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Poly(vinyl chloride) degradation: identification of acidic degradation products, their emission rates, and implications for heritage collections

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The degradation of poly(vinyl chloride) (PVC) is a potential risk to the objects themselves and their surroundings. In this work, we study the acidic emissions produced during the thermal degradation of PVC to assess their contribution to indoor pollution and to improve the understanding of hydrogen chloride (HCl) emissions. With surface emission experiments, we have shown that the process of HCl emissions exhibits a two-phase behaviour. Prediction of HCl emission rate at 25 °C and modelling the steady-state concentration of HCl in a museum storage box enabled us to conclude that PVC objects emit HCl at rates that are too low to significantly contribute to environmental pollution in heritage collections. However, we demonstrated significant formation of formic and acetic acid. The latter is likely the main acidic compound responsible for the negative impact in the paper Oddy test, observed for all the tested PVC materials.

Poly(vinyl chloride) (PVC) is among the most versatile and widely used synthetic polymers, integral to numerous applications spanning construction, packaging, medical devices, toys, clothing, and consumer goods^{1–4}. Its extensive range of uses arises from versatile material properties that can be tailored and optimized to sector-specific requirements by including additives. Plasticizers increase the polymer's softness and flexibility by reducing its density, melting viscosity, and glass transition temperature (T_g). They can represent up to 50% of the total mass of PVC and are therefore often the subject of research^{5–11}. Due to the instability of PVC at high temperatures and UV light, heat stabilizers and antioxidants are used. The majority of heat stabilizers include metallic soaps, which react with HCl and prevent further PVC degradation. PVC materials also include fillers to thicken the material, increase its strength, and lower production costs. For practical or aesthetic reasons, PVC often also includes pigments, which change the colour of the material^{14–6,12}.

Despite the widespread use of PVC, it was recognized as one of the polymeric materials most prone to degradation in heritage collections^{13,14}. With ageing, it undergoes chemical degradation, a process that is exacerbated by environmental factors such as heat, light, and humidity. Chemical degradation leads to the release of acidic gases, notably hydrogen chloride (HCl), which not only compromises the integrity of the PVC objects themselves but also poses significant risks to surrounding materials and organisms^{14,15}. The dehydrochlorination reaction is well-known and originates from structural irregularities in the polymer

chain, such as allyl and tertiary chloride, which are usually formed during the polymer synthesis^{16–18}. The HCl elimination reaction is most often described as ionic or quasi-ionic with an autocatalytic character, which leads to the formation of a polyene sequence. This causes changes to the mechanical and optical properties of the material, gradually turning the object yellow, orange, red, brown, and lastly almost black, as the absorption peak shifts from the UV to the visible region, i.e., 350–550 nm^{19–22}.

The degradation of PVC and the associated emissions are influenced by several factors, including the chemical composition of PVC and its additives, the physical properties of the object (thickness and surface area), and the environmental conditions²³. Specifically, lower relative humidity and lower temperatures are associated with lower degradation rates^{24,25}. Due to the wide use of PVC, multiple studies have been conducted on its degradation. The vast majority are focused on high processing temperatures, due to their relevance for pyrolysis, incineration, and waste management^{26–31}. Investigating the mechanism behind the degradation at said conditions provides a comparison of formulation stability under stress and evaluates the effectiveness of stabilizers and other additives. These studies are usually performed with pyrolysis, thermogravimetric analysis, and combustion testing and do not offer the determination of HCl emission rates, especially not at conditions relevant for heritage institutions. There have been a few studies on the degradation of PVC in the heritage field, such as Shashoua's research on the degradation of the PVC at 70 °C with a focus

on discoloration¹⁹, the work of Royaux et al. with a temperature cycle at 80 °C and 25 °C³², and our work on modelling the yellowing of PVC collections²⁴. Klempová et al. studied plasticized PVC samples exposed to accelerated UV-vis and thermal aging at 50 °C and 90 °C³³. Artworks made of PVC may also require specific conservation approaches^{34–38}. On the other hand, PVC is a construction material that causes concern when used in museum display and storage cases^{39,40}. However, none of these studies have attempted to quantify the HCl emissions produced during the degradation of PVC.

HCl is a highly corrosive compound with significant implications for both human health and the environment. The Occupational Safety and Health Administration (OSHA) stipulates a permissible human exposure limit of 5 ppm as the highest allowed threshold for workplace environments⁴¹, while the European Chemical Agency (ECHA) sets the occupational exposure limits at 10 ppm for short-term exposure (STEL) and 5 ppm for long-term exposure (LTEL)⁴². Recommended threshold values of HCl concentrations for museum and gallery environments have not been declared, although acidic gases pose a threat to many objects as they can accelerate the corrosion of metals, cause discoloration and embrittlement of organic materials such as paper and textiles, and lead to the degradation of other synthetic polymers^{43–47}. Museums, therefore, endeavor to keep the concentration of pollutants at manageable levels. In its guidelines for museums, galleries, libraries and archives, the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) recommends a maximum average concentration of 400 ppb for acetic acid, 0.7 ppb for hydrogen sulfide, 5 ppb for nitrogen dioxide, 5 ppb for ozone and 10 µg/m³ for fine particles, but does not mention a threshold for HCl^{47,48}.

There are no international standards on storage environments specific to polymeric materials. Current preservation strategies recommend dark storage with stable humidity at 40–60% and low temperature. Ideally, each polymeric material should be stored separately, and segregation of those emitting harmful volatile compounds is recommended. However, the long-term effectiveness of such approaches remains unclear^{49–53}. Without a better understanding of material emissions, it is difficult to develop evidence-based guidelines for the management of PVC objects in heritage collections.

The aim of this work is to improve the understanding of acidic emissions from heritage PVC, to quantify the emission rate of HCl, and to evaluate the risk of its emission at room temperature. In order to assess the general performance of the material on the surrounding materials and objects, a variation of the Oddy test was performed. Quantitative experiments of HCl emission testing at temperatures from 90 °C to 120 °C allowed us to make predictions at room temperature and explore their implications for heritage collections.

Methods

Reference PVC samples used in the study

Five different transparent PVC document folders from the plastics reference collection of the Heritage Science Laboratory, Ljubljana, were selected based on their differences in yellowing, age, and plasticizer content⁵⁴. All were characterized in previous studies in terms of plasticizer type and concentration, polymer molecular weight, thickness, heat stabilizers, and antioxidant content. Furthermore, their natural yellowing at room temperature was assessed^{9,24,55}. The collection of various plastic objects is available for further research⁵⁶.

Samples PVC1 and PVC2 were produced in 2019, while samples P423, P430A, and P415 are dated between the 1980s and the 1990s. Their thickness is between 0.14 mm and 0.20 mm. PVC1, P423, and P430A contained less than 0.5% plasticizer, while PVC2 included 18.9% diethyl terephthalate (DOTP) and P415 16.2% bis(2-ethylhexyl) phthalate (DEHP). All the selected materials were commercially produced and contained antioxidants and 10–30 µmol/g heat stabilizers, which is considered representative of typical PVC objects encountered in museum environments²³. PVC1 was chosen as a primary working material, as it was commercially available in large quantities and at that time showed no visible signs of degradation.

For optimization of the sampling parameters and as an additional verification of identified acidic compounds, commercially available powdered PVC (Poly(vinyl chloride), Sigma-Aldrich, CAS-No.: 9002-86-2) was used. It did not contain any plasticizers, heat stabilizers, or antioxidants.

Cross-infection test

A variation of the Oddy test, according to Curran et al.⁵⁷ was carried out as a cross-infection test. A piece of PVC folder (500 ± 15) mg) and a piece of reference cellulose ((250 ± 10) mg; Whatman filter cellulose No. 1, Maidstone) were placed in a Schott glass vial (nominal volume 100 mL). A control without the PVC sample was also performed. The vials were sealed and left in a fan-assisted oven (model ED 115, Binder) at 80 °C for 14 days. The degradation of the cellulose was then evaluated by viscometry as a change to the degree of polymerisation (DP). The values were expressed as a percentage by comparing the DP of each test cellulose with the DP of the control cellulose (i.e., DP/DPcont. × 100%).

Emission experiments using microchambers

The emissions from PVC folders were sampled using the Markes Micro-Chamber/Thermal Extractor µCTE120 in surface emission mode. The PVC samples were cut into circles with a diameter of 4.5 cm (12.8 cm² surface area was exposed to air flow) to fit into the micro-chamber. For powdered PVC bulk mode was used, where the samples were enclosed in pouches made from Tyvek (1442 R).

After optimization, the sampling was performed at 100 mL/min airflow. The airflow was monitored using an Aalborg mass flow meter GFM. The experiments were carried out at temperatures between 80 °C and 120 °C without relative humidity control.

According to the OSHA standards^{58,59}, silica sorbent tubes (SKC, Specially cleaned silica sorbent tubes, 226-10-03; 7 × 110 mm in size, 2 sections, 400/200 mg of sorbent) were used for HCl emissions and charcoal tubes (Zefon International, Activated coconut shell charcoal sorbent tubes, ZST-001; 6 × 70 mm in size, 2 sections, 100/50 mg of sorbent) for organic acids.

For studying the dynamic changes of HCl emissions in time, consecutive sampling was used. A PVC sample was enclosed in a micro-chamber for a selected amount of time, and the sorbent tubes used to collect the emissions were changed several times in between. Each sorbent tube, therefore, represents its own sampling period for the same sample at given conditions.

The uncertainty of the HCl determination was calculated as the average of 5 replicates of PVC1 at 110 °C sampled at 100 mL/min for 24 h. The calculated value is 18% and represents the combined value of instrumental and random error, inhomogeneity of the sample, and possible variability between the sorbent tubes. The observed uncertainty is consistent with established standards for HCl measurements (OSHA 174-SG)⁴¹, and is considered acceptable for the purpose of this study.

Sorbent extraction

After the emission experiments, each part of the sorbent tube was extracted separately with 5 mL of 10 mM NaOH prepared by dilution (Fisher Scientific, 50% w/w). The mixture was vortexed for 20 min and placed on a shaker for 30 min. The solution was filtered through a 0.45 µm nylon filter (Chrom4, Germany) into a vial.

Ion chromatography

The extracts were analyzed using an ion chromatograph (IC) Dionex ICS-5000 (Thermo, USA), consisting of an eluent generator, an electrochemical suppressor, and a conductivity detector. In total, 25 µL of sample was injected into a Dionex IonPac AS11-HC 4 mm × 250 mm analytical column (Thermo, USA), where the mobile phases were (A) MQ and (B) KOH at a flow rate of 1.5 mL/min. The separation was performed as follows: After equilibration at 3 mM of B for 5 min, isocratic conditions were maintained at 3 mM B for 6 min, followed by an increase in the concentration of B to 10 mM in 7 min and then to 40 mM in 3 min, where isocratic conditions

were held for 4 min, followed by a decrease in B concentration to 3 mM in 2 min and further 2 min at the said conditions.

The mass of adsorbed compound was calculated from the peak areas and calibration curves. Solutions for calibration were prepared weekly in a range of 0.1–10 mg/L by dilution in MQ water. Ammonium formate ($\geq 99.0\%$) and sodium acetate ($\geq 99.0\%$) were purchased from Supelco, Sigma-Aldrich, and sodium chloride ($\geq 99.5\%$) from Merck Millipore.

High-performance liquid chromatography

The high-performance liquid chromatography (HPLC) analyses of the filtered extracts from the emission experiments were carried out using an Agilent Technologies series 1100 high-performance liquid chromatography system coupled with a diode array detector. The separation of the injected 25 μL sample was performed on an ion-exclusion Supelcogel C-610H (9 μm) 30 cm \times 7.8 mm column (Supelco, USA). The mobile phase used was 18 mM H_3PO_4 with a flow rate of 0.500 mL/min for the first 24 min and 0.800 mL/min for the following 4 min. After a total of 29 min of analysis time, 1 min of post-run time was applied to reset the conditions to the initial state.

Mid-infrared spectroscopy

The Fourier transform infrared spectroscopy (FTIR) analyses of the solid PVC samples before and after the emission experiments were performed with a Bruker Alpha II FTIR spectrometer with attenuated total reflectance (ATR). The spectra were recorded in a mid-IR range between 4000 cm^{-1} and 450 cm^{-1} with a spectral resolution of 4 cm^{-1} . Each of these spectra was obtained by co-addition of 10 scans and with air as the background spectrum.

Results

Cross-infection test

The results of the cross-infection test used in this study are shown in Fig. 1 and are expressed as the ratio between test and control cellulose. The acidic emissions produced by the tested material cause degradation of the cellulose and reduce its DP value. It can be observed that emissions from all tested PVC have a moderate to severe negative impact on the reference, as classified by Curran et al.⁵⁷

Comparing the results of the tested newer (blue monochromatic column) and older (orange monochromatic columns) unplasticized PVC, the emissions of the latter can be categorized as causing severe negative cross-infection of the cellulose. These results indicate that older objects made of unplasticized PVC cause more damage to the surrounding objects than newer materials. We hypothesize this is due to consumption of heat stabilizers, reducing their capacity to trap HCl and making aged PVC more prone to degradation²³.

Plasticizers seem to have a beneficial effect (column with a striped pattern) and reduce the harmful effect of emissions even in older samples (orange) compared to unplasticized samples (monochromatic columns). The role of the identity and concentration of plasticizers in the degradation of PVC is not yet fully understood, but plasticizers may react with HCl by undergoing acid-catalysed hydrolysis. The results of this study are consistent with the observations described during the modeling of the damage function, where higher concentrations of plasticizers were associated with lower yellowing rates²⁴.

However, it is not possible to determine the components that cause the damage to the cellulose paper using the variation of the Oddy test alone. As cellulose is susceptible to acid-catalyzed degradation, we can only state that the damage is caused by acidic compounds emitted from PVC.

Optimization of the emission experiment

To determine the identity and quantity of acidic emissions from PVC, emission experiments were performed with microchambers, followed by analysis with ion chromatography. Microchambers are commonly used for emission studies as they provide a controlled set-up for the assessment of emissions of volatile organic compounds from different materials^{60,61}. In our

work, we focused on the effect of temperature on HCl emissions, as the previous study conducted to model a damage function showed that temperature had the biggest effect on the rate of degradation, while the influence of relative humidity was about an order of magnitude smaller²⁴.

Four sampling rates within the working range of the device were investigated (25, 50, 100, and 150 mL/min) to optimize the sampling set-up (Fig. 2). The sampling rate had no significant effect on the mass of chloride emitted, as the emission rates are not volume, but time dependent. That indicates that the emission rates are lower than the investigated sampling rates. Therefore, a value of 100 mL/min was chosen as the sampling rate for further emission experiments, as it sits in the middle of the working range of the microchambers.

Since the mass of emitted HCl does not change with different flow rates, we can deduce that the process of HCl emissions is not evaporation-controlled. Therefore, changing the airflow or air-exchange rates in museum storage does not affect the emission rates of HCl from PVC.

The results from the emission experiments are reported as surface emission rates (SER). These were calculated as $\text{SER} = \frac{m(\text{sample}) - m(\text{blank})}{S \times t}$, where m represents the mass of emitted compound of interest from a PVC sample or a blank, S the area of samples (12.8 cm^2 , defined by the micro-chamber size), and t the sampling time.

Emissions at room temperature could not be detected within a reasonable time, as more than 10 years of sampling would be required to conduct experiments at the given conditions. Consequently, higher temperatures were used to determine the behavior of emissions and then to extrapolate the results to lower temperatures. As the micro-chambers used in this study allow heating up to $120\text{ }^\circ\text{C}$, the temperature of $110\text{ }^\circ\text{C}$ was chosen as the basis for the experiments. It enabled rapid analysis with satisfactory amounts of emitted compounds.

As the majority of experiments were performed for the determination of HCl in surface emission mode, the experiment with silica sorbent tubes was more thoroughly characterized. Based on 14 replicate measurements of blank sorbent tubes with no PVC sample (blank sample), the limit of detection (LOD) and quantification (LOQ) were calculated as $\text{LOD} = \bar{m} + 3.3 \times \text{sd}$ and $\text{LOQ} = \bar{m} + 10 \times \text{sd}$, where \bar{m} represents the average mass of HCl and sd the standard deviation ($n = 14$) of the blank sample. The values $0.2\text{ }\mu\text{g}$ for LOD and $0.5\text{ }\mu\text{g}$ of HCl for LOQ were determined.

Sorbent tubes have two sections, the first (main) one, two times larger than the second (backup) one. If the latter contains more than 25% of the amount of analyte in the main section, breakthrough has occurred⁶². According to that, the capacity of the silica tubes was calculated. 5 replicates of powdered PVC (approximately 1.5 g) were enclosed in Tyvek pouches and sampled for 1–6 days at $110\text{ }^\circ\text{C}$ in the bulk emission mode to ensure the maximum emissions. All the sorbent tubes exhibited a breakthrough, so we can claim that the main section was saturated with HCl. The capacity of the silica sorbent tubes was calculated as the average mass, $(30 \pm 5)\text{ }\mu\text{g}$ of HCl.

Determination of HCl emissions from PVC and their time dependence

HCl is a well-known degradation product of PVC, and our initial experiments were designed with a specific focus on this acidic compound. However, because we wanted to improve the understanding of the emission process, we used consecutive sampling (Section “Emission experiments using microchambers”) to capture the dynamic changes of HCl evolution. This approach allowed us to observe that the emission of HCl from PVC proceeds in two phases, which, to the best of our knowledge, has not been reported yet (Fig. 3).

The first phase of HCl emissions consists of an initially high surface emission rate, which rapidly decreases to a minimum. This phase likely reflects the release of HCl accumulated within the material structure, formed either during manufacturing or previous degradation, and remained trapped until the experiment. Elevated temperatures led to its emission. In contrast, the second phase exhibits a stable SER within the uncertainty

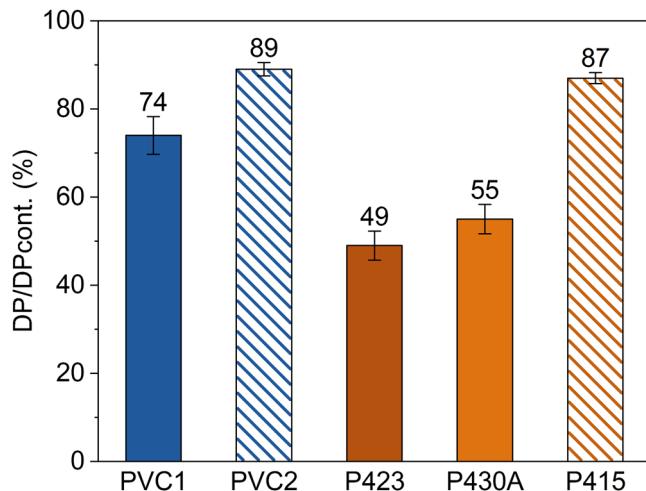


Fig. 1 | Results of the cross-infection test as a percentage comparing the DP value of the reference cellulose with the DP of the control cellulose. The final ratio is an average of two samples, both of which were analyzed twice, and is presented with the corresponding standard deviation. The labels on the x-axis represent the PVC material with which the respective reference cellulose was used in the experiment.

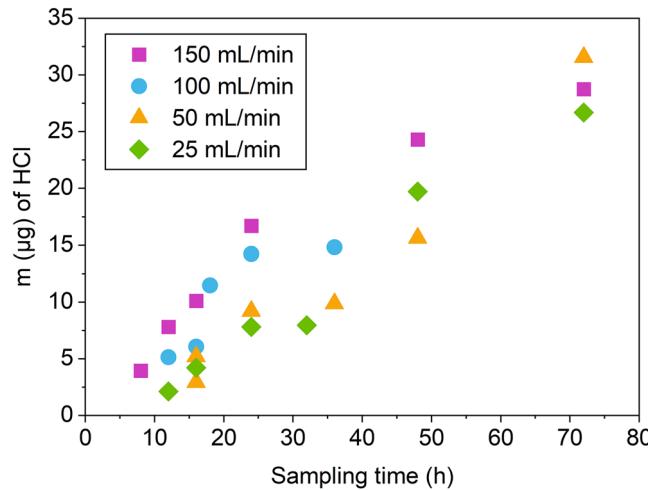


Fig. 2 | Influence of the flow rate on the mass of emitted chloride from PVC1 at 110 °C. Four flow rates were tested in a 3-day experiment with consecutive sampling periods.

interval. During this phase, HCl is actively produced and emitted as a result of ongoing PVC degradation during the experiment.

A similar trend of a two-phase process was also observed with all the other tested PVC samples. We applied two characteristic sampling periods, one for each phase, and carried out an experiment shown in Fig. 4 at the same temperature and flow as Fig. 3. Older unplasticized samples show the same pattern as PVC1 with higher SER in the second phase than in the first phase. The values of PVC1 are the same as in the more detailed Fig. 3 and are discussed above. When comparing the two older unplasticized samples, a significant difference between them is observed. We hypothesize this may be due to differences in their prior storage conditions and trace chemical composition, as their major chemical components are otherwise similar. However, without complete knowledge of the samples' histories, the causes of the observed differences cannot be unambiguously determined.

On the other hand, emissions from plasticized PVC are clearly detectable only in the first phase, meaning that no HCl was detected as a product of active degradation even at 110 °C for the duration of the experiment. The glass transition temperature (T_g) of pure, unplasticized PVC is typically around 80–85 °C^{63–66}, which decreases with increasing

plasticizer content, meaning that the experiments were performed above the T_g for all the tested materials. Below it, the material exists in a rigid, glassy state where the polymer chains have limited mobility. When the temperature exceeds the T_g , PVC transitions to a more flexible rubber-like state with increased molecular movement⁶⁴. Plasticizers penetrate in-between polymer chains and increase the free volume between the polymer chains, which leads to increasing diffusion of small molecules and could therefore facilitate the initial steps of dehydrochlorination and accelerate the degradation of PVC. However, plasticizers are believed to generally decrease the rate of HCl formation by reacting with HCl. The roles of plasticizer type and concentration in PVC degradation are therefore not yet fully elucidated^{8,63,65}. The two-phase nature of HCl emissions is crucial for understanding the material behavior and for the interpretation of experimental results. This characteristic should be taken into consideration when designing research questions and experimental plans. Experimental parameters are case-specific, as the sampling periods vary with temperature and material composition.

Activation energy of HCl emission from PVC

To determine the temperature dependence of HCl emissions from PVC, experiments were carried out in a wider temperature range at 90, 100, 110, and 120 °C. As expected, the emissions of HCl decreased at lower temperatures. The two-phase behaviour of HCl emission could be observed at all of the investigated temperatures, but the first period of emission was prolonged at lower temperatures. Therefore, the sampling periods needed to be adjusted to the individual experiment. At each of the four temperatures investigated, a stable SER value was reached in the second phase, which was used to fit the Arrhenius equation with good linearity (Fig. S1). The activation energy was calculated from the slope of the $\ln(\text{SER})$ vs. the inverse temperature as 205 kJ/mol (6% relative error). This value is relatively high because it reflects the combination of several phases of the process—the formation of HCl, its migration through the bulk, and emission from PVC into the surrounding air. It should be noted that the much lower activation energy of degradation observed as yellowing²⁴ suggests chemical degradation is occurring, but emission of the produced HCl in the gaseous form is thermodynamically unfavorable.

The calculated activation energy was then used to predict SER at lower temperatures, e.g., the calculated SER of HCl from PVC1 at 25 °C is 0.02 µg/m²/year, which is well below the LOD of the used method. The activation energy was calculated based on experiments with temperatures above T_g , where mobility is considerably higher than in the glassy state; therefore, the calculated SER at room temperature is likely a worst-case scenario.

Calculations of equilibrium HCl concentration in a storage box

The calculated HCl emissions at room temperature were used to predict the equilibrium concentrations of HCl in a box as a possible storage option for PVC folders in repositories. The model used for the prediction was adapted from Grøntoft⁶⁷, and is expressed as:

$$\frac{\delta c_i}{\delta t} = \frac{ER}{V} - v_d c_i \frac{A}{V} - N c_i$$

$\delta c_i / \delta t$ represents the partial derivative of the HCl concentration over time (mg/m³/h), ER is the emission rate (mg/h), c_i is the concentration of HCl in the steady state in the enclosure (mg/m³), A is the surface of the enclosure (m²), and V volume (m³) of the enclosure, v_d is the gravitation-driven deposition velocity of HCl on the surface (m/h) and N is the air exchange rate of the enclosure (h⁻¹). For the purpose of the prediction, a surface-coated storage box of 35 cm × 25 cm × 10 cm was used as a worst-case scenario with the lowest N of 0.2 h⁻¹ according to the study by Novak et al.⁶⁸. v_d for HCl of 2.4 cm/s was used according to Erisman⁶⁹.

If we hypothetically fill the described box with 250 A4 (ISO 216) sheets made of PVC1 at 25 °C and calculate the c_i using SER at room temperature (Section “Activation energy of HCl emission from PVC”),

Fig. 3 | Surface emission rates of HCl from sample PVC1 in consecutive time periods at 110 °C. The values are plotted as the average of two measurements with standard deviation. The sampling intervals used were optimized for this sample, as well as the experimental parameters, to clearly distinguish between the two phases, which are also shown in the plot. The experiment is explained in Section "Emission experiments using microchambers".

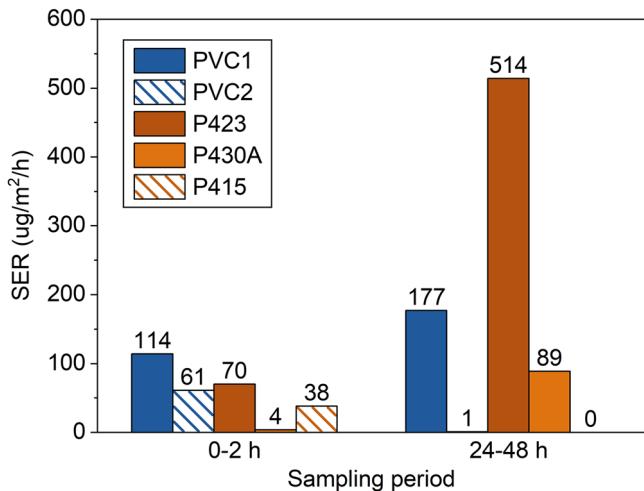
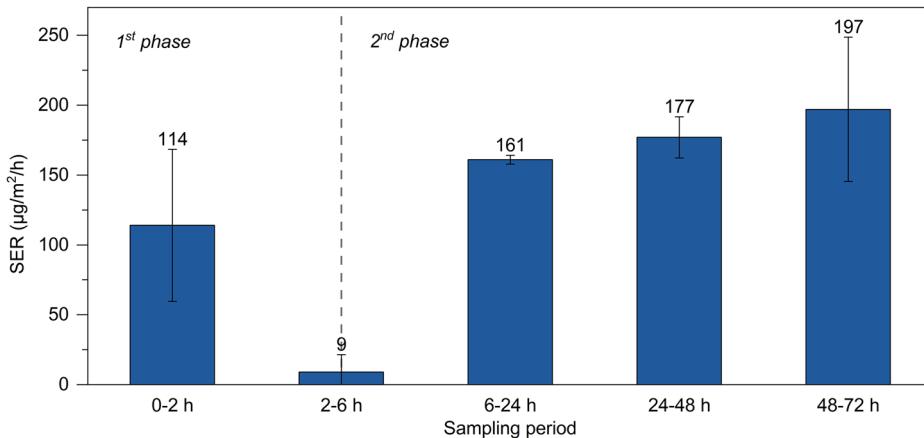


Fig. 4 | Emission rates of HCl at 110 °C from the PVC samples from 2019 (blue columns) and the 1980s/1990s (orange columns), that are plasticized (columns with the pattern) or unplasticized (monochromatic columns). Two sampling periods were selected based on the experiment shown in Fig. 3 to represent the two phases. One replicate was performed for each determination. The uncertainty of the method is 18%, which accounts for instrumental and random error as well as sample and sorbent tube inhomogeneity.

the calculated equilibrium concentration amounts to approx. 2 ppq (parts-per-quadrillion), i.e., 2×10^{-6} ppb (2.8×10^{-6} µg/m³) HCl. The value is far below the human exposure limit defined by OSHA⁴¹ and at the same time far from exceeding the maximum average concentration for acidic pollutants defined by ASHRAE⁴⁸. Accordingly, it could be argued that the HCl emissions are too low to significantly contribute to the pollution in real environments where heritage collections are displayed and stored.

Determination of other acidic emissions

Considering the low rate of HCl emission, we hypothesize that HCl alone could not degrade the reference cellulose paper in the cross-infection test as extensively as observed (Section "Cross infection test"), thus indicating the potential emission of other acidic compounds. Indeed, in the ion chromatograms, two additional peaks matching the retention times of formate and acetate were observed besides chloride (Fig. S2). Since there is no mention of formic and acetic acid as PVC degradation products in the reviewed literature, their identity was unambiguously confirmed by an additional orthogonal HPLC analysis (Fig. S3). The presence of C–O and C=O as indicators of oxidative processes was also observed in FTIR spectra (Fig. S4).

To match the quantity of organic acids with the results of the cross-infection test, an emission experiment was performed at 80 °C with one sampling period of 14 days on charcoal sorbent tubes. LOD and LOQ for formic acid were 4 µg and 8 µg, and for acetic acid, 0.9 µg and 2 µg, respectively. The results are presented in Fig. 5, illustrating that all studied PVC samples emitted both formic and acetic acid. Notably, acetic acid emissions were significantly higher, particularly in the case of the older unplasticized samples (P423 and P430A). Among the detected acids, acetic acid is the weakest, which reasonably explains its prominence as the most emitted compound. HCl, the strongest acid among the three, could not be detected under these conditions.

To determine which acid had the greatest impact, we assessed the relationship between the emitted acidic gases at 80 °C from the emission experiments and the DP/DP_{cont.} values obtained from the cross-infection test. Figure 6 highlights this relationship for acetic acid, showing a clear trend: the more acetic acid was emitted, the more severely the reference cellulose paper degraded. In contrast, no such correlation was observed for formic acid. HCl was below the limit of detection at the conditions of the experiment. This leads to the conclusion that acetic acid had the most significant contribution to the observed damage to the cellulose reference.

To verify that the acetic and formic acids originate from PVC itself and not its additives, we repeated the emission experiment using commercial powdered unplasticized PVC without stabilizers. The material was enclosed in Tyvek pouches and sampled in bulk emission mode at 110 °C. The results consistently showed the presence of the same three peaks in the IC chromatogram (Fig. S5), confirming our hypothesis that these acids are produced directly from the PVC and not from any additives.

The reviewed literature does not mention formic or acetic acid as emission products of unplasticized PVC. On the other hand, the formation of the same two organic acids has been reported during the degradation of polypropylene in oxidative environments. The degradation of polypropylene leads to the formation of oxygenated products, including carboxylic acids, following the scission of the polymer chain to smaller fragments^{70–72}. However, it is unclear whether a similar pathway takes place in PVC.

Discussion

The aim of this work was to better understand the acidic emissions of heritage PVC, focusing on HCl as a well-known acidic degradation product. Five PVC samples, differing in age and plasticizer content, were analyzed in cross-infection tests and multiple complementary emission experiments.

We report the first study establishing the methodology for the assessment of the degradation of PVC by measuring HCl emission rates, which can be easily adapted for use in other fields. Cross-infection tests were performed to assess the impact of the total emissions on cellulose as a reference. The results showed a moderate to severe negative impact on all the investigated samples, with the older, unplasticized samples having the

Fig. 5 | Surface emission rates of acetic and formic acid at 80 °C for 14 days of sampling. The sampling conditions (temperature and time) were selected to match the cross-infection test. The experiment is described in Section “Emission experiments using microchambers”.

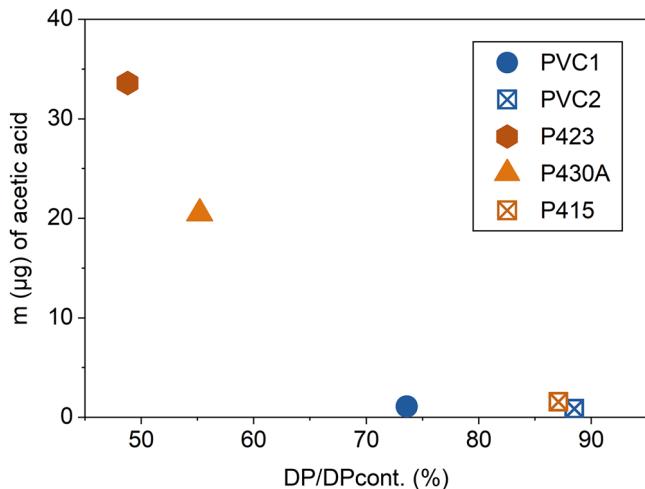
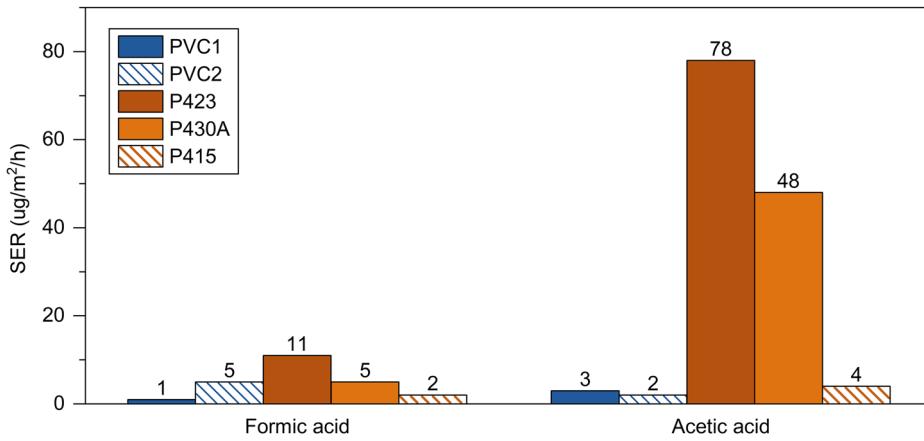


Fig. 6 | Correlation of the emission experiment with results of the cross-infection test. The mass of emitted acetic acid (14 days at 80 °C) is presented as a function of DP/DPcont. value.

biggest negative impact. The results indicate that older objects made of unplasticized PVC cause more damage to the surrounding objects than newer materials. Further experiments with emission testing were performed to elucidate the identity and concentration of the harmful degradation products.

Performing experiments in the surface emission mode allowed us to successfully demonstrate that the process of HCl emissions at elevated temperatures consists of two phases. The first phase is related to the release of previously accumulated HCl. The second phase corresponded to ongoing dehydrochlorination at the conditions of the experiment. This conclusion should be considered while designing future emission experiments.

Quantifying ongoing surface emission rates from the model PVC material at temperatures within the range of 90–120 °C allowed us to calculate the activation energy of 205 kJ/mol. This high value is due to several processes required for the emission of gaseous HCl from PVC, including the formation of HCl from the polymer, its migration from bulk to the surface, and the following emission into the surrounding air. The observed high temperature dependency prevented us from performing emission experiments at lower temperatures.

To assess the impact of HCl emissions from PVC at conditions relevant to heritage collections, we predicted the emission rate at room temperature and created a simple model to calculate the equilibrium concentration in a standard storage box for a worst-case scenario. The equilibrium

concentration of HCl was in the range of parts-per-quadrillion, which is well below the recommended concentration thresholds for other acidic pollutants in heritage environments. According to the emission experiments performed on the selected samples and the modelling, we can conclude that emissions of HCl from PVC are too low to meaningfully and significantly contribute to the pollution of the environment in which heritage collections are displayed and stored. The results are based on samples dated from the 1980s to 2019, varying in yellowing, age, and plasticizer content, which we consider representative of heritage PVC objects of this age.

Additionally, we discovered that emissions of acids from PVC also include formic and acetic acid. The amount of acetic acid was the largest and showed a good correlation with the results of the cross-infection test. To unequivocally determine the origin of formic and acetic acid, the dynamics of their emissions from PVC, and to assess the extent of the damage caused during the PVC degradation, further experiments will be conducted in the future.

The discovery that formic and acetic acids are products of PVC degradation holds significant implications for PVC collections, as the compounds are associated with the degradation of organic and inorganic heritage materials. This will contribute to informing future material selection choices in storage and display, and lead to the development of better preservation strategies for PVC heritage objects.

Data availability

All data generated or analyzed during this study are included in this published article and its supplementary information file.

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Competing interests

The authors declare no competing interests.

Additional information

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