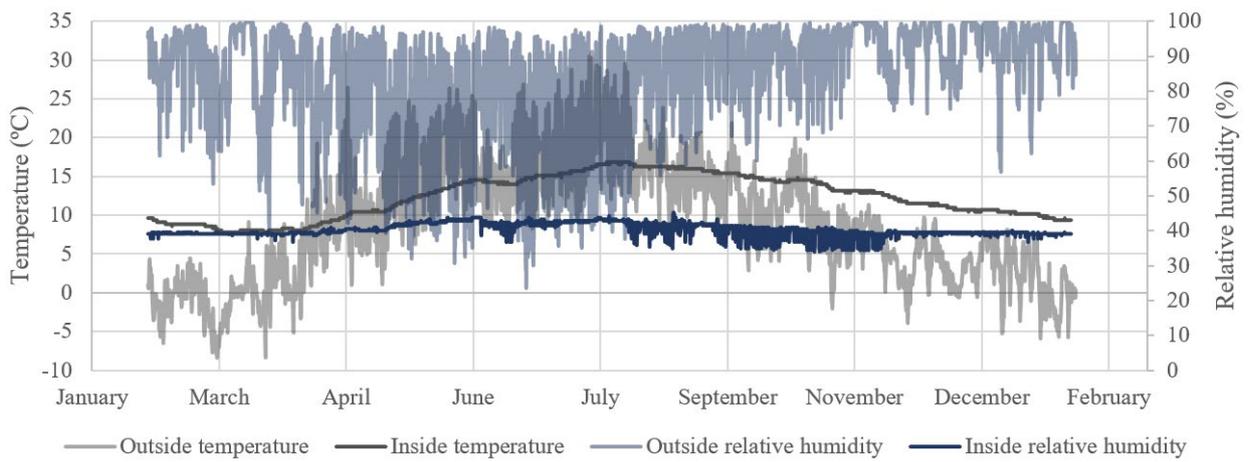
Supplementary information 1

The temperature and RH in a central measurement location within Storage I and II as well as outdoors. The measurements were running from January 2018 to February 2019.

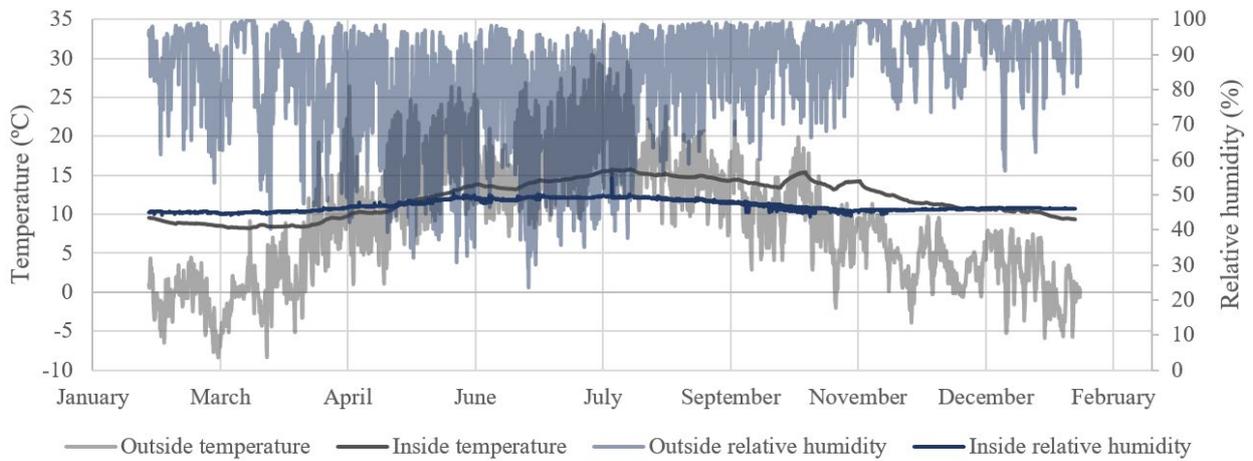
Storage I



Storage II - archival collection



Storage II - mixed collection



Supplementary information 2

The formic and acetic acid concentrations ($\mu\text{g m}^{-3}$) in Storage I and the room with archival and mixed collections in Storage II. (*Due to a large museum object in the corner of the room with mixed collections in Storage II measurement location 1 was left out). The results were corrected using ambient temperature (14°C in Storage I and 16°C in Storage II), and standard pressure.

Storage I		
Sample No.	HCOOH ($\mu\text{g m}^{-3}$)	CH ₃ COOH ($\mu\text{g m}^{-3}$)
Outdoor	1.4	2.1
1	9.1	5.4
2	8.4	8.0
3	6.3	3.3
4	4.2	<1.0
5	<1.0	2.0
6	4.4	2.3
7	5.7	2.3
8	3.6	1.8
9	2.3	<1.0
10	4.5	4.3
11	6.0	2.9
12	9.6	5.1
13	10.5	8.0
14	2.3	<1.0
15	7.5	3.6

16	9.0	4.7
17	11.7	5.7

Storage II - archival collections		
Sample No.	HCOOH ($\mu\text{g m}^{-3}$)	CH₃COOH ($\mu\text{g m}^{-3}$)
Outdoor	1.3	2.1
1	1.7	6.2
2	1.7	6.3
3	5.3	6.1
4	6.4	6.5
5	6.6	8.0
6	2.3	1.7
7	4.1	6.0
8	3.5	8.7
9	2.2	6.0
10	2.5	3.0
11	1.7	2.7
12	4.6	4.3
13	3.4	5.7
14	3.1	2.0
15	8.8	12.7
16	4.5	5.8

17	4.2	4.3
18	<1.0	4.6
19	3.8	2.9
20	4.2	15.8
21	<1.0	2.8
22	<1.0	2.4
23	<1.0	3.7

Storage II - mixed collections		
Sample No.	HCOOH ($\mu\text{g m}^{-3}$)	CH₃COOH ($\mu\text{g m}^{-3}$)
Outdoor	1.3	2.1
1*	-	-
2	11.6	69.8
3	16.1	106.9
4	12.8	71.8
5	5.6	39.8
6	2.0	43.9
7	15.9	107.0
8	14.0	75.9
9	17.5	108.8
10	15.6	85.3
11	9.7	45.8

12	12.3	64.3
13	18.5	101.3
14	15.6	80.2
15	20.3	113.1
16	21.6	81.6
17	19.2	79.1
18	14.1	75.7
19	15.2	101.6
20	11.6	87.3
21	17.1	85.4
22	16.6	79.9
23	11.6	70.6
24	9.4	56.4
25	14.4	85.5
26	10.9	57.8
27	21.2	91.9
28	8.0	52.1
29	6.0	50.2
30	7.1	56.0
31	20.1	110.2
32	13.2	57.7
33	10.8	61.9

34	7.0	48.4
35	13.8	96.4

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Paper VII

Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J.

‘Comparing the air quality performance in unoccupied storage buildings with mechanical ventilation and semi-passive climate control’

In Proceedings from the *19th International Council of Museums - Committee for Conservation (ICOM-CC) Triennial Conference*, 14-18 September 2020, Beijing, China (submitted 15.11.2019).

Comparing the air quality performance in unoccupied storage buildings with mechanical ventilation and semi-passive climate control

Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J.

Abstract

Air pollution can damage heritage collections. This study examines the air quality performance in one store with mechanical ventilation and one with semi-passive climate control. Air pollution was measured with passive diffusion samplers during summer and winter. The atmospheric corrosivity was determined gravimetrically using copper, zinc and lead coupons as well as with a real-time electrical resistance monitor over one year. The concentration of outdoor generated air pollution was low in both stores. The emission of formic acid and acetic acid from internal sources led to a higher concentration indoors. The total acid concentration was $15 \mu\text{g m}^{-3}$ in the store with mechanical ventilation and $97 \mu\text{g m}^{-3}$ in the store with semi-passive climate control. The indoor atmospheric corrosivity was determined as very low by both methods. The study demonstrated that stores using mechanical ventilation with air filtration and semi-passive climate control provide an acceptable air quality for the preservation of heritage collections.

Keywords air pollution, acetic acid, formic acid, air exchange rate, emission, corrosion monitoring, lead dosimeter.

1. Introduction

Air pollution can cause damage to heritage collections and many metals and their alloys are as an example prone to atmospheric corrosion. Formic acid and acetic acid are among the most critical indoor air pollutants (Brimblecombe and Grossi, 2012). Lead is particularly sensitive to organic acids (Tétreault *et al.* 2003) and white corrosion products due to formic acid and acetic acid exposure have been detected on many different types of lead objects (for example; Padfield *et al.* 1982; Tennent and Cannon, 1993; Chiavari *et al.* 2008).

The ability of the indoor atmosphere to increase corrosion (*'the indoor atmospheric corrosivity'*) is classified in the international standard ISO 11844-1:2006. The standard contains five atmospheric corrosivity categories from IC1 (very low corrosivity) to IC5 (very high corrosivity). In ISO 11844-2:2005 a method is described on how to measure the indoor atmospheric corrosivity using metal coupons. The standard includes silver, copper, zinc and carbon steel coupons. Ryhl-Svendsen (2008) additionally showed that lead coupons can be used to evaluate the indoor atmospheric corrosivity particularly from formic acid and acetic acid. The metal coupons function as dosimeters that deteriorate in a way similar to objects found within the collections. The weight increase due to corrosion is measured gravimetrically several times over the course of one year, and the development in mass is converted into a corrosivity category (ISO 11844-2:2005, Table 2.2).

Various transportable real-time sensors have also been developed to assess the indoor atmospheric corrosivity in heritage institutions. One is the AirCorr™ monitoring system, which measures the corrosion rate over time as the increase in electrical resistance due to corrosion on a thin metal track made of zinc, copper, silver, iron or lead. The metal track thickness depends on the desired sensitivity and service life of the sensor where increasing thickness increases the service life but decreases the sensitivity (Kouril *et al.* 2014). Prosek *et al.* (2013) proposed an indoor atmospheric corrosivity classification for electrical resistance type lead sensors. Class L1 is pure air causing no visible lead corrosion and with a corrosion rate $< 3 \text{ nm per month}$. The

classification ends with Class L4 representing polluted air causing very visible corrosion and a corrosion rate ≥ 50 nm per month. The AirCorr™ monitor and sensor are more expensive than the coupon method but provide detailed information on how the rate of corrosion progresses over time.

This study compares the air quality performance in one store with mechanical ventilation (Storage I) and one with semi-passive climate control (Storage II). The air exchange rate and the mean age of air were measured as the concentration decay of perfluorocarbon tracer gas over time. Passive diffusion samplers were used to measure the concentration of ozone and nitrogen dioxide from outdoor sources and the concentration of formic acid and acetic acid off-gassing from internal sources during a winter and summer period. The atmospheric corrosivity was measured gravimetrically with copper, zinc and lead coupons together with a real-time electrical resistance monitor with a 400 nm lead sensor over one year.

2. Field measurements

2.1 Sites

Storage I contained a 15th to 17th century book collection from the Royal Library in Denmark stored densely packed on movable shelves. The storage facility was located in central Copenhagen surrounded by heavy traffic. The room was about 600 m³. A mechanical ventilation system with carbon filtration serviced the room. A building management system (BMS) controlled the outdoor air intake and the recirculation rate. The mechanical ventilation consumed 67 kWh m⁻³ year⁻¹ (personal communication: Danielsen, N.).

Storage II contained a mixed material collection with objects made of among other materials wood, paper, leather, glass, metal, stone and plastic stored densely packed on movable shelves. The storage room was part of the shared storage facility at the Centre for Preservation of Cultural Heritage located in a rural area outside Vejle in Denmark. The room was about 4800 m³. Infiltration through leaks in the building envelope dominated the air exchange rate. The storage facility was built on the concept for semi-passive climate control where the building construction ensures a stable temperature that varies seasonally (Ryhl-Svendsen *et al.* 2011; Bøhm and Ryhl-Svendsen, 2011). The relative humidity (RH) was kept constant with periodic mechanical dehumidification. The energy use for mechanical dehumidification was 1.1 kWh m⁻³ year⁻¹ (personal communication: Knudsen, L.R.).

2.2 Method

Constant dosing with perfluorocarbon tracer gas and sampling on passive samplers provided by PentIAQ, Sweden, were used to measure the air exchange rate (ASTM E741-11:2017). The mean age of air (the average time air spends inside the store) was calculated according to ISO 16000-8:2007.

The concentration of air pollution was measured with passive diffusion samplers from Gradko International Ltd, UK, (ozone and nitrogen dioxide), and the Swedish Environmental Research Institute IVL (formic acid and acetic acid). The limit of detection was 2.0 µg m⁻³ for ozone, 0.4 µg m⁻³ for nitrogen dioxide, 1.4 µg m⁻³ for acetic acid and 1.0 µg m⁻³ for formic acid. The concentration was measured as an average over three weeks in the middle of each storage room and outdoors using samplers placed in duplicate at each location. The measurements were conducted in winter (February) and summer (August).

The temperature and RH were measured from February 2018 to January 2019 (TinyTag View 2 climate sensors, ± 0.4 °C and $\pm 3\%$ RH, Gemini Dataloggers, UK).

The corrosivity of the atmosphere was measured gravimetrically as the mass increase of copper, zinc and lead coupons during the one year measurement period from February 2018 to January 2019. All coupons were made from pro analysis above 99.9% pure metal (MERCK and Alfa Aesar, Germany). The copper and zinc coupons were prepared as described in ISO 11844-2:2005 and the lead coupons as described by Ryhl-Svendson (2008). The metal was cut into 50 x 30 mm (copper) and 50 x 20 mm (zinc and lead) coupons. Three coupons from each metal were placed approximately in the centre of each storage room and weighed every three months using a Mettler Toledo MT5 balance (accuracy $\pm 1 \mu\text{g}$). The atmosphere's corrosivity towards lead was additionally measured continuously (15 min intervals) from February 2018 to January 2019 as the increase in electrical resistance on a 400 nm lead sensor with an AirCorr™ I Indoor Datalogger (Institut de la Corrosion / NKE Instrumentation, Brest, France).

3. Results

3.1 Air pollution

Table 1 shows the air exchange rate and the mean age of air. The mean age of air was almost 40 times higher in Storage II with semi-passive climate control than in Storage I with mechanical ventilation.

	Storage I	Storage II
Air exchange rate (hours⁻¹)	0.3	0.01
Mean age of air (hours)	4	151

Table 1. Air exchange rate and mean age of air in Storage I and II.

Table 2 shows the concentration of ozone, nitrogen dioxide and organic acids in Storage I and II. The concentration of ozone was below detection limit in both stores except for Storage II in summer. The concentration diminished indoors to less than 5% of the ambient level. Also, the concentration of nitrogen dioxide was below detection limit within both stores in summer. In winter, the concentration diminished to 9-4% of the ambient level.

	Storage I				Storage II			
	Indoor		Outdoor		Indoor		Outdoor	
Season	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
Ozone ($\mu\text{g m}^{-3}$)	< LOD	< LOD	61.3	74.1	< LOD	2.4	58.4	60.7
Nitrogen dioxide ($\mu\text{g m}^{-3}$)	1.8	< LOD	19.4	10.9	0.5	< LOD	12.5	5.4
Organic acid ($\mu\text{g m}^{-3}$)	6.5	14.7	< LOD	3.5	28.3	96.5	< LOD	3.5

Table 2. Concentration of air pollution in summer and winter in Storage I and II. Organic acid is the sum of formic acid and acetic acid concentrations. <LOD indicate measurements below the limit of detection (ozone < $2.0 \mu\text{g m}^{-3}$, nitrogen dioxide < $0.4 \mu\text{g m}^{-3}$, acetic acid < $1.4 \mu\text{g m}^{-3}$ and formic acid < $1.0 \mu\text{g m}^{-3}$).

The concentration of organic acids (formic acid + acetic acid) was always higher indoors than outdoors. The concentration additionally varied from summer to winter. The concentration decreased 56% from summer to winter in Storage I and 71% from summer to winter in Storage II.

The BMS controlled the temperature and RH inside Storage I. The temperature varied slowly from 7 °C in winter to 16 °C in summer and with a constant $45 \pm 10\%$ RH throughout the year. In Storage II, the structure of the building passively controlled the indoor temperature changing slowly from 9 °C in winter to 16 °C in summer, while the RH was kept constant at $46 \pm 7\%$ RH using periodic mechanical dehumidification.

3.2 Corrosivity measurements

Figure 1 shows the average increase in mass of the metal coupons after one year's exposure. For copper it was 1.9 mg m^{-2} in Storage I and 2.5 mg m^{-2} in Storage II, while for zinc it was 7.9 mg m^{-2} in Storage I and 17.7 mg m^{-2} in Storage II. Lead coupons increased in mass with 70.1 mg m^{-2} in Storage I, and 483.5 mg m^{-2} in Storage II.

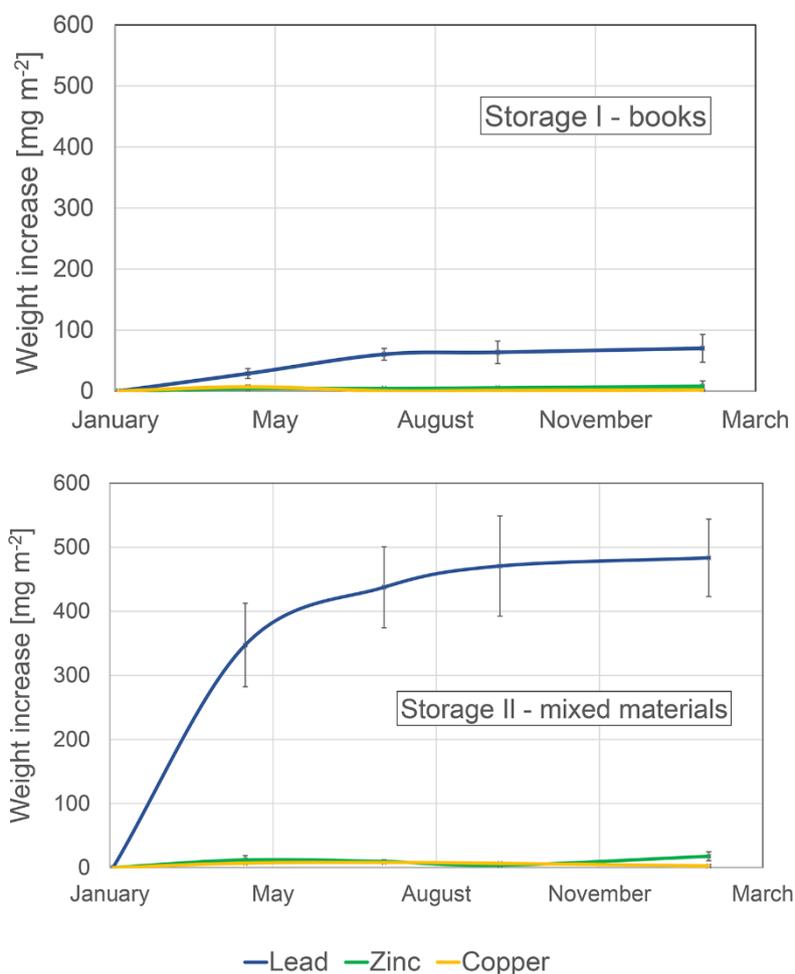


Figure 1. The average increase in mass of copper, zinc and lead coupons in Storage I and II, as measured every three months from February 2018 to January 2019 (one year). Error bars display the standard deviation of each set of measurements (three coupons of each metal).

Figure 2 shows the increase in corrosion thickness on the AirCorr™ lead sensor. The corrosion thickness increased with 5 nm within Storage I with a book collection and 13 nm in Storage II with a mixed material collection after one year's exposure.

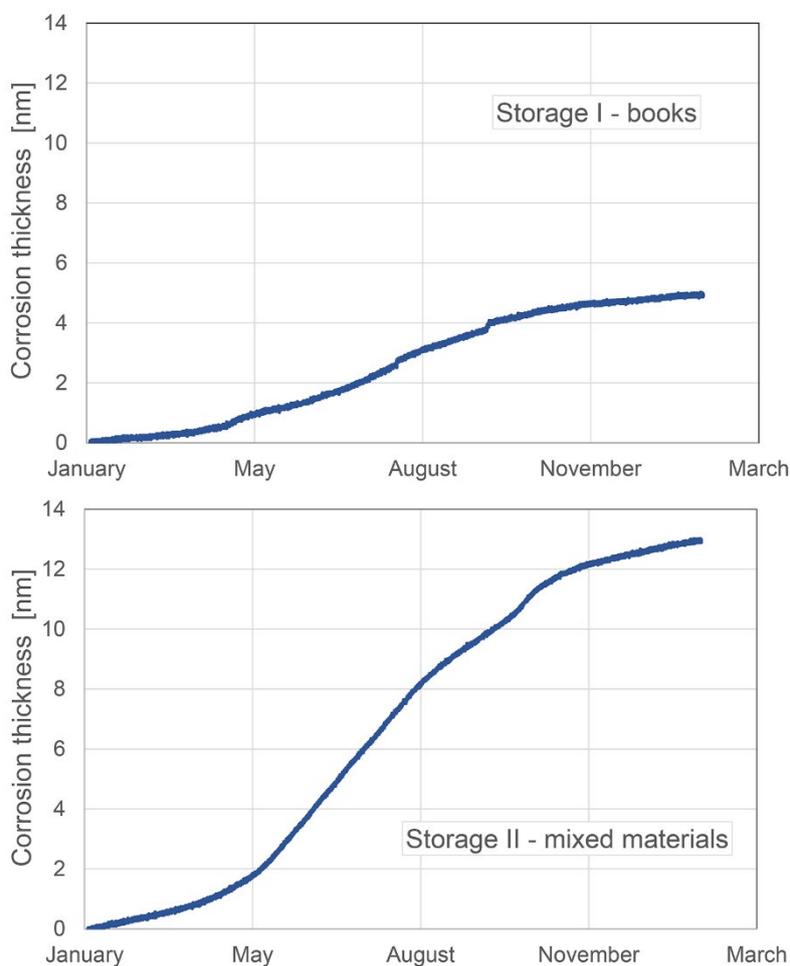


Figure 2. The increase in corrosion thickness on a 400nm lead AirCorr™ sensor measured from February 2018 to January 2019 (one year) in Storage I and II.

4. Discussion

The concentration of ozone and nitrogen dioxide in Storage I with mechanical ventilation and Storage II with semi-passive climate control are in the low end of the values reported for other storage buildings (Ryhl-Svendsen, 2006). Ozone is a strong oxidant that react readily with interior surfaces and is known to cause damage to rubber, textile and fade dyes among other materials in heritage collections (Jaffe, 1967). Ozone is more reactive than nitrogen dioxide and the concentration of ozone will therefore typically diminish more as air infiltrates the building than the concentration of nitrogen dioxide. Ozone can also react with pollutants in air as nitrogen oxide producing nitrogen dioxide. This reaction will further reduce the ozone level in storage buildings and contribute to the concentration of the less reactive nitrogen dioxide indoor (Brimblecombe *et al.* 1999). The indoor ozone level diminished to below 5% of outdoors, while the nitrogen dioxide concentration decreased to below 9% in both stores. The reduction in outdoor air pollution is in line with observations elsewhere; e.g. Kontozova *et al.* (2005) measured a decrease in ozone concentration to below 3% from ambient

at the Musical Instrument Museum in Belgium, and Blades *et al.* (2000) found a similar 9% decrease in nitrogen dioxide concentration from outdoor in a store at the Dreadnought Study Collection Centre, UK. Our study underlines that despite the higher concentration of ozone and nitrogen dioxide outside Storage I in central Copenhagen than for Storage II located in a rural area both ventilation forms effectively blocked outdoor air pollution from entering the storage buildings. In Storage I with mechanical ventilation, outdoor air pollution was removed by air filtration with activated carbon filters located in the air intake. In Storage II with semi-passive climate control, outdoor air pollution was supposedly removed by deposition onto construction materials as the air slowly infiltrated through leaks in the building. Comparing the air quality performance in the storage building with mechanical ventilation and with semi-passive climate control also showed a very low atmospheric corrosivity IC1 for copper and zinc (ISO 11844-2:2005) inside both stores. The American Society of Heating, Refrigerating and Air-Conditioning Engineers provide various levels for air pollution control in heritage institutions based on the ventilation form used in the building and the sensitivity of materials in the collections (ASHRAE, 2019). This study confirmed that air filtration in mechanical ventilation systems as well as storage buildings with semi-passive climate control can be used as valid control methods to reduce the concentration of outdoor generated air pollution in unoccupied storage buildings with heritage collections.

The concentration of formic acid and acetic acid in both storage buildings corresponds to values reported for other storage buildings (Ryhl-Svendsen *et al.*, 2014). The concentration of formic acid and acetic acid was six times higher in Storage II with semi-passive climate control compared to Storage I with forced ventilation. The low air exchange rate in Storage II can lead to a higher organic acid concentration (Ryhl-Svendsen *et al.*, 2014). The type of materials within the collections could additionally contribute to the increase in organic acid concentration in Storage II. Smedemark *et al.* (2020) measured the area-specific emission rates of formic acid and acetic acid from naturally aged wood and paper objects under ambient storage conditions and found an up to 30 times higher emission rate from wood than from paper. In heavily loaded storage rooms, this difference in emission rates will have a significant impact on the air quality. Furthermore, Smedemark *et al.* (2020) measured the highest emission rates of formic acid and acetic acid from newly manufactured wood packaging material used to transport and store collections, such as pallets. The book collection in Storage I is stored on metal shelves whereas the mixed material collection in Storage II is stored on close to 1600 highly emissive wood pallets corresponding to above 35.000 kg. We attribute the higher concentration of organic acid in Storage II to a combination of a low air exchange rate and highly emissive wood present in the collection and as storage material compared to the less emissive paper-based collection in Storage I.

Kouril *et al.* (2014) measured the atmospheric corrosivity with an AirCorr™ monitor and a 400 nm lead sensor in stores with archival collections. The corrosion thickness increased with 1 nm over four months from January to May. The results correspond well with the increase in corrosion rate measured in Storage I containing a book collection. After one year's exposure, the higher organic acid concentration in Storage II resulted in an almost seven times larger corrosion thickness increase on the real-time electrical resistance sensor, as compared to Storage I. The lead coupons showed a similar trend with a seven times higher mass increase in Storage II compared to Storage I after one year's exposure. While the corrosion of the zinc coupons was much less severe than that of lead, zinc corrosion was about two times higher in Storage II than for Storage I. Storage I and II both had a pure atmosphere according to the classification by Prosek *et al.* (2013). The study demonstrated that, despite a higher concentration of organic acid than in ambient air, both stores with mechanical ventilation and with semi-passive climate control can provide an acceptable air quality for the preservation of heritage collections. The forced ventilation helped to dilute the organic acids in Storage I. The steady-state concentration in Storage II was the result of a balance between the organic acids emitted from

materials and the rate at which it was lost again, either by ventilation (little) and uptake by sorption on interior surfaces (probably the dominating factor) and this could account for the relative low concentration in air.

The temperature and RH variations were almost equal in the two buildings. Storage I, however, used 60 times more energy in order to maintain the climate conditions using the mechanical ventilation system than Storage II with semi-passive climate control.

Figure 3 shows the monthly increase in corrosion thickness of the AirCorr™ lead sensor together with the monthly average temperature and monthly average RH. The real-time electrical resistance sensor provided instant results and can give detailed information on the increase in corrosion rate as time progresses. The curve's shape reveals periods with a higher or lower corrosivity rate (steeper or gentler slope), which can be hard to detect from the coupon measurements unless the coupons are weighed much more frequently.

The increase in corrosion thickness was associated with both the temperature and RH. In Storage I with a book collection, the corrosion rate increased from 0.1 to 0.8 nm per month when moving from winter to summer. In Storage II, with a mixed material collection, the corrosion rate increased from 0.3 nm in winter to 2.1 nm per month in summer. Prosek *et al.* (2013) also found a correlation between the increase in temperature, RH and the corrosion rate of an AirCorr™ monitoring system, when using a copper sensor.

Month	Storage I			Storage II		
	Corrosion thickness (added) [nm]	Temperature [°C]	RH [%]	Corrosion thickness (added) [nm]	Temperature [°C]	RH [%]
February	0.1	7.3	41	0.3	9.4	45
March	0.1	7.4	41	0.4	8.9	44
April	0.4	9.8	44	0.8	10.0	46
May	0.4	12.8	47	1.5	12.2	47
June	0.6	12.6	50	2.0	14.0	48
July	0.8	14.8	50	2.1	15.2	49
August	0.8	15.3	47	1.8	15.8	49
September	0.7	15.1	46	1.2	15.0	47
October	0.4	13.1	47	1.5	14.6	46
November	0.2	11.4	43	0.7	13.5	45
December	0.1	9.7	43	0.5	11.5	45
January	0.1	8.1	41	0.3	10.6	46

Figure 3. Increase in corrosion thickness of the AirCorr lead sensor per month together with the monthly average temperature and monthly average RH from February 2018 to January 2019. Increased colour intensity means higher values.

Several studies have shown that organic acid emission from internal sources depend on temperature (Krupinska *et al.* 2013; Ryhl-Svendsen *et al.* 2014). In our study, we observed an increase in organic acid concentration parallel to an increase in temperature and RH in both stores. This altogether contributed to the higher lead corrosion rate in summer. An increase in temperature to maintain normal indoor room conditions about 21°C for human comfort or even higher summer temperatures in storage buildings with heritage collections is expected to further increase the emission rate and the concentration of formic acid and acetic acid in air.

5. Conclusion

The concentration of outdoor generated air pollution diminished to below 9% from ambient and the atmospheric corrosivity was very low for copper and zinc in both stores. The emission of formic acid and acetic acid from internal sources gave rise to higher concentration indoors than outdoor. The organic acid concentration was $15 \mu\text{g m}^{-3}$ in the storage with mechanical ventilation and a book collection and $97 \mu\text{g m}^{-3}$ in the storage with semi-passive climate control and a mixed material collection. The atmospheric corrosivity corresponded to Prosek *et al.* (2013) Class L1 (pure atmosphere) for lead despite the higher organic acid concentrations indoor.

The study demonstrated that storage buildings with mechanical ventilation and outdoor air filtration as well as storage buildings with semi-passive climate control and a well-sealed building envelope can provide an acceptable air quality for the long-term preservation of collections. A well-sealed building envelope in stores with semi-passive climate control in combination with a large amount of emissive materials can however, lead to a higher organic acid concentration and an increase in the corrosion rate of lead. Furthermore, the increase in corrosion thickness observed with higher temperature and RH underlined that control of these parameters can be used to improve the air quality performance in storage buildings with heritage collections.

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Paper VIII

Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J.

‘Removal of organic acids from indoor air in museum storage rooms by active and passive sorption techniques’

Studies in Conservation (submitted 29.01.2020).

Removal of organic acids from indoor air in museum storage rooms by active and passive sorption techniques

Smedemark, S.H., Ryhl-Svendsen, M. and Toftum, J.

Abstract

Adsorbent materials can be used for the removal of organic acids from air in storage rooms with heritage collections. The organic acid removal efficiency of two commercially available activated carbon air-filters were tested *in situ* in two unoccupied stores with densely packed collections. One filter was designed for outdoor type pollutants (Filter A), while the other was designed for organic acids in indoor air (Filter B). Furthermore, the acetic acid removal efficiency of a desiccant silica gel rotor used for dehumidification was measured in a laboratory at different relative humidity levels. Finally, passive removal of acetic acid by silica gel and unfired clay brick were tested in a chamber, and for clay brick at room level as well. Filter B had the highest removal efficiency. The removal efficiency of both filter types depended on the airflow and the filter performance varied considerably *in situ* from the values reported from standard laboratory tests. Increasing the airflow rate through the filter reduced the removal efficiency from 77% and down to 7% for Filter A, and from 92% to 24% for Filter B. There was almost no effect of active air filtration on the concentration of organic acids, when this was measured in the middle and in the corner of the storage rooms away from the ventilation inlets. The desiccant dehumidifier removed 98-100% of the acetic acid from the air, independently of the relative humidity. The desiccant rotor will, however, only be running when there is a need for dehumidification and as a result will only periodically remove pollutants. The high acid removal efficiency by dry silica gel was furthermore demonstrated in a chamber test. A clay brick wall in a test room established a concentration gradient across the room, and reduced the concentration of organic acids by 56% compared to close to the emission source.

Keywords heritage collections, storage buildings, formic acid, acetic acid, air filtration, silica gel, clay, removal efficiency of adsorbents, clean air delivery rate, passive adsorption, energy use.

1. Introduction

Organic acids can cause damage to sensitive materials in heritage collections. Formic acid and acetic acid have been reported to cause efflorescence on calcareous materials, such as glass, limestone, ceramic and shells, corrosion on metals; particularly lead, and to damage varnish (Clarke and Longhurst, 1961; Gibson *et al.*, 1997; Thickett and Odlyha, 2000; Robinet *et al.*, 2004; Halsberghe *et al.*, 2005; Gibson and Watt, 2010; Bonaduce *et al.*, 2013). For example, Robinet *et al.* (2004) measured a formic acid and acetic acid concentration of about 830 $\mu\text{g m}^{-3}$ in a room previously used to store glass objects showing signs of deterioration while Thickett and Odlyha (2000) measured an acetic acid concentration between 1071 and 2880 $\mu\text{g m}^{-3}$ in wooden cupboards used to store copper alloys forming pale blue corrosion products.

The emission from people's activities, building interior and the collections themselves can be sources of formic acid and acetic acid in heritage institutions. Among other volatile organic compounds (VOCs), cleaning agents emit acetic acid (Wolkoff *et al.*, 1998). Building interior made of wood is also known to emit organic acids. Ryhl-Svendsen and Glastrup (2002) measured the area-specific emission rate of formic acid and acetic acid from wooden museum furniture materials at the National Museum of Denmark. The emission rate ranged from

63 $\mu\text{g m}^{-2} \text{h}^{-1}$ from a newly produced pine wood shelf to 267 $\mu\text{g m}^{-2} \text{h}^{-1}$ from a coin collection drawer made of Masonite and maple wood. The area-specific emission rates of formic acid and acetic acid from heritage collections were measured in a few studies under normal indoor room conditions. Smedemark *et al.* (2020a) measured the emission rate of formic acid and acetic acid from naturally aged paper and wood kept in heritage collections. The emission rate ranged from 10 $\mu\text{g m}^{-2} \text{h}^{-1}$ from a newspaper printed in 1914 to 259 $\mu\text{g m}^{-2} \text{h}^{-1}$ from a 19th century wood sample.

One method to control unwanted air contaminants in a room is to recirculate the indoor air through filters. In this study we examined the formic acid and acetic acid removal efficiency of two commercially available activated carbon air-filters measured *in situ* in storage buildings with heritage collections. The acetic acid removal efficiency of a desiccant silica gel rotor used for dehumidification was also measured and finally the passive removal of acetic acid onto silica gel and clay brick were examined.

2. Background

Commonly used adsorbents include molecular sieves, silica gel, activated alumina and activated carbon produced as a powder, granulates, pellets or embedded into a fabric (Gustavsson *et al.*, 2010; Schieweck, 2012). The air pollutants will diffuse from the air stream while it penetrates the pore structure, and into the adsorbent material in air-filters. Adsorbent materials are often treated (activated) to increase their surface area and thereby its adsorption capacity. For example, carbon can be injected into a hot air stream to create activated carbon. The hot air stream will create a large amount of small pores that will increase the surface area. Activated carbon will have a typical surface area between 800 and 1600 $\text{m}^2 \text{g}^{-1}$ (ASHRAE, 2019).

Organic acids are removed from indoor air through two mechanisms: physical and chemical adsorption. Physical adsorption involves the reversible formation of weak Van der Waals forces between the pollutant and the adsorbent material whereas chemical adsorption involves an irreversible chemical reaction between the pollutant and the adsorbent. Adsorbent materials can be impregnated with a chemical to target specific pollutants and increase the chemical adsorption (Gustavsson *et al.*, 2010). It has been a concern that adsorbent materials may re-release pollutants back into the indoor air. However, Thickett and Short-Traxler (2010) detected no evidence of desorption from passive adsorbents such as activated carbon used in display cases, despite the reversible Van der Waals interactions formed during physical adsorption.

The removal efficiency of adsorbents can be used as a measure to compare the performance of different adsorbent materials as well as other air-cleaning devices. The single-pass removal efficiency η (%) of an adsorbent can be calculated as (Siegel, 2016):

$$\eta = 1 - (C_{\text{downstream}} / C_{\text{upstream}}) * 100 \quad (1)$$

where $C_{\text{downstream}}$ is the concentration ($\mu\text{g m}^{-3}$) of air pollution downstream of the air-cleaning device and C_{upstream} is the concentration upstream.

The removal efficiency of adsorbent materials for outdoor generated air pollution have been extensively studied. A literature review on adsorbent construction materials and coatings used to passively remove ozone from indoor air points to inorganic materials such as clay-based brick and plaster, calcareous stone and ceiling tile made of mineral fibres or volcanic perlite as the most promising adsorbents (Darling *et al.*, 2016). Parmar

and Grosjean (1991) examined the outdoor generated air pollution removal efficiency of activated carbon, molecular sieves, and silica gel, used both passively in display cases and actively as filters in heating, ventilation and air-conditioning (HVAC) systems. The study showed that activated carbon removed 100% of the outdoor generated air pollutants ozone, nitrogen dioxide, sulphur dioxide and hydrogen sulphide, whereas other widely used adsorbents as molecular sieves and silica gel failed to remove one or more target compounds from the air. For example, when using silica gel the removal efficiency was only 28% for ozone while the removal efficiency decreased from 82% to 0% for nitrogen dioxide within 24 hours, and from 100% to 36% for sulphur dioxide after less than three hours. Grosjean and Parmar (1991) also examined the removal efficiency of mixtures of ozone and peroxyacetyl nitrate (PAN) as well as nitrogen dioxide, ozone, PAN, nitric acid, aldehydes and organic acids on adsorbents as activated carbon, molecular sieves, silica gel and Purafil (4% potassium permanganate on neutral activated alumina). Their study also showed that activated carbon filters had the highest passive as well as active removal efficiency while adsorbents as silica gel only removed 74% of the nitrogen oxides (nitrogen dioxide, PAN, methyl nitrate and other nitrogen containing intermediates and products).

Only a few studies have measured the removal efficiency of adsorbent materials with regard to formic acid and acetic acid. Cruz *et al.* (2008) measured the impact of acetic acid onto lead in a test tube with and without an adsorbent. The measurements showed that activated carbon was the most efficient adsorbent causing a 50-70% decrease in lead corrosion. Schieweck (2012) showed that out of 39 adsorbents used in display cases, zeolites, activated carbon, and activated carbon with an alkaline impregnation had the highest removal efficiency for formic acid and acetic acid. Grøntoft *et al.* (2015) also measured the decrease in concentration of formic acid and acetic acid in display cases with activated carbon cloth, foam, and granulates. The activated carbon cloth, which was the most effective of the three types, reduced the concentration of formic acid and acetic acid with 78-96% inside the display case. Ryhl-Svendsen and Clausen (2009) demonstrated that sheets of activated carbon embedded in a non-woven polyester filament can be used as an adsorbent wall covering to reduce the concentration of formic acid and acetic acid at room scale in storage buildings with heritage collections. As previously mentioned the removal efficiency of adsorbent materials will depend on the exposed surface area. Ryhl-Svendsen and Clausen (2009) showed that passive adsorbents performed better in small rooms compared to larger rooms due to the ability to reach a higher surface-area-to-volume ratio in the smaller rooms. Ryhl-Svendsen (2011) measured the passive adsorption of organic acid onto a clay brick wall at room scale and found that passive adsorption onto clay brick reduced the organic acid concentration in the room air by 71%.

Several standard test methods exist to determine the particle and gas-phase removal efficiency of filters under laboratory conditions (ASHRAE standard 52.2; ISO 16890-2:2016; ISO 10121-2:2013; ASHRAE standard 145.2-2016). Information on the removal efficiency of target compounds based on such standard tests is often provided by the filter manufacturer. Only a few studies have investigated the removal efficiency *in situ*. Weschler *et al.* (1994) observed a decrease in the ozone removal efficiency of activated carbon filters from 85% to 60% after 37 months of use in a clean room. Di Pietro and Mentzel (2012) measured the concentration of acetic acid to assess the effectiveness of active air filtration at the National Library in Bern, Switzerland. Their study showed that active air filtration only gave rise to a 20% reduction in the acetic acid concentration when measured away from the ventilation inlets but close to the paper-based library collections stored on shelves. The large discrepancy between the removal efficiency of activated carbon filters measured in the

laboratory and its operation *in situ* makes it difficult to predict the effectiveness of active air filtration in complicated structures such as in unoccupied stores with heritage collections densely packed on shelves.

The removal efficiency of air-filters will depend on the airflow through the filter or the so-called residence time. The residence time is the theoretical time a pollutant in air is in contact with the adsorbent medium while the air flows through the filter structure. The longer the residence time the higher the removal efficiency (ASHRAE, 2019). Destailats *et al.* (2012) measured the VOC removal efficiency of photocatalytic oxidation (POC) air purifiers with an airflow from 178 to 878 m³ h⁻¹. The VOC concentration decreased only marginally across the POC air purifiers at high airflow rates while a decrease in the airflow rate led to an increase in the VOC removal efficiency from 5% to 44%. The clean air delivery rate (CADR) is a measure which combines the removal efficiency with the airflow rate through the filter (m³ h⁻¹). Although originally proposed as a measure for particle filters, it has also been used to evaluate the performance of activated carbon filters and other air-cleaning devices for gas filtration in real buildings (see the review by Zhang *et al.*, 2011).

Silica gel has primarily been used to maintain a stable relative humidity (RH) in display cases in heritage institutions. Silica gel is also used in desiccant rotors to dehumidify air at room level. One example of such use is the shared storage facility at the Centre for Preservation of Cultural Heritage in Vejle, Denmark (see 3.1). A desiccant silica gel rotor contains two sections. One section physically adsorbs moisture from the process air supplied from and returned to the room, while the other section is heated to reactivate (dry out) the silica gel. The removed water is then discarded away from the building (Wolfrum *et al.*, 2008).

As a side-effect a desiccant rotor can also remove pollutants from indoor air. Fang *et al.* (2008) measured the co-sorption effect of a desiccant silica gel rotor for improving the VOC removal and sensory perception of the air quality in an office building. The experiments revealed that the desiccant rotor removed all the measured VOCs with an efficiency of 94% or higher. Fang *et al.* (2005, 2006) showed that the pollution removal in the rotor was independent of the concentration of air pollution, as well as independent of the relative humidity .

The reactivation temperature for dehumidification of a desiccant silica gel rotor is between 60 and 100°C, which corresponds with the temperature needed to remove VOCs (Ge *et al.*, 2018). Zhang *et al.* (2008) found that using a high temperature above 90°C to reactivate the desiccant silica gel rotor improved the VOC removal. As a result, the desiccant silica gel rotor can provide dehumidification while also contributing to the effective removal of air pollution without additional energy use.

Several previous studies point to activated carbon as the most effective adsorbent for outdoor generated air pollution as well as for formic acid and acetic acid in display cases (Parmar and Grosjean, 1991; Cruz *et al.*, 2008; Schieweck, 2012; Grøntoft *et al.*, 2015). Only a few studies have however, measured the formic acid and acetic acid removal efficiency of activated carbon filters *in situ* and compared the results with the energy use.

3. Intervention 1: activated carbon filter tests

The two activated carbon filters tested were designed as a “two-in-one” cartridge system for combined particulate and molecular filtration, where the carbon medium was embedded in a particulate-filter structure. Both filters tested were from Camfil AB Sweden (Table 1). Filter A is designed to remove outdoor air pollution in a ventilation outdoor air intake, whereas filter B is specifically designed to remove organic acids in indoor

heritage environments. All filters were new. The formic acid and acetic acid removal efficiency of the activated carbon filters were calculated using Equation 1.

	Product name	Size (mm)	Cost (2018)	Classification*	Energy class**
Filter A	CityCarb I (CIZP-7I)	592 x 287 x 292	277 €	F7	E
Filter B	CityCarb CH (CIZP7CH)	592 x 287 x 292	295 €	F7	E

Table 1. The product name and cost of the two activated carbon filters, their classification and energy class. *Both filters have been classified as F7 according to EN 779:2012, now replaced by ISO 16890:2016, and the performance tested by ISO 10121-1:2014 and ISO 10121-2:2013. **Filter A and B have been certified as energy class E according to EUROVENT with A+ having the lowest energy use and E the highest (Ecob, personal communication).

3.1 The storage buildings

Storage I contained a book collection from the 15th to 17th century belonging to the Royal Library in Denmark. The storage room was about 600 m³. A separate HVAC system serviced the room with a building management system controlling the outdoor air intake as well as the recirculation rate. The HVAC system consumes 67 kWh m⁻³ year⁻¹ (Smedemark *et al.* 2020b).

Storage II was part of a shared storage facility at the Centre for Preservation of Cultural Heritage in Vejle, Denmark. The storage room was about 4800 m³ and contained a mixed material collection with materials ranging from archaeological waterlogged wood to modern plastic. The storage building was almost airtight with an infiltration rate of 0.01 h⁻¹. The storage building had no mechanical ventilation except for a desiccant rotor used for periodic dehumidification. The energy use in Storage II was 1.1 kWh m⁻³ year⁻¹ (Smedemark *et al.* 2020b).

3.2 Ventilation systems

The activated carbon filters were tested *in situ* using the HVAC system in Storage I, and by recirculation through three mobile stand-alone filter units in Storage II. Each mobile stand-alone filter unit consisted of a fan connected to a filter cartridge with a flexible duct outlet.

The airflow through the mobile stand-alone filter units was measured with constant emission of tracer gas (Freon_{134a}) in the filter unit using an Innova Photoacoustic Multi-gas Monitor type 1312 connected to a Multipoint Sampler and Doser type 1303, both from Bruel & Kjaer, Denmark. Unfortunately, the airflow through the filters in the HVAC system in Storage I could not be determined with tracer gas as the system used a too high rate of recirculation and the tracer gas was therefore detected in the return air immediately after release into the supply air. The formic acid and acetic acid removal efficiency was tested at normal ventilation conditions (50% fan power) as well as with the fans running at full power (100% fan power).

3.3 Measurement set-up

The concentration of formic acid and acetic acid were measured in the air upstream and downstream of the activated carbon filters (Figure 1). A 0.144 m³ sample of air was drawn through a 0.1 M sodium hydroxide solution in a washing bottle at 100 mL min⁻¹ using a calibrated pump. The air was sampled over 24 hours. The concentrations collected in the sodium hydroxide solution were quantified by ion chromatography (IC) analysis on an 881 Compact IC pro instrument with an 863 Compact Auto sampler, using an anionic precolumn (art.-no. 6.1005.250) and a column for organic acids (art.-no. 6.1005.200) from Metrohm (Herisau, Switzerland). An acceptable baseline separation between formic acid and acetic acid was achieved with a column temperature of 30°C and a flow rate of 0.4 mL min⁻¹ using 0.33 mmol L⁻¹ sulphuric acid as eluent and 0.1 mol L⁻¹ lithium chloride as suppressor. The method has a limit of quantification (LOQ) of 5 µg m⁻³ for both formic acid and acetic acid.

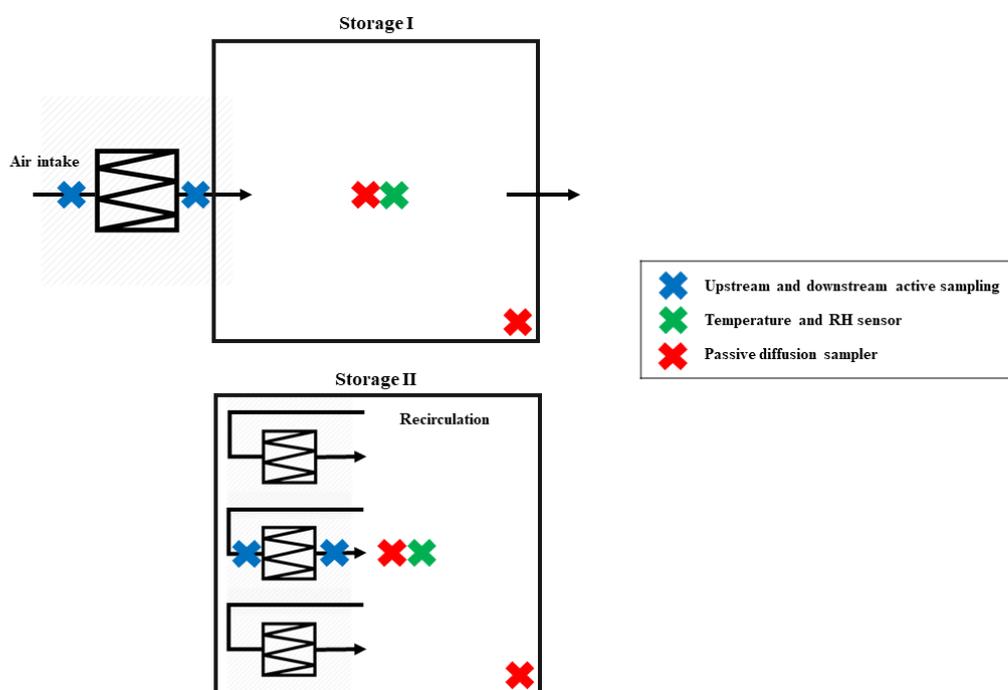


Figure 1. Set-up showing the measurement locations upstream and downstream of the filters as well as the passive diffusion samplers in the middle and in the corner of Storage I and II and the temperature and RH sensor.

In both rooms, the formic acid and acetic acid concentrations were measured as an average over ten days using passive diffusion samplers from the Swedish Environmental Research Institute IVL. These measurements determined the impact of active air filtration on the concentration of organic acids close to sensitive collection objects within the storage rooms. The method has a LOQ of 1.4 µg m⁻³ for formic acid and 4 µg m⁻³ for acetic acid. Duplicate samplers were placed at shelves in the middle and in the corner of each room (Figure 1). The temperature and relative humidity were also measured in the middle of each storage room with a Gemini TinyTag View 2 climate recorder (accuracy about ±0.2°C and ±3% RH).

Before the filter tests the undisturbed concentration of organic acids in each room was measured with passive diffusion samplers. The activated carbon filters were then placed in the HVAC system in Storage I, and in the three stand-alone filter units in Storage II, and the concentration of formic acid and acetic acid measured again

during the filter test. After each test the carbon filters were removed and the storage rooms left for ten days without filtration before another test was conducted. The test were running from August to late November 2018.

4. Intervention 2: desiccant rotor test

The acetic acid removal efficiency of a desiccant silica gel rotor was measured in a laboratory at different relative humidity levels. The dehumidifier tested was a commercially available silica gel rotor from HB Cotes A/S, Denmark, type CR 160A. The tested dehumidifier was not new, but had been used for some years in a storage room with heritage collections. It was estimated to be in the middle of its service life.

4.1 Measurement set-up

The concentration of acetic acid was measured in the air upstream and downstream of the desiccant rotor (Figure 2). The air supply to the desiccant dehumidifier was passed through a humidity-controlled chamber, in which the relative humidity was maintained at 25%, 50% and 70% RH, respectively. The temperature and relative humidity were measured in the air upstream and downstream of the desiccant rotor using a climate datalogger with an external sensor (Gemini TinyTag View 2, accuracy about $\pm 0.2^\circ\text{C}$ and $\pm 3\%$ RH). Degraded cellulose acetate film sheets were used as an emission source, releasing acetic acid at a high rate into the air supply.

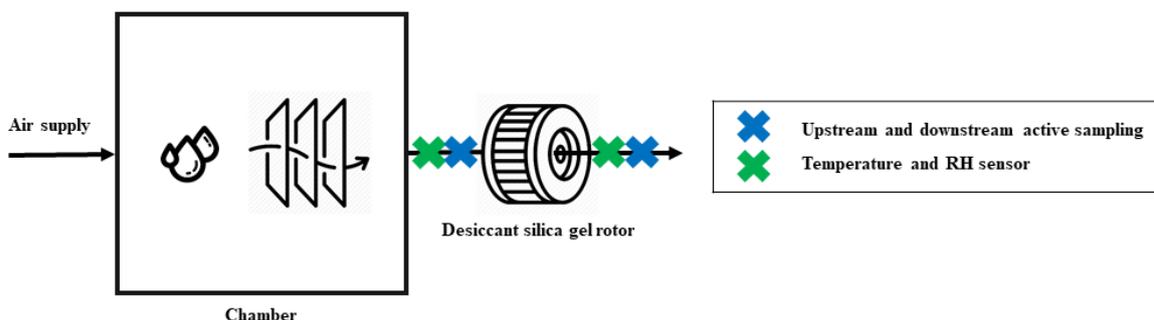


Figure 2. Set-up showing the RH controlled chamber with cellulose acetate films off-gassing acetic acid to the air stream as well as the measurement locations upstream and downstream of the desiccant silica gel rotor and the temperature and RH sensors.

The concentration of acetic acid was measured by passing air through a 0.1 M sodium hydroxide solution in a washing bottle at 500 mL min^{-1} using a calibrated pump. The air was sampled over 2 hours. The concentration of acetic acid collected in the sodium hydroxide solution was determined by IC analysis (see description in section 3.3). The acetic acid removal efficiency of the desiccant silica gel rotor was calculated using Equation 1.

5. Results and discussion

The formic acid and acetic acid removal efficiency of Filter A and B in Storage I with a HVAC system running at normal operating conditions and with the fan running at full power, as well as in Storage II with three mobile stand-alone filter units, are shown in Figure 3. Furthermore, the acetic acid removal efficiency of the desiccant silica gel rotor is shown at 25%, 50% and 70% RH.

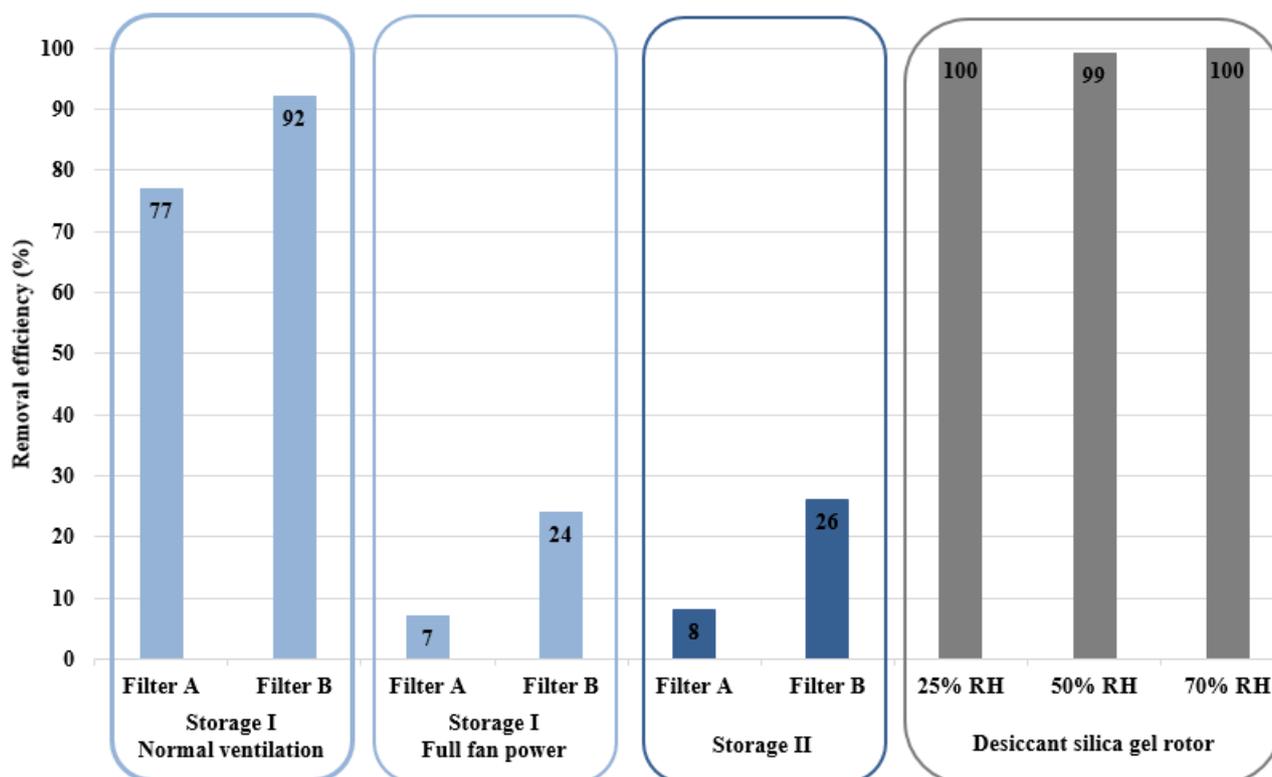


Figure 3. The formic acid and acetic acid removal efficiency of Filter A and B under normal ventilation conditions and with the fan running at full power in Storage I (light blue) and in Storage II with three mobile stand-alone filter units (dark blue). In grey is shown the acetic acid removal efficiency of the desiccant silica gel rotor at 25%, 50% and 70% RH.

Filter B, which was specifically designed to remove formic acid and acetic acid, performed better than Filter A in all measurements. The removal efficiency for Filter B was 15-18% higher than for Filter A.

Under normal ventilation conditions the organic acid removal efficiency of Filter B in Storage I was 92%. This corresponds with the initial removal efficiency measured by the filter manufacturer at an airflow rate of $0.94 \text{ m}^3 \text{ s}^{-1}$ under laboratory conditions (Ecob, personal communication). The removal efficiency measured *in situ* in Storage I with fans running at full power and in Storage II with mobile stand-alone filter units vary considerably from the efficiency obtained using laboratory standard test methods.

The removal efficiency of both filters diminished as the airflow through the filters increased. An increase in the airflow through the activated carbon filters in Storage I with a HVAC system from normal ventilation conditions to full fan power (from 50% to 100%) reduced the organic acid removal efficiency from 77% to 7% for Filter A, and from 92% to 24% for Filter B. A similar trend has been observed for other filter-types and air-cleaning devices (e.g. Destailats *et al.* 2012). The CADR that combines the removal efficiency with the airflow through the filter is therefore a more useful measure than the removal efficiency alone, for the determination of the performance of active air filtration *in situ*. In Storage II the airflow through each mobile stand-alone filter unit was $0.39 \text{ m}^3 \text{ s}^{-1}$ and the organic acid removal efficiency only 8% for Filter A and 26% for Filter B. The CADR for each mobile stand-alone filter unit was $112 \text{ m}^3 \text{ h}^{-1}$ for Filter A and $365 \text{ m}^3 \text{ h}^{-1}$ for Filter B. The CADR could not be calculated for Storage I due to the unknown airflow through the filters.

A reduction in the concentration of formic acid and acetic acid measured in the middle and in the corner of both storage rooms would reveal whether active air filtration influenced the air quality close to the collection objects. No significant impact could however be determined, as the possible decrease in the concentration by filtration did not stand out from the natural variation. Natural variation was expected as a decrease in room temperature from summer to winter will lead to a reduction in the emission rate from interior surfaces. The intervention study spanned several months from August to late November. The formic and acetic acid concentrations decreased from 15 to 7 $\mu\text{g m}^{-3}$ in Storage I and from 97 to 28 $\mu\text{g m}^{-3}$ in Storage II when going from summer to winter. The indoor temperature decreased with 7 to 8°C within the same time period. The average formic acid and acetic acid concentration was $17 \pm 7 \mu\text{g m}^{-3}$ in Storage I and $60 \pm 15 \mu\text{g m}^{-3}$ in Storage II during the intervention study. Our measurements indicated that a decrease in room temperature from summer to winter lead to a larger decrease in the concentration of organic acids in indoor air than could be accomplished by active filtration. A subject for future work could be to further examine the CADR *in situ* and the distribution of clean air close to densely packed collections, in order to establish the true benefit of air filtration on a room, shelf, or collection object level.

The desiccant rotor efficiently removed 98-100% acetic acid from the process air. The air was at the same time dried out to 13% RH or less. The removal efficiency was independent of the relative humidity in the air supply measured upstream from the desiccant rotor. This corresponds with measurements conducted by Fang *et al.* (2005).

The literature points to activated carbon as the most efficient adsorbent for formic acid and acetic acid, whereas silica gel has been shown to be less effective (Parmar and Grosjean, 1991; Schieweck, 2012). One explanation for the high formic acid and acetic acid removal efficiency we observed for the silica gel in the desiccant rotor could be that the removal efficiency depend on the moisture content of the silica gel. While silica gel is usually conditioned to about 50% RH when used in display cases, the desiccant rotor silica gel is completely dried out before use, which could increase the removal efficiency.

6. Intervention 3: passive adsorption on wall

The passive removal of acetic acid onto silica gel and clay brick were measured in a laboratory test chamber, and for clay brick at room scale as well. Our previous measurements (Intervention 2) confirmed that silica gel used for dehumidification in a desiccant rotor efficiently removes acetic acid from indoor air. Several studies have also shown that mineral based construction materials such as unfired clay are effective adsorbents for the passive removal of pollutants from indoor air (e.g., Darling *et al.*, 2016; Ryhl-Svendsen, 2011).

6.1 Laboratory test chamber

The passive adsorption of acetic acid onto silica gel and a clay brick were measured in a closed 7 L glass test chamber. One measurement was conducted in the empty test chamber, one in the chamber with a cellulose acetate film sample releasing acetic acid, and one with a cellulose acetate film sample together with the adsorbent material; either dry silica gel, or clay from an unfired brick. The clay contained about 20% calcium carbonate. The silica gel was dried out while the clay brick was conditioned in chamber air to about 42% RH (Table 2).

Material	Mass (g)	Surface area (m ²)	Loading (m ² m ⁻³)
Cellulose acetate	1.15	0.0094	1.34
Silica gel	260	0.0154	2.2
Clay brick	442	0.0154	2.2

Table 2. The amount and surface area of the cellulose acetate film (acetic acid source) and the adsorbent silica gel and clay brick. The clay brick was processed into a powder. Although the mass of silica gel and clay varied, the volume and exposed surface area of each material was identical and corresponded to the chamber area.

The acetic acid concentration was measured as an average over six days with passive diffusion samplers (as described in 3.3). The temperature and relative humidity were measured with a Gemini TinyTag View 2 climate sensor (accuracy about $\pm 0.2^{\circ}\text{C}$ and $\pm 3\%$ RH).

Description	Acetic acid ($\mu\text{g m}^{-3}$)
Empty chamber	<6
Chamber with cellulose acetate	63
Chamber with cellulose acetate and silica gel	<6
Chamber with cellulose acetate and clay brick	40

Table 3. The concentration of acetic acid in the empty chamber, in the chamber with emissive cellulose acetate film as well as with cellulose acetate film and either silica gel or clay brick as an adsorbent.

The concentration of acetic acid in the test chamber decreased with more than 92% for silica gel while the clay brick only reduced the concentration of acetic acid by 37%. The closed test chamber could have affected the measured acetic acid concentration, as stagnant air will reduce the diffusion into the passive sampler and by this underestimate the true concentration within the chamber. The drying out of the air (down to 5% RH) by the silica gel probably led to a decrease in the emission of acetic acid from the cellulose acetate film, which together with the adsorption of acids from the air onto the silica gel resulted in the large decrease in concentration. The possible decrease in emission rate due to a low relative humidity may have led to an overestimation of the adsorption capacity for silica gel. The large decrease in the concentration of acetic acid indicates however, that dry silica gel can be used as an efficient adsorbent for organic acids as is also clear from the desiccant rotor test (Intervention 2).

Silica gel will adsorb moisture from indoor air and can therefore not be used as an adsorbent to passively remove organic acid without also considering the impact on the relative humidity in heritage environments. Other studies have shown that silica gel also fails to remove some outdoor generated air pollutants (Parmar and Grosjean, 1991). Construction materials as clay brick might therefore be a more suitable adsorbent than silica gel to remove organic acids from indoor air while maintaining a moderate relative humidity level.

6.2 Clay wall in test room

The passive removal of acetic acid onto a clay brick wall and the acetic acid distribution within a room were also examined in a full-scale test room (Figure 4). The room volume was 28 m³. One wall was partly covered with 8.7 m² unfired clay brick (the same clay brick as was used in the chamber test in 6.1). The loading factor was 0.31 m² m⁻³. The air exchange rate was measured by releasing carbon dioxide into the test room and measuring its decay in concentration over time, using a Gemini Tinytag TGE-0011 Monitor (ASTM E741-11). The background concentration of carbon dioxide was subtracted. The air exchange rate, mainly through leaks in the building envelope, was about 0.1 - 0.2 h⁻¹.

The acetic acid concentration was measured as an average over three weeks using passive diffusion samplers (as described in 3.3). The concentration was measured in four locations within the room; one close to the emission source, one in the middle of the room and two close to the adsorbent wall about 10 cm from the wall surface. 25 g of degraded cellulose acetate film sheets (0.12 m²) were used as the emission source. The temperature and relative humidity were measured with a Gemini TinyTag View 2 climate sensor (accuracy about ±0.2°C and ±3% RH) in the middle of the room.

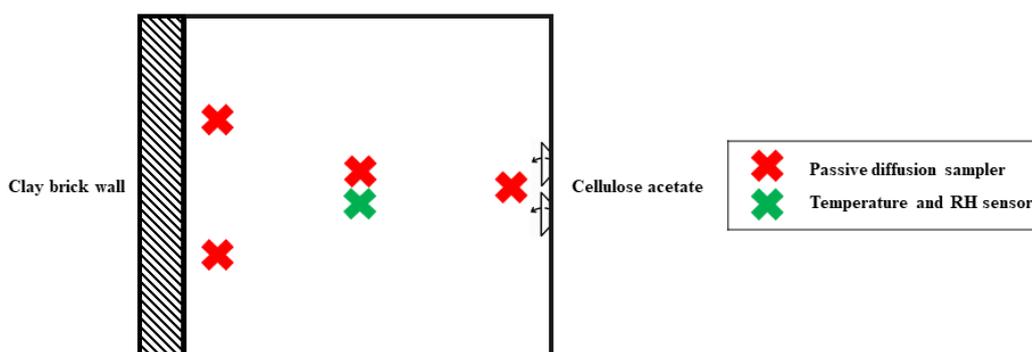


Figure 4. The test room with an adsorbent clay brick wall to the left. The concentration of acetic acid was measured in four locations: one at the emission source, one in the middle of the room and two at the clay brick wall. The temperature and RH were measured in one location. Floor dimensions were 2.7 x 2.4 m.

The concentration of acetic acid was below LOQ in the empty test room (background). Introducing the cellulose acetate films into the room led to an increase in the concentration of acetic acid to 31 µg m⁻³ as measured close to the emission source and in the middle of the test room. The concentration only increased to 14 µg m⁻³ in the two measurement locations close to the clay brick. The passive acetic acid removal of the clay brick wall thus led to a 56% decrease in the concentration across the test room. The higher passive acetic acid removal measured in an earlier study by Ryhl-Svendsen (2011) with a similar set-up could be due to a higher loading of adsorbent clay brick (0.46 m² m⁻³) compared to our study (0.31 m² m⁻³), and by this a higher adsorption capacity. Overall, both studies showed however, that clay brick can be used as a passive adsorbent to remove acetic acid from indoor air.

7. Energy considerations

The energy use is an important parameter, besides the removal efficiency or CADR, to support decisions on suitable control method for indoor air quality. The overall cost of active air filtration in HVAC systems depend on the installation, maintenance and operational lifetime of the filters as well as the energy needed to overcome

the pressure drop across the filter (ASHRAE, 2011). As the pollution load on activated carbon filters increases, the rate of adsorption decreases and the filter will eventually become saturated (Muller, 2007). The operational lifetime for activated carbon filters is difficult to estimate and the filters are therefore often routinely replaced once a year as a precaution. Di Pietro *et al.* (2016) estimated a cost of 489 € per 1000 m³ year⁻¹ for filter replacement in a storage building with semi-passive climate control at the National Museum of Denmark. This corresponds with the filter costs in this intervention study of 277-295 € for the 600 m³ room of Storage I (461-492 € per 1000 m³).

It has traditionally been assumed that filters account for 21-100% of the total pressure loss in HVAC systems in light commercial and residential buildings (Stephens *et al.*, 2010). Di Pietro *et al.* (2016) estimated the energy use for active air filtration in an unoccupied store with semi-passive climate control at the National Museum of Denmark to 1.7 kWh m⁻³ year⁻¹. This corresponds with the energy use in Storage II with semi-passive climate control. The energy use for climate and air quality control in Storage I with a HVAC system was 67 kWh m⁻³ year⁻¹ under normal ventilation conditions. The energy use for air filtration accounted for 8 kWh m⁻³ year⁻¹ or 12% of the total energy use for climate and air quality control. From a cost-benefit perspective, Di Pietro *et al.* (2016) concluded that the use of active air filtration in storage buildings with library and archival collections should be discouraged. Further research is still needed to examine in more detail the performance of activated carbon filters *in situ* and the energy use.

Our study demonstrated that a desiccant silica gel rotor effectively removed acetic acid from indoor air. The desiccant rotor will remove organic acid without consuming additional energy, as the rotor will be running to control air humidity. It will, however, only be running when there is a need for dehumidification and as a result it will only remove organic acids periodically.

Clay brick wall does not consume energy and will furthermore help buffering the relative humidity of the room (Padfield and Aasbjerg Jensen, 2011). It may require a higher installation cost if the clay brick material must be added to an existing structure, but the material has a much smaller carbon footprint than normal brick as it has not been fired.

8. Conclusion

Our study showed that the formic acid and acetic acid removal efficiency of activated carbon filters depend on the airflow through the filter and that the performance varies considerably *in situ* from the removal efficiency obtained using standardized test methods in a laboratory. The organic acid removal efficiency was highest for Filter B in all measurements. Filter B was specifically designed to remove formic acid and acetic acid in heritage environments. An increase in the airflow through the filters from normal ventilation conditions (50% fan power) to full fan power (100%) reduced the organic acid removal efficiency from 77% to 7% for Filter A, and from 92% to 24% for Filter B. The effect of active air filtration on the concentration of formic acid and acetic acid in the middle and in the corner of the storage rooms, both densely packed with collections, was almost non-existent. The measurements indicated that a decrease in temperature from summer to winter led to a larger decrease in the concentration of organic acids in indoor air than active filtration. Further work is needed in order to establish the true benefit of active air filtration on a room, shelf, or object level. The CADR that combines the removal efficiency with the airflow through the filters could be a more useful measure than the removal efficiency to evaluate the performance of filters *in situ* in heritage institutions.

Our study also demonstrated that a desiccant silica gel rotor can remove organic acids from indoor air without additional energy use. The desiccant rotor efficiently removed 98-100% acetic acid from the process air. The removal efficiency was independent of the relative humidity in the range between 25% to 70%. However, the desiccant rotor will only be running when there is a need for dehumidification and as a result will only remove organic acids periodically.

Silica gel can, together with unfired clay brick, also be used as a passive adsorbent to reduce the concentration of organic acids in indoor air. Our clay brick test wall reduced the concentration of acetic acid close to the wall with 56%, as compared to the free room air. Passive adsorbents will continuously remove organic acids from air without consuming energy. However, such passive control materials may pose practical challenges on use (surface area loading or extra installation cost).

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