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Indoor air pollutants and their seasonal monitoring in European museums

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Abstract

The monitoring of indoor air pollutants is an important part of the management of heritage collections. In this work, acetic acid, formic acid, formaldehyde, acetaldehyde and NO_2 were measured with passive samplers along with temperature and relative humidity once per season in seven European institutions of different sizes with different types of objects. The measurements were carried out in a variety of locations, from modern and old display cases in exhibition rooms of different sizes to storage rooms and their enclosures for different types of objects. The results were evaluated based on the characteristics of the sampling locations and the extent to which the changing seasons affect pollutant concentrations were estimated. The dataset obtained from this study can be a valuable asset as a snapshot of the current state of the environment in European heritage collections.

Keywords Volatile pollutants, Air monitoring, Museum collections, Seasonal changes

Introduction

Volatile pollutants are an inescapable part of indoor environments, including those housing heritage collections. In recent years, the presence of pollutants [such as acetic acid (AcOH), formic acid (HCOOH), formaldehyde (FDH), acetaldehyde (ADH), ammonia, NO_x, SO_2, H_2S, O_3, and other volatile organic compounds (VOCs)] in heritage environments has come under the spotlight due to their ability to contribute to the degradation of various materials the heritage objects are made from [1–5]. Air quality in institutions housing heritage objects including museums, libraries, archives [6–18] and storage locations [12, 19–22] has already been investigated as a part of the ongoing development of preventive conservation requirements.

The compounds of concern for preventive conservation are generally categorised by their prevalent source as outdoor-generated pollutants (entering the collection environment mainly from the outside of buildings, e.g. NO_x, SO_2, O_3) and indoor-generated pollutants (emitted mainly from the building materials, display and mounting materials, old conservation treatments, and the materials of the objects themselves, e.g. acetic acid, formic acid, formaldehyde, acetaldehyde) [23]. Accordingly, the pollutant concentrations are affected differently by parameters such as enclosure airtightness and ventilation rate: while the outdoor pollutant concentrations are usually low in spaces with low ventilation rates [24], the opposite is usually true for indoor pollutants in near-airtight locations such as microclimate frames [6] or display cases [7, 8].

Similar to parameters such as air temperature (T) and relative humidity (RH), the air pollutant concentrations in museum environments fluctuate on an annual basis. It has already been noted that organic acid concentrations measured in the summer are higher than those measured in the winter, and the opposite is true for NO_2 [11, 13, 25–27]. In museum galleries in Belgium, it was reported that organic acid concentrations were 5–6 times higher in the summer than in the winter, while outdoor concentrations were comparable between seasons [11]. In the

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Czech Republic, AcOH and HCOOH concentrations in a historical library were found to be 4 times and 10 times higher, respectively, in July than in February [13]. In storage locations in Denmark, organic acid concentrations were 2–3 times higher in the summer than in the winter [25]. Similar trends were also found in an archive [26] and in display cases [23, 27].

The annual air temperature and humidity fluctuations are considered the main cause of these concentration variations, as more organic compounds are released from paper, paints, and wooden materials at higher temperatures [11, 23, 28]. Other relevant parameters affected by the seasonal changes in T and RH include unassisted outdoor air infiltration rates into the building, which depend on T differences between indoors and outdoors, and changes in the ventilation regimes of buildings (e.g. window opening, air conditioning systems) [13], both of which can affect the dilution of indoor pollutants and the influx of outdoor pollutants.

While there are several guidelines for the pollutant concentration limits available, their values should be considered with caution, because they generally do not consider the synergistic effects between various parameters (such as T, RH, light, and object conservation history) and are usually not material specific. Also, the material response to the pollutants more accurately depends on their dose than the concentration (dose = time × concentration). Therefore, the guidelines listed in Table 1 are stated as "necessary to prevent damage to objects for at least 1 year [29]" or for "long-term storage [30]". Where the measured concentrations are compared to the guideline values in this work, it must be also taken into account that a shorter sampling time can only result in estimates of yearly concentrations.

The monitoring of the collection environment can have several objectives: to ensure that conditions are acceptable for the preventive conservation of objects; to investigate the causes of detectable damage to the objects; to evaluate the effectiveness of the measures to prevent further damage; to ensure the health and safety of the staff and visitors alike; to support the studies of material degradation; and others [1, 31].

Table 1 Guideline values for the maximum allowable concentrations of pollutants in museums (in μg/m^3)

	General collections [1]	Sensitive collections [1]	General collections [29]	Long-term storage [30]
Acetic acid	100–700	12.5	1000	2500 (250 for sensitive materials)
Formic acid	10–40	9.5	–	1000
Formaldehyde	12.5–25	0.1–6	–	375
Acetaldehyde	–	2–37	–	–
NO_2	4–20	0.1–5	10	20
SO_2	1–5	0.1–1	–	3

Various methods are available for the monitoring of pollutants, usually separated into active and passive types. Active sampling requires the use of a pump that produces a continuous flow of air at a known flow rate. The sampling time is short and provides a snapshot view of the environment, which can be less representative of long-term conditions. In this work, passive samplers were used for all pollutants. Such samplers are typically exposed for an extended period of time (several days to weeks) but they are small and do not require an external supply of power. As a result, sensitive but time-averaged data is collected that is representative of the long-term conditions of the object environment and is less affected by short term variations or spikes in the concentrations [1, 31].

In this work, we aimed to evaluate the pollutant concentrations in seven European museums of different sizes, many of which have never before conducted such measurements. While many institutions nowadays monitor T and RH, due to budget constraints, pollutants are investigated at best occasionally.

Our goal was to estimate the magnitude of error that can be obtained due to the seasonal changes in museums where measurements can only be performed once. We also wanted to investigate the effects of the seasonal changes in different types of locations: galleries/display rooms, storage rooms, display cases and storage enclosures such as boxes, crates, and cupboards. Additionally, the results of the monitoring were used to select the locations where novel mitigation methods (VOC absorbers of different types, modified cardboard material for boxes, graphene membrane coatings) developed as a part of the project APACHE (Active & intelligent PAckaging materials and display cases as a tool for preventive conservation of Cultural Heritage [32]) could best be applied. The effect of these mitigation actions can also be later evaluated against the results of this work. Finally, the data set obtained during our research covers a wide variety of locations and will be a valuable resource for future research in the field.

Experimental

Acidic gases sampling and analysis

AcOH, HCOOH, as well as NO_2 and SO_2 were sampled with UMEx 200 passive samplers (SKC, USA) with triethanolamine, each containing a sampling and a blank strip. Sampling was performed by the staff of respective institutions, while analysis was performed in a single laboratory after the samplers were transferred by post. The samplers were exposed for 7 days. The extraction procedure was described in detail elsewhere [33], but briefly: the strips were ultrasonicated in 2 mL of ultrapure water (MQ; Millipore, USA) for 20 min. The extracts were filtered through 0.45 µm filters (Chrom4, Germany) before injection into an ion chromatograph, Dionex ICS-5000 (Thermo, USA), consisting of an eluent generator, an electrochemical suppressor, and a conductivity detector. For SO_2 analysis, the extract was diluted 1:1 with H_2O_2 prior to the injection, as specified in the manufacturer's instructions for use [34].

Aldehydes sampling and analysis

For the sampling of aldehydes, UMEx 100 passive samplers (SKC, USA) with DNPH were used, each containing a sampling and a blank strip. The samplers were exposed for 7 days, then closed and transported to the laboratory. Aldehyde DNPH-derivatives were eluted from the strips with 3 mL of acetonitrile and the solutions were analysed by HPLC with UV–VIS detection at 365 nm (Agilent Series 1100, Agilent, USA). An YMC Triart C18 column (150 × 4.6 mm × 5 µm) was used with the HPLC method from [9]. The calculations were performed as specified in the manufacturer's instructions for use [35].

Locations

The sampling locations (Table 2) were selected by the staff of the collection institutions, with the guidelines to select one display case (DC) and one storage enclosure (SE), each in their respective rooms (display room (DR) and storage room (SR)). In total, 33 locations were monitored in 7 different institutions in four European countries: Fondazione Scienza e Tecnica, Florence (FST); Peggy Guggenheim Collection, Venice (GGH); Chieti State Archive, Abruzzo (MB) in Italy; Centre Georges Pompidou (PPD) and Quai Branly Museum (QB) in Paris, France; National Museum of Slovenia, Ljubljana (NMS) and Hungarian National Museum, Budapest (NMH). Additional information on the museum locations is provided in Additional file 2: S2.

Information about the locations such as ventilation, materials present, T and RH was also provided by the museum staff. Due to the pandemic, the museums were closed to the public for most of the measuring period. The sampling was performed between February 2020 and July 2021 (the detailed sampling intervals are available in Additional file 2: S2); the samplers were exposed in duplicates.

An additional DC and its DR was investigated in FST, while in PPD two DCs were evaluated without the DR location. MB is an archive that has no display rooms, so two SR and two SE locations were investigated instead. In GGH, in addition to DR and SR, the conditions on the outside of DC and SE containers were also measured (BE and NE), attached to the enclosures, but DR and SR were not measured in summer.

Average outdoor concentrations of NO_2 during the measuring intervals were calculated from the publicly available data of respective national environmental agencies for locations of FST, GGH, NMH and NMS.

Air temperature and relative humidity were measured using HOBO MX 1101 loggers (Onset Corp., USA) with a time step of 30 min.

Results and discussion

The average concentrations of the pollutants in all locations and seasons were 27.2 µg/m^3 for FDH (with the maximum value of 251 µg/m^3), 4.84 µg/m^3 for ADH (max 29.7 µg/m^3), 411 µg/m^3 for AcOH (max over 9000 µg/m^3), 58.9 µg/m^3 for HCOOH (max 812 µg/m^3) and 8.87 µg/m^3 for NO_2 (max 39.6 µg/m^3), while SO_2 was not detected above the limit of detection (LOD) in any location. The average repeatability between duplicate samplers was 6.83% FDH, 22.2% ADH, 11.9% AcOH, 10.1% HCOOH, 15.7% NO_2, expressed as the average relative standard deviation (%RSD) of all locations, which is acceptable in all cases except for ADH, where RSD is over 15% in connection to the low concentrations determined. The measured temperatures ranged from 10.7 to 28.9 °C, and the relative humidity ranged from 42.9 to 75.2% during sampling. All collected information is available in Additional file 1: Dataset.

Generally, the organic pollutants were measured in higher concentrations in museums FST, GGH and PPD (see Fig. 1), and lower in MB, NMH, NMS and QB. In most cases, higher concentrations of the indoor pollutants were present in storage environments than in display (except in PPD), which could be due to the usually higher object density in the storage than on display, resulting in higher emissions. In almost all museums, NO_2 concentrations were higher in the display environments than in the storage, the only exception being NMS.

FST

Large seasonal variations in T were measured in this museum, especially in the storage environment (10.7–28.9 °C). This is probably due to the museum being housed in a historical building, with the storage area located just below the roof. A strong source of AcOH appears to be present in the SR and SE, leading to high concentrations in both locations (over 3000 µg/m^3 in the summer), which exceeded all the recommended guideline values. The same source could also be the origin of HCOOH (concentrations were about 10-times lower

Table 2 Sampling locations in the selected European museums with the description of their collection objects and the environmental management conditions

Museum (no. of locations)	Display case (DC)	Display room (DR)	Storage enclosure (SE)	Storage room (SR)	Additional location	Additional location
FST (6) Fondazione Scienza e Tecnica, Florence	Scientific instruments (wood, metal, ceramic) inside wooden DC (18.2 m^3)	Natural ventilation, historical building	Herbarium in cardboard box	Inside wooden cupboard with natural ventilation (0.24 m^3)	Additional DC (ADDC): polymeric plant models in wooden DC	Additional DR (ADDR): Natural ventilation, historical building (10.2 m^3)
GGH (6) Peggy Guggenheim Collection, Venice	Sculpture in modern DC	Climate control, renovated historical building	Painting in a modern frame	Climate control	Outside DC (BE)	Outside SE (NE)
MB (6) Chieti State Archive, Abruzzo	–	–	SE1: documents inside metal box SE2: documents inside synthetic material box	SR1,4: archive of metal shelves with documents, no ventilation SR2,3: historical books on metal shelves of archive, natural ventilation		
NMH (4) Hungarian National Museum, Budapest	Ceramics, paper, leather in wooden DC (7.6 m^3)	Library room in historical building, ventilated daily through windows (776 m^3)	Acetate film negatives and paper in metal storage drawer (0.03 m^3)	Climate controlled photo storage room (547 m^3)		
NMS (4) National Museum of Slovenia, Ljubljana	Silk and silver thread object in modern DC (0.72 m^3)	Climate control with filtration, new building (95 m^3)	Mixed materials in metal storage drawer (0.06 m^3)	Climate controlled mixed storage room, filtration (186 m^3)		
PPD (3) Centre Georges Pompidou, Paris	DC1: Artist's workroom—large display case with many objects, no ventilation (sampled in multiple spots) (72.1 m^3)	–	PVC design pieces in wooden crate	–	DC2: documents and small mixed objects in modern DC (1.2 m^3)	
QB (4) Quai Branly Museum, Paris	Metal and textile objects in modern DC	Climate control, new building	Wool and plastic in wooden box	Climate control		

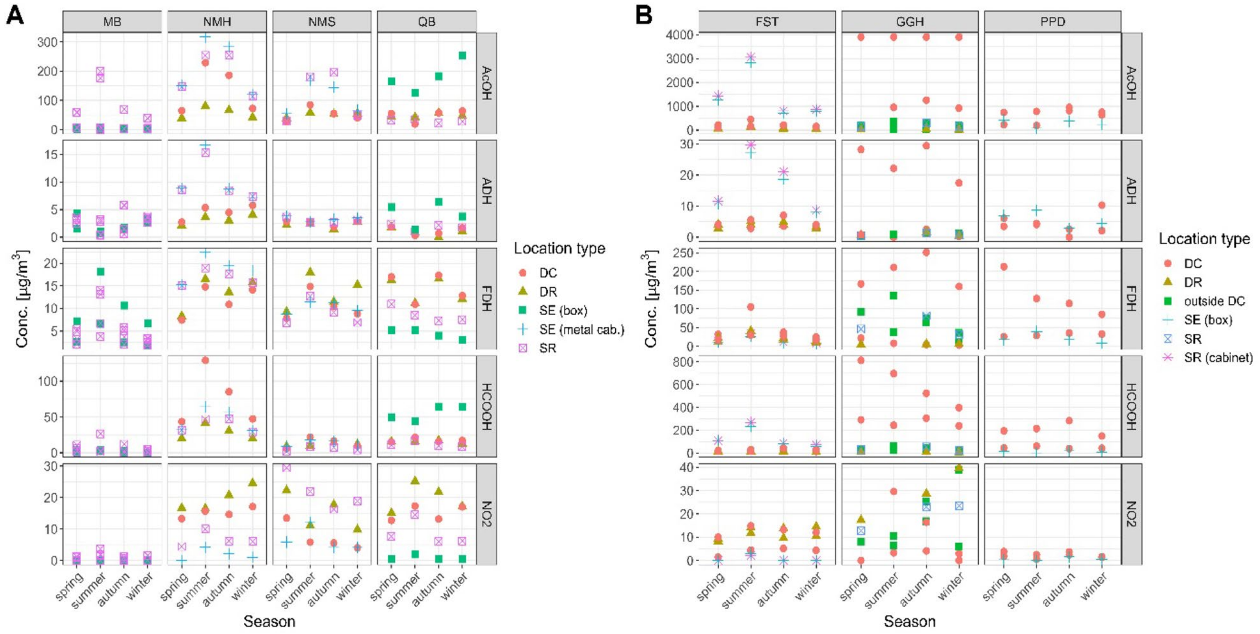

Fig. 1 Pollutant concentration by museum, season, and location type (**A** MB, NMH, NMS, QB; **B** FST, GGH, PPD)

than those of AcOH) and ADH. Mitigation actions such as the use of sorbents were recommended in this location and the source was narrowed down to the cardboard box container SE. NO_2 concentrations and the derived ratio of indoor vs. outdoor concentration (I/O ratio, see also Table 3) were the highest in the ADDR and ADDC environment; this room is located close to the main entrance, through which the NO_2 presumably enters. NO_2 concentrations in SR/SE were much lower than elsewhere, which is probably because SR is an enclosure of itself (a cupboard), thereby containing an additional wall towards the outside. This also leads to a high %RSD in the calculated I/O presented in Table 3 (107%, calculation based on [13]).

GGH

The highest concentrations of all organic pollutants were determined in this museum, FDH in the DC, and AcOH, HCOOH and ADH in the SE frame, with AcOH concentrations exceeding the sampler linear capacities and all the recommended values in several measurements. In comparison to the concentrations, determined in painting frames by Grøntoft et al. [36], the concentrations determined here were comparable or higher for AcOH (925 to over 9000 µg/m³) and HCOOH (239–697 µg/m³) and much higher for FDH (4–251 µg/m³). Considering the much lower levels of these pollutants in the respective rooms of the enclosures (see Fig. 1), and the materials the contained objects are made from, the objects themselves were considered to be the main source of these pollutants, probably the canvas or the wood of the painting frame and stretcher in the SE [36], and the wood and the cardboard of the sculpture in the DC. A comparison between both acids' levels close to the enclosures and in the bulk rooms (NE vs. SR and BE vs. DR) shows lower concentrations the latter, further confirming the possible presence of a strong source inside the enclosures. Both enclosures are relatively airtight, leading to an accumulation of the emitted compounds. This could be mitigated for example by regular airing out (with a short-term effectiveness) or by opening the back of the frame, but the objects could then be exposed to harmful effects from RH, ozone or particulate matter [37], which have not been investigated in this research. Mitigation with pollutant absorbers was undertaken instead. The NO_2 concentrations were found to correlate well with the outdoor values in DR (yearly average I/O ratio 0.96), but less in SR (yearly average I/O ratio 0.69), indicating a lower air exchange rate (AER), a more effective air filtration or a higher deposition velocity in SR. Higher concentrations were determined in the bulk of both rooms than close to the enclosures, indicating that concentrations reduce further away from the outdoor sources.

MB

In this institution, a high relative humidity was noticed (53–75%), and all of the pollutants were measured in low concentrations, often <LOD (Fig. 1). Mitigation efforts to reduce the humidity, such as air de-humidifiers, were recommended. The AcOH and HCOOH concentrations

Table 3 I/O ratios (standard deviation in parentheses), calculated from NO_2 concentrations (nd—no data; standard deviation could not be calculated for data, collected from respective environmental agencies)

Museum	DR/outdoor	DC/DR	SR/outdoor	SE/SR	additional	additional
FST	Spring 0.41	0.18 (0.03)	0.022	< LOD	0.46	1.07 (0.06)
	Summer 0.55	0.38 (0.15)	0.10	1.39 (nd)	0.66	1.05 (0.04)
	Autumn 0.32	0.54 (0.07)	0.016	1.74 (1.07)	0.48	0.96 (0.07)
	Winter 0.25	0.42 (0.12)	0.009	0.31 (0.52)	0.34 (ADDR/out)	0.83 (0.10) (ADDC/ADDR)
GGH	Spring 0.98	ND	0.72	ND		
	Summer/		–			
	Autumn 1.04		0.83			
	Winter 0.88		0.52			
NMH	Spring 0.69	0.80 (0.04)	0.18	< LOD		
	Summer 0.90	0.95 (0.10)	0.54	0.42 (0.69)		
	Autumn 1.32	0.71 (0.06)	0.39	0.33 (0.45)		
	Winter 0.82	0.70 (0.03)	0.20	0.16 (0.09)		
NMS	Spring 0.79	0.61 (0.47)	1.05	0.20 (0.08)		
	Summer 0.97	0.52 (0.07)	1.92	0.55 (0.16)		
	Autumn 0.88	0.31 (0.11)	0.81	0.26 (0.29)		
	Winter /	0.41 (0.23)	–	0.22 (0.03)		
QB	ND	Spring 0.85 (0.04)	ND	0.057 (0.64)		
		Summer 0.69 (nd)		0.13 (nd)		
		Autumn 0.60 (0.32)		0.089 (0.60)		
		Winter 0.99 (0.17)		0.061 (0.70)		

were highest in the locations SR2 and SR3, where a temperature-induced emission from the nineteenth century books could be a source of these organic acids. A good linear correlation between the temperature and the concentrations of these acids was noticed in these locations (AcOH $R^2=0.87$, HCOOH $R^2=0.86$).

NMH

A source of AcOH in the form of acetate film negatives is known to be located in the SR and SE environments, and indeed increased concentrations were confirmed in both locations, in the summer and autumn over the limit of 250 µg/m^3 for sensitive materials (yearly averages were 192 µg/m^3 in SR and 218 µg/m^3 in SE). Higher values in the SE than in SR (Fig. 1) indicate that the AcOH may originate from the collection materials but diffuses well into the room. NO_2 concentrations exceeded the recommended 20 µg/m^3 in DR in the autumn and winter, but the yearly average was just below this value. Generally, the values inside DR were comparable to the outdoor values, this pollutant likely enters through the daily opened windows (yearly average I/O 0.93). The concentrations in SR were the highest in summer but did not exceed 10 µg/m^3 (yearly average I/O 0.33), proving the effectiveness of the air filtration used in this storage.

NMS

The concentrations of the volatile organic pollutants were low in all locations (Fig. 1). NO_2 concentrations were the highest in SR, with the yearly average of 21.6 µg/m^3 exceeding the recommended values. The concentrations inside SR were higher than those outdoors in the spring and summer, but lower in the autumn (outdoor data was not available in winter), resulting in the yearly average I/O value of 1.3. This was unexpected, since the central air-conditioning system includes gas filtration modules. It is possible that the outdoor value is not correct for this location and that the contribution of the traffic to the outdoor NO_2 is larger near the museum than at the meteorological station (which is about 1 km away). An abundance of nitrous acid (HONO) formed from surface reactions inside the museum could also contribute to an overestimation of the NO_2 sampled with the sampler [38], although this compound is not declared as an interferant for the type of sampler used. NO_2 can be also regenerated inside large rooms from NO and ozone [39] or secondary atmospheric pollutants such as peroxyacetyl nitrate [40], which could be an important contribution in the summer, when the ozone concentrations outdoors are the highest (max. reported value 59 µg/m^3). These options indicate that the filtration system might not be working as expected. Other options for the higher inside NO_2 concentrations, including a significant unfiltered air intake and strong emissions from materials [29], are less likely in this case. In DR, the yearly average I/O ratio was 0.9, which is quite high for a controlled environment and again indicates a high AER with the outdoors or a contribution from the reactions of other compounds.

PPD

DC1 was selected for sampling by the museum staff due to a strong smell detected inside. Indeed, the concentrations of volatile organic pollutants were found to be quite high (Fig. 1), probably due to a large number of objects present inside the closed display case. This large display case was sampled in four different micro-locations, where the pollutant concentrations deviated up to 25% from the display case average. FDH concentrations in DC1 were among the highest in all investigated museums, indicating a strong source is present (possibly the stuffed animals). HCOOH concentrations in DC1 are 5-times higher than in DC2, exceeding the recommended value of 250 $\mu g/m^3$ in the summer, which could be due to the large number of emitting objects inside DC1. NO_2 concentrations in all locations are very low, indicating that the building and all enclosures act as good shields toward NO_2.

QB

In this museum, the location SE differed from the other locations as it had higher concentrations of AcOH, HCOOH, ADH, but not of formaldehyde and NO_2 (Fig. 1). The source of these organic compounds could be the SE box itself, as it is made from wood, which could also contribute to lowering the NO_2 concentrations by deposition. Additionally, the AER is likely low (as observable from the low I/O ratios), and the emitted compounds do not dissipate with the ventilation. The NO_2 yearly average concentration in DR was just below the recommended value of 20 $\mu g/m^3$.

Note that while generally the NO_2 I/O ratio increases when the AER increases [13], the relation should be considered indicative only, due to NO_2 not being an inert gas, but a reactive compound that participates in several indoor air reactions with other pollutants [40].

Concentrations by location type

The investigated locations were very heterogenous in influential parameters such as the AER, surface-to-volume ratios, object density, types and amounts of emissive and absorptive materials present, [13, 29] resulting in difficulties for statistical analysis. The obtained results were used in PCA analysis, but the separation of the different locations was poor (PC1 described 50.5% variability, PC2 23.2%, PC3 19.8%, PC4 5.4%; see Additional file 2: S2). Instead, the method of t-distributed stochastic neighbour embedding (tSNE) [41] was used to better visualise the similarities of the different locations by museum and by location type.

In the first tSNE plot (Fig. 2A), a green group can be observed on the right, comprised of the measurements performed in MB. This location is distinguished from the others by the very high humidity (exceeding 75% in summer) and generally very low pollutant concentrations. Additionally, NMH measurements (marked with green triangles) are distributed in two groups, one consisting of storage and the other of display locations, implying that although all locations are physically present in the same building, the conditions are quite different. Similar can be observed for NMS and FST. For all museums except MB, the results are not well grouped, showing that the separation according to the location of the museum or building type is weak, and that the results must be investigated according to the sampling location type.

This can be observed better in the second tSNE plot (Fig. 2B). A strong distinction between the DR and SE "box" locations is noticeable, based mainly on NO_2 concentrations (see also Fig. 2C), which are low in boxes and high in display rooms. DR locations are grouped in the lower left part of the plot and are further characterised with medium concentrations of volatile organic pollutants. A slight separation into two groups can be noticed, correlating with the presence or absence of air conditioning in the rooms. The SE "metal cabinet" locations are not grouped together, probably due to their starkly different contents (the cellulose acetate negatives in NMH SE vs. the mixed plastics, wood, and textile in NMS SE). SR locations are loosely grouped into four groups: a MB group on the far right, separate QB and NMH groups in the middle and an NMS/GGH group on the bottom left of the plot, thus indicating that this type of location is very loosely defined; some locations are more similar to DR, while others are closer to SE. Finally, DC locations are also separated into 4 groups. The top left and rightmost groups include locations with very high AcOH and HCOOH concentrations from two different institutions separated on the basis of FDH and ADH concentrations: the left group (I.) has higher FDH and lower ADH concentrations and includes modern display cases housing mixed wooden materials (PPD DC1, GGH DC), while the right group (II.) consists of a modern painting frame with higher ADH and lower FDH concentration, housing a painting on a canvas frame (GGH SE). The third DC group on the bottom left (III.) appears to be similar to the DR locations, with high NO_2 and medium organics concentrations (QB DC, NMH DC, FST ADDC), while the fourth group (IV.) in the middle includes locations with

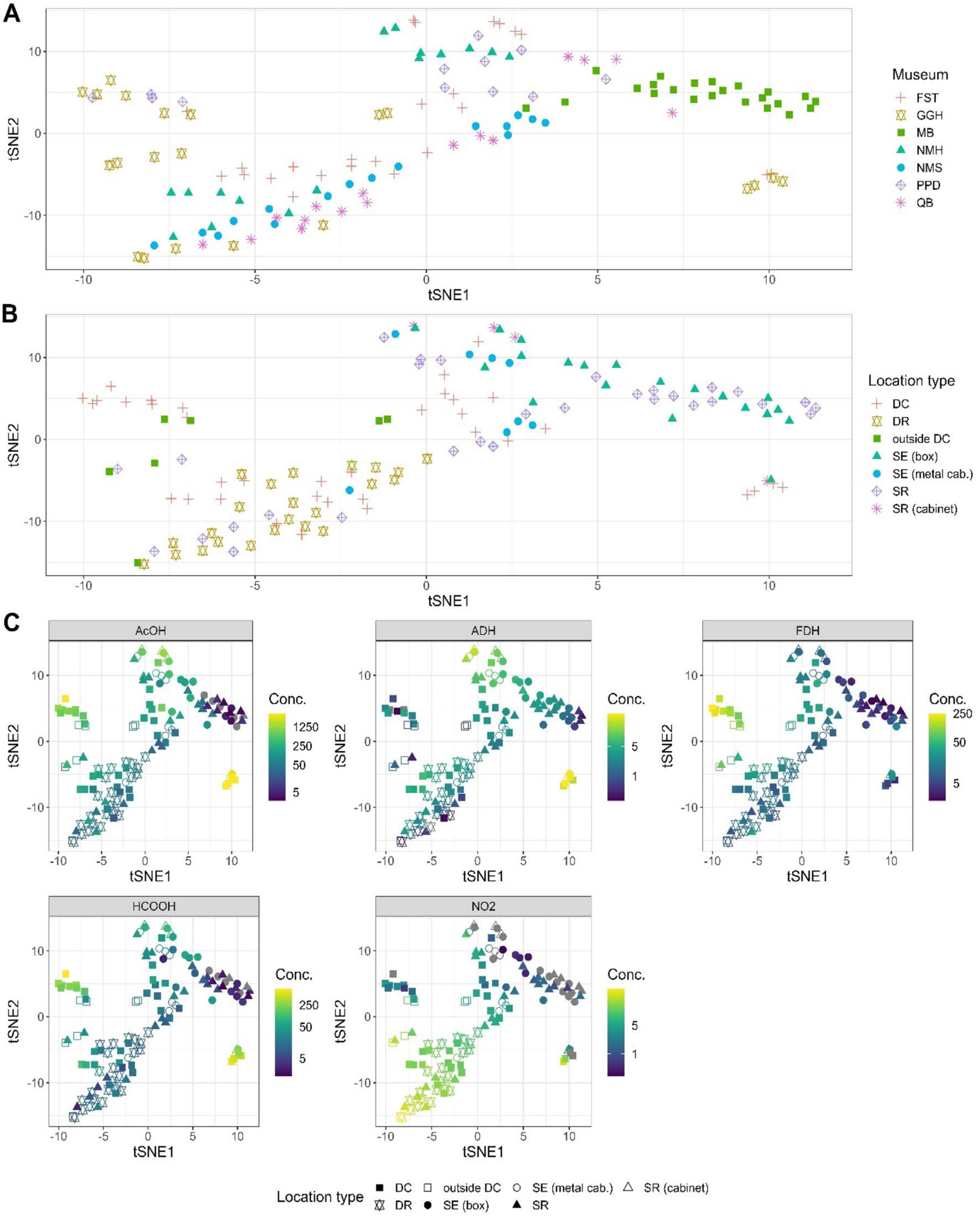

Fig. 2 tSNE analysis (**A** by museum, **B** by location type, **C** pollutant concentration map, where low concentrations are represented in blue and high concentrations in yellow)

lower NO_2 and medium organics concentrations (NMS DC, FST DC, PPD DC2). The groups of DC seen in the tSNE can be also classified according to their I/O ratio for NO_2: groups I and II have the yearly average I/O of < 0.25, group III 0.3–0.5 and group IV > 0.75.

In rooms, the concentrations of indoor pollutants are usually reduced by the application of a ventilation system [42], where the spaces are flushed with clean air (filtered for the outside pollutants or for the indoor pollutants if circulation is applied). The action might be less effective in the cases where there are major sources of the pollutants present or where the air flow rate is low [29]. In our cases, both higher concentrations and larger seasonal variations of indoor pollutants were detected in the three DR locations without air conditioning (AC), than in the three DRs with AC. For NO_2, the distinction was not as clear, which can be observed also in the I/O ratios (Table 3): the non-AC NMH-DR location appears to be more similar to the AC locations, than the non-AC FST museum, where the I/O ratios and NO_2 concentrations are much lower. This could correlate the concentration of indoor pollutants not only with the presence of AC, but also with building materials, since all non-AC locations are housed in older buildings; or with the fact, that FST was not intentionally ventilated at all during the measurements. The effect of ventilation on AcOH concentrations can be seen in the Fig. 3, where a correlation is observed between the yearly averages of AcOH concentrations and the I/O ratios of respective DR locations.

All SR locations (except MB) had AC, therefore this comparison was not possible. Generally, the indoor pollutant concentrations were higher in SR than in DR, which could be due to a combination of a larger object density and lower AER in SR, the latter is also indicated by the lower NO_2 concentrations.

In DC, the concentrations of the outdoor pollutants are usually reduced in comparison to the room levels due to an effect of AER and deposition onto surfaces, resulting in lower pollutant concentrations at lower AERs [24, 43], as described in Weschler's equation for ozone [44]. Inversely, the indoor pollutant concentrations are usually higher at lower AERs [24]. These effects can be directly observed in two of our investigated locations: (i) display cases DC and ADDC in FST are of similar age (nineteenth century), placed in the same museum, but have different constructions (ADDC has wide gaps in the glass doors of the case), resulting in higher NO_2 concentrations in ADDC than in DC (Fig. 1) and different I/O ratios between the display cases and their respective rooms (the yearly average I/O of 0.98 in ADDC vs. 0.38 in DC, see also Table 3); and (ii) GGH DC, where the heritage object was moved for the last campaign from the original into a new DC of the same type and materials, but sealed closed. Consequently, the I/O ratio was reduced from 0.07–0.14 to effectively 0 (NO_2 was < LOD), but the organic acid concentrations surged from 925–1258 µg/m^3 AcOH and 239–305 µg/m^3 HCOOH in the original to > 7950 µg/m^3 AcOH and 812 µg/m^3 HCOOH in the new DC. This confirms that the object is a strong source of these organic acids, and the effect of low AER is exacerbated by the low sorption capacity of these compounds by glass and steel [24] that are the main constituents of the DC. In contrast, FDH and ADH concentrations did not increase in the new DC, possibly the object could function both as a source and as a sink for the aldehydes.

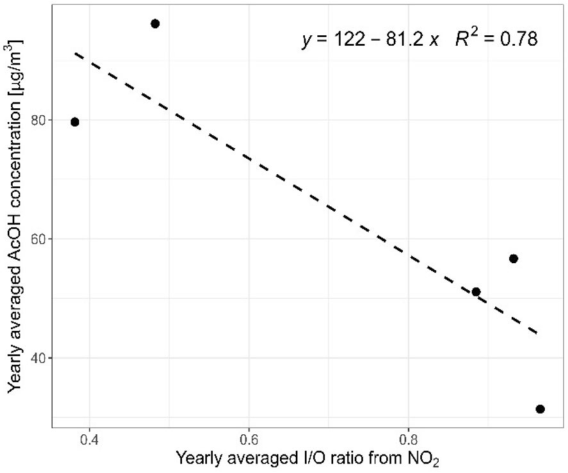

Fig. 3 Relation between yearly averaged AcOH concentration and NO_2 I/O ratio for investigated DRs (FST DR, FST ADDR, GGH DR, NMH DR and NMS DR)

SE containers are ruled by the same rules as DC but are strongly influenced by the different materials they are made of. Although it has been reported, that SE usually have higher AERs than in DCs (a wooden box from eighteenth to nineteenth century AER of 1–2 h^{-1} vs 0.02–0.04 h^{-1} for well-constructed DC [45]), the NO_2 I/O ratios in our experiments show lower average values for SEs than for most DCs (NMH SE 0.24, NMS SE 0.31 and QB SE 0.08), which would indicate lower AERs, especially in QB SE, where the SR NO_2 concentration was reduced on average by 90%. The NMH and NMS SE enclosures were of the same type (metal drawer cabinets) and show similar I/O ratios, but differ especially in the organic acid concentrations, probably due to the different materials housed in the drawers (emissions from the photographic materials contribute to the higher AcOH concentrations in NMH SE [20]). QB SE and PPD SE are both wooden crates, containing different materials, which are expected to emit low to no organic acids (wool, polypropylene, polyethylene, PVC). Concentrations ranged 127–252 µg/m^3 for AcOH and 44–65 µg/m^3 for HCOOH in QB, and 86–422 µg/m^3 AcOH and 2–21 µg/m^3 HCOOH in PPD (Fig. 1), which is comparable to or higher than in literature [45]. While the SR information is not available in PPD, in QB SR, the organic acid concentrations were 2.6- to 9-times lower than in QB SE. This indicates that the wood of the crates is a source of AcOH and HCOOH in these locations. Similarly, the cardboard box of FST SE was also shown to be a strong source of both compounds.

Seasonal effects

Concentrations of the volatile pollutants followed in this work change with seasons. For the organic compounds, the highest concentrations were expected in the summer, the lowest in the winter and medium in the spring and autumn (due to the changes in T, RH, airflows, desorption and adsorption rates). At least partially (with one deviation, e.g. an extreme in the spring or autumn) this was found to be true for FDH in 82% of locations, AcOH in 70%, HCOOH in 87%, but only in 27% for ADH, indicating a difference in the mechanisms governing the ADH concentrations. For NO_2, the outside concentrations are usually the highest in winter and the lowest in summer (due to the stronger anthropogenic sources and the lack of UV light for photolysis in winter [46]). Indoors, this trend was followed at least partially only in 35% of locations for NO_2 and was actually the opposite (similar to organics) in 32% of locations.

Averaged across all locations, the differences between seasonal concentrations ranged between 1% (for NO_2) and 40% (for AcOH), falsely suggesting that the seasonal effects are generally of low importance (this was calculated as the difference between the highest and lowest average concentrations of each season for all locations combined, as obtained from the 7-day measurements). A closer look at the separate types of locations indicates that the seasonal differences can be much larger. Table 4 shows the ratios between the averages of the concentrations per location type, obtained in the seasons with the highest and the lowest concentrations. An example of the distribution and mean values of the seasonal measurements for AcOH is shown in Fig. 4. It is observable, that the relative concentration differences between the seasons are larger in the storage environments than in the display environments, and are larger for AcOH, HCOOH and FDH than for ADH and NO_2. The highest ratios of the concentrations between the seasons in any single location reached up to 9.9 for ADH, 9.5 for FDH, 7 for AcOH, 5.8 for NO_2 and 5.1 for HCOOH (Fig. 1). These results indicate that, although generalisation by the location type is possible, up to 10-times higher concentrations may occur during the passing of a year than the concentrations determined in a single measurement campaign in one location.

Table 4 Ratios between the average concentration per location type in the season with the highest and the lowest concentrations of pollutants (value for NO_2 in SE not available due to most concentrations below LOD)

	DR	SR	DC	SE
AcOH	1.93	2.35	1.57	2.4
HCOOH	1.60	2.26	1.53	2.16
FDH	1.93	1.84	1.54	3.48
ADH	1.4	1.12	1.13	1.75
NO_2	1.3	1.06	1.67	/

It is difficult to assign specific environmental parameters as the causes for seasonal changes. Most commonly regarded as important are temperature and humidity, therefore we have also investigated the effect of these parameters on the pollutant concentrations.

Changes in temperature are a driving force for many processes influencing the pollutant concentrations. Figure 5 shows the relation between AcOH concentration and temperature in all measured locations, together with linear correlation attempts within the same locations. While a general positive correlation between the temperature and AcOH concentration can be observed, the poor correlation coefficients confirm that the temperature is not the only factor affecting the concentration and the correlation is probably not linear. Similar results are obtained for the other pollutants (available in Additional file 2: S2). The effect of temperature is more noticeable in locations with strong sources of AcOH and low ventilation, for example in FST SE and SR, PPD DC1 and NMH DC, indicating that material emission is an important factor. Between the DRs investigated, the slope of the correlation appears to depend on the presence of AC, with the non-AC locations having steeper slopes than the AC locations. This could be correlating also with other factors such as the age of the building and the materials in use (all non-AC locations are housed in older buildings) and was also observed with ADH, but not with HCOOH or FDH.

Relative humidity can also influence some of the processes involved in pollutant production, for example the emission rates from materials are higher both at higher temperature as well as higher RH [20, 24, 47]. In our measurements, the relations between RH and pollutant concentrations were even less clear than for the temperature, with the trends reversing depending on location for all pollutants (example for HCOOH shown in Fig. 6).

Temperature changes lead also to changes in the AER between the outdoors and the indoors, either driven by temperature differences or by higher mechanical ventilation [13]. The NO_2 I/O ratio increases when the AER increases, therefore for most of the investigated locations the highest AER appears to be in the summer (Table 3), which is both in agreement [48] and disagreement [13] with literature.

In select locations, for example the GGH museum that is located on the seashore, seasonal variations in other compounds such as ozone may influence the concentrations of other pollutants. For this museum, the highest concentrations of ADH were determined in the autumn

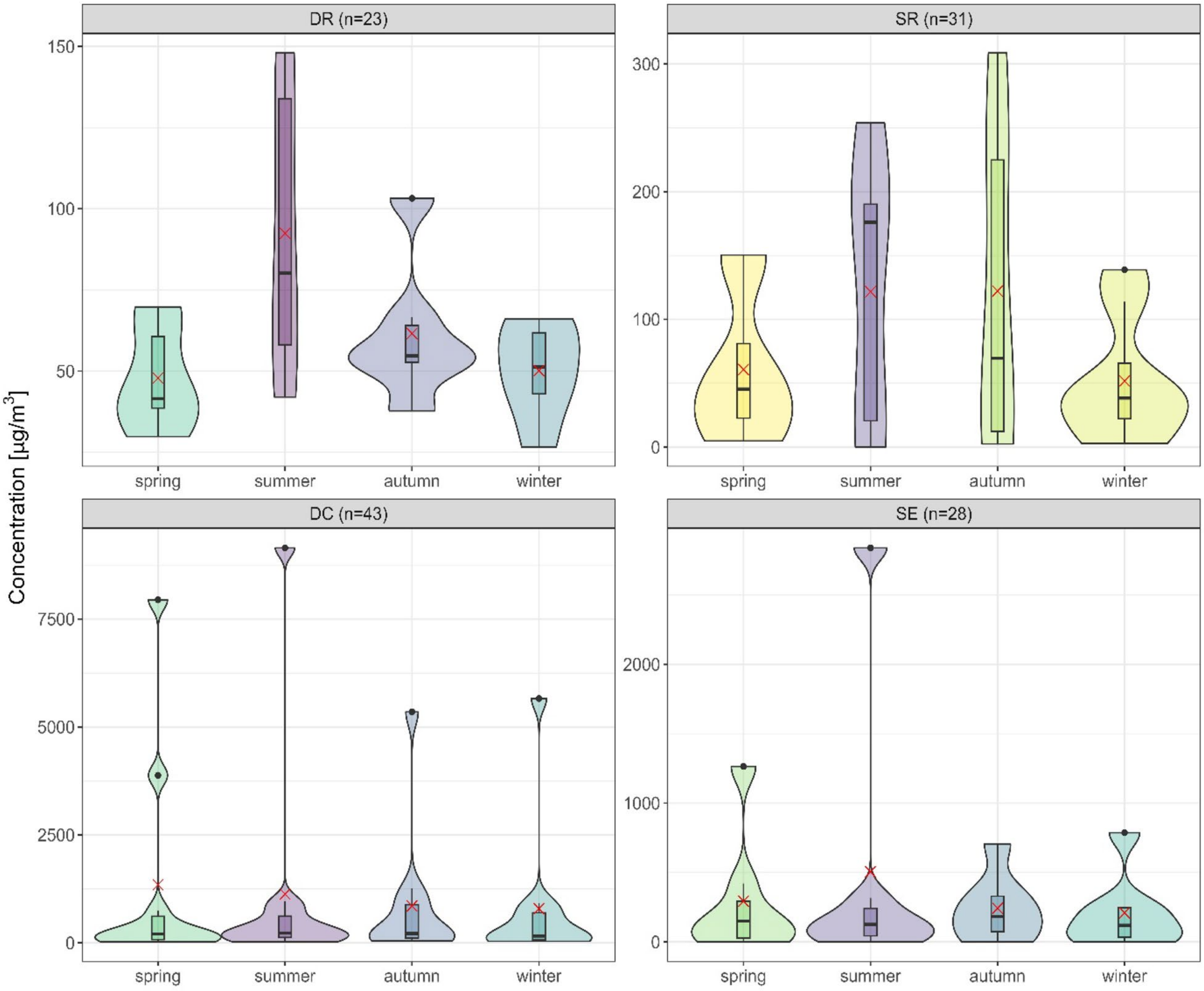

Fig. 4 Distribution of AcOH concentrations by location type and season (red X—average value), the width of the violin plot shows the distribution of datapoints in the concentration ranges. The high concentration locations GGH DC and FST SE can be identified as the outliers in the distributions. [Location FST SR (cabinet) was omitted from the SR graph due to the distinct difference in the character between this location and the other SR locations.] Plots for the other pollutants are available in Additional file 2: S2

in all locations, which could be due to an oxidative effect of the high ozone concentrations in the summer oxidating ADH to AcOH, but this effect lessening in the autumn when the ozone concentrations lessen.

Conclusions

Five volatile pollutants were determined in seven European museums. Generally, higher concentrations of indoor pollutants were determined in the storage locations than in the display locations, while the opposite was true for the outdoor pollutant NO_2. Very high concentrations of acetic acid were determined in several of the monitored locations and mitigation actions were recommended to the institution personnel.

Average seasonal pollutant concentrations per location types were found to differ for a factor of 2–3 between the seasons, but for single locations, the concentration ratios between seasons for a single pollutant could reach up to 10. Therefore, while measuring the pollutant concentrations in museums and other collection institutions with the aim to evaluate the air quality in specific locations, care should be taken to perform the measurements in the seasons when the highest concentrations are expected, or the location should be monitored for multiple seasons.

While the pollutant concentrations could be grouped according to the location, further evaluation of the factors influencing the concentrations was difficult due to the large variations between the monitored locations,

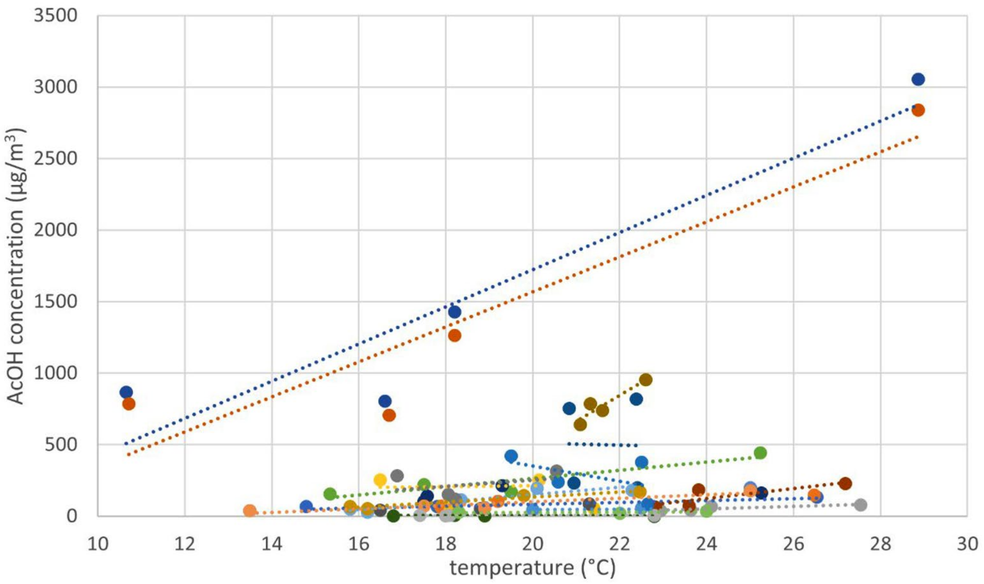

Fig. 5 Concentration of AcOH in correlation to the average temperature at the time of measurement. Colours mark the sampling locations

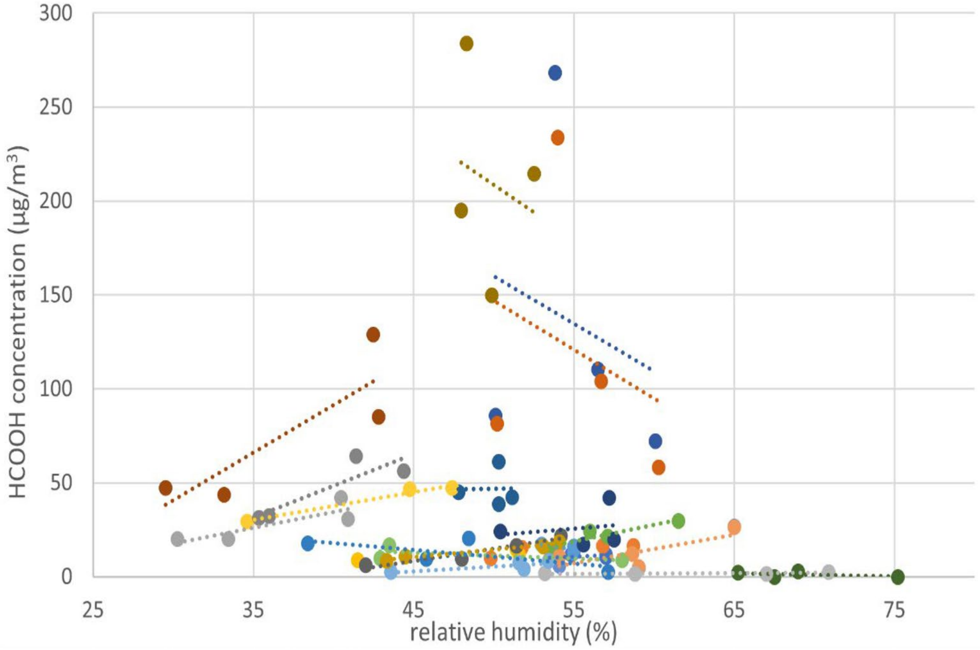

Fig. 6 Concentration of HCOOH in correlation to the average RH at the time of measurement. Colours mark the sampling locations

which reflects the reality in the field. The museum institutions investigated are housing a wide range of objects and materials in various types of enclosures, are of different sizes and are housed in different types and sizes of buildings. The acquired dataset, available fully in Additional file 1: Dataset, is therefore a valuable asset as a snapshot of the current status of environment in European collections. It can be of use to museum professionals with limited capabilities for their own monitoring, as well as to future researchers in the field. Nevertheless, it could be further improved with the use of additional sampling methods, such as sensors [49].

Abbreviations

AC	Air conditioning
AcOH	Acetic acid
ADDC	Additional display case
ADDR	Additional display room
ADH	Acetaldehyde
AER	Air exchange rate
DC	Display case
DNPH	2,4-Dinitrophenylhydrazine
DR	Display room
FDH	Formaldehyde
FST	Fondazione Scienza e Tecnica
GGH	Peggy Guggenheim Collection
HCOOH	Formic acid
HPLC	High performance liquid chromatography
I/O	Ratio of indoor vs. outdoor concentration of NO_2
LOD	Limit of detection
MB	Chieti State Archive
NMH	Hungarian National Museum
NMS	National Museum of Slovenia
PCA	Principal component analysis
PPD	Centre Georges Pompidou
QB	Quai Branly Museum
RH	Relative humidity
RSD	Relative standard deviation
SE	Storage enclosure
SR	Storage room
T	Temperature
tSNE	t-distributed stochastic neighbour embedding
VOC	Volatile organic compound

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-024-01164-x.

Additional file 1. Dataset.

Additional file 2. Sampling details and additional results.

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Author contributions

IK designed the sampling protocol in cooperation with museum institutions, processed the samples, interpreted experimental data, and drafted the manuscript. JM carried out the processing and interpretation of data. AE contributed to the interpretation of data and manuscript writing. IKC acquired the funding, supervised the work and provided critical revision of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The data collected for this study is available as a data set in Additional file 1: Dataset.

Declarations

Competing interests

The authors declare no competing interests.

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