

Environmental dose-response functions of silk and paper exposed in museums.

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ABSTRACT

This paper reports 1 year of data of the environments and changes in the molecular weight of silk and the degree of polymerization of sensitive paper measured externally and indoors in 10 European museums, and the dose-response functions that were obtained by statistical analysis of this data. The measurements were performed in the EU FP5 project Master (EVK-CT-2002-00093). The work provides documentation of deterioration of silk by NO₂ and O₃, and alternatively in combination with UV radiation. The indoor deterioration of the silk was only observed in one location with high UV radiation. The indoor deterioration of sensitive paper correlated with the UV radiation, the concentrations of NO₂ and O₃, and in addition with an SO₂ concentration of 4 μgm⁻³ and a formic acid concentration of 50 μgm⁻³ in two different locations. If the observed dose-response effects are linear to lower doses and longer exposure times, then the lifetime to intolerable deterioration of the paper and silk would be 6–7 times longer overall in the enclosures than in the galleries.

1. Introduction

To reduce the deterioration of silk and paper in museums and archives, it is important to understand the relative influences of environmental factors on the deterioration, and the aging mechanisms. A short review of the ageing of silk [1] describes complex and changeable deterioration mechanisms involving interacting mechanical, physical, photochemical, chemical, thermal, and biological factors. Photo-oxidative degradation by especially ultraviolet (UV)-radiation can break the hydrogen bonds and covalent bonds in the proteins in the fibroin macromolecules in the silk, and denature, discolor, make it more brittle, and reduce its strength. Amino acids in silk proteins, like serine and tyrosine, are prone to oxidation that results in denaturation of silk fibers. Silk is susceptible to chemical attack by a multitude of compounds. The chemical degradation will happen in synergy with other environmental agents, like temperature, and increase as the higher chemical diversity of more degraded silk triggers more molecular reactivity. In accelerated ageing experiments of silk and estimations by the Arrhenius equation, it was found that silk was little aged by UV filtered light in typical display conditions, but that elevated temperatures and relative humidity significantly enhanced the deterioration [2]. It has been found that thermo-oxidation at elevated temperatures (125

°C) can mimic the state of degradation of historic silk textiles, and that oxidation, hydrolysis, chain scission and chain rearrangements (physical ageing) were the main degradation mechanisms [3].

Paper collections are mainly deteriorated by acid-catalyzed hydrolysis, that causes cleavage of cellulose molecular chains and reduction in the average molecular weight and degree of polymerization of cellulose. The deterioration rate is influenced by the environment, and acidity and other properties of the paper [4]. Accelerated exposure of paper-based materials from museums, archives, and libraries to sulfur dioxide (SO₂) and nitrogen dioxide (NO₂), has been found to degrade paper into more water-soluble organic compounds by increasing the acidity, the total organic carbon (TOC) value, the conductivity, and the copper number [5]. A review found no evidence of effects of small fluctuations of temperature ($\Delta T = 10$ °C) and ($\Delta RH = 20$ %) on the degree of polymerization of historic paper [6]. It stated that acetic acid and NO₂ might significantly contribute to degradation, but that no general dose-response functions (DRFs) were available taking into account the most important agents of deterioration: T, RH, pollutants and the paper composition, with the acidity probably being the most important parameter. DRFs that included the effects of T, RH and the paper acidity were later developed [7]. An extensive study exposed a variation of papers outdoors in ten European sites and Cairo over 1.5 years,

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protected from rainfall and direct or reflected sunlight (including UV radiation) [8]. Environmental DRFs were developed by multilinear regression analysis. This study showed complex interactions between the environment and the deterioration of paper seemingly related both to the interactions between the parameters in the environment and in their combined interaction and reactions with the paper. They measured the temperature, relative humidity, and light illuminance continuously with electronic meters, and the pollution gases NO₂ and ozone (O₃) in the first 4 weeks per monitoring period of three months. The study did not measure SO₂ since “in post-industrial environments the concentrations of this pollutant are generally very low and in most of the environments used in this research do not exceed the value of 1 ppb [9], which is commonly the value considered safe for paper collections according to several standards and guidelines [10].” The study measured deterioration as the change along the yellow-blue coordinate, Δb^* in the CIE L*a*b* colour space, and the viscometrical average change in the degree of polymerization of the papers, $\Delta(1/dP)$, which were used as dependent variables in the statistical dose-response analysis.

Increasing ΔdP changes of the paper in these exposures were explained by higher concentrations of NO₂ together with T, and by higher concentrations of O₃. The synergistic effect of NO₂ and T was found to decrease at higher values of the two parameters and the effect of O₃ was found to be higher at low pH of the paper. The decreasing synergistic effect of NO₂ and T could be interpreted as a decreasing Arrhenius effect, and maybe by a reduction in the reaction rate of NO₂ with the paper when its concentration increased (at constant T). Lower gaseous deterioration rates are typical as initially fresh surfaces become saturated with adsorbents and reaction products build up and hinder further reaction [11]. The higher effect of O₃ at lower pH of the paper may be related to similar causes, as a more acidic paper, with fewer hydroxyl (OH) groups, may have more surface sites accessible for atmospheric oxidation. On the other hand, high levels of relative humidity and daily illuminance tended to slow down the degradation, but antagonistically so that increasing values of one of these parameters nullified the effect of both. This could be interpreted as a reduction in the surface humidity of the paper when light levels increased, and a reduction in a degrading effect associated with the light exposure by the interaction of the light with the surface humidity. These results seemed to illustrate well the complexity of such deterioration mechanisms [12], and are interesting to compare with this work.

There seems still to be few reports available of the environmental deterioration and DRFs of silk and paper exposed in situ indoors in museums or other heritage institutions. This work, therefore, finally reports the observed aging of samples of silk and paper that were exposed indoors, with two references outdoors, in ten European museums in the EU MASTER project in 2004–2005 [13], together with measurement of the environments in these sites. Besides the reports of the silk, this adds observations at lower environmental loads on paper than in the work of Pastorelli et al. [9], in museum environments, and also of singular observed effects of UV radiation, sulfur dioxide, and formic acid that can occur in museums. Comparisons of the observed deterioration with recommended levels of the environment are presented. The work did not investigate the physical or chemical mechanisms of the observed deterioration of the silk and paper samples.

2. Experimental measurements and methods

2.1. Sites, environments, and recommended levels

Samples of silk and paper were exposed in 10 museums and historical houses from the 1st March 2004 to the 1st March 2005 (Table 1).

The samples were exposed outdoors (a), in galleries (b) and inside enclosures (c) in these galleries. Fig. 1 shows the mounting of the samples at site no.9. Photos of the other sites/locations are available in Table A.5 in the Appendix.

The silk and paper slide samples were mounted vertically on matt

Table 1

The EU MASTER project museums.

Name of museum/ historic building	Site, Country
1. The Museum of Decorative Arts & Design	Oslo, Norway
2. Trøndelag Folk Museum	Trondheim, Norway
3. Blickling Hall	Norfolk, UK
4. Tower of London, Bloody Tower	London, UK
5. Haus der Geschichte Baden-Württemberg	Stuttgart, Germany
6. Schwarzwälder Trachtenmuseum	Haslach, Germany
7. National Museum in Krakow, The Jan Matejko House	Krakow, Poland
8. The Karol Szymanowski Museum “Atma”	Zakopane, Poland
9. Wignacourt Collegiate Museum	Rabat, Malta
10. The Historical Museum of Crete	Heraklion, Greece

black anodized Al-racks (Fig. 1) for one year. The silk samples were exposed outdoors (a) at all the 10 sites. The paper samples were exposed outdoors at two of the sites. Both the silk and paper samples were exposed in the galleries (b) and inside protective enclosures (c) in these galleries at all the 10 sites. The slides with the paper samples included one sample that was exposed to light (U = unshielded) and one sample that was shielded from light (S). Thus, in total 30 silk samples, 22 unshielded paper samples and 22 shielded paper samples were exposed. An Al-shield covered the samples outdoors to avoid direct exposure to sunlight and precipitation (Fig. 1A). It seemed that some stray and diffuse radiation would still reach the samples at many of the outdoor locations, with different lighting conditions during the days, months, and year. Eight of the enclosures were showcases, and two were wooden storage compartments: a cupboard with openings to the gallery (3c) and a wooden cabinet (4c). Except for the samples at locations 4b and 4c, all the samples were permanently positioned at their mounting locations for the whole year. Due to refurbishments at site 4, the samples in locations 4b and 4c were relocated in the same types of locations in a different gallery closed to the public during October 2004. From November 2004 the samples in location 4b were relocated to the original location, and the samples in location 4c were relocated to a different but similar wooden cabinet in the original room. The passive pollution sampling followed the relocations. However, due to this irregularity some increased uncertainty in the representativeness of the annual assessment of the RH, T, light- and UV radiation in location 4b might be expected. Below the passive gas samplers in Fig. 1, Al-holders with so called early warning organic (EWO) dosimeters [14] can be seen. Between the paper and silk samples blue wool (BW) light dosimeters [15] are seen. The results of the EWO are not discussed in this work. The results of the BW dosimeters were correlated with the assessed UV and light doses. The UV-dose was substituted with the BW parameter in developed DRFs with a significant effect of the indoor UV-dose, as a check of the radiation effect.

The paper samples were held in plastic slide mounts, with openings of 24 × 36 mm. Behind the front paper that was exposed to light (U), a central sheet of the same paper was placed to absorb light that might pass through the unshielded sample. The central piece was not analysed. The shielded sample (S) was mounted behind the central sheet (Fig. 2).

The concentrations of sulfur dioxide [SO₂], nitrogen dioxide [NO₂], and ozone [O₃] ($\mu\text{g m}^{-3}$), and the temperature, T (°C), and relative air humidity, RH (%), were measured in all the 30 locations. In addition, UV radiation, UV (mWm^{-2}), and visible light, VI (Lux) were measured in the galleries (b), and inside the enclosures (c). The concentrations of acetic acid [CH₃COOH] and formic acid [HCOOH] were measured inside the enclosures (c). The acetic acid will be termed AcAc and formic acid as FoAc in the text in the following, but CH₃COOH and HCOOH in the diagrams and tables. The gases were measured with duplicate passive badge samplers of the IVL type [16] (Fig. 1). The detection limits (dl) of the monthly gas sampling were reported from the laboratories to be 0.03 $\mu\text{g m}^{-3}$ of SO₂ and NO₂, 0.5 $\mu\text{g m}^{-3}$ of AcAc and FoAc and 1.0 $\mu\text{g m}^{-3}$ of O₃.

The T and RH were recorded with the electronic loggers in normal

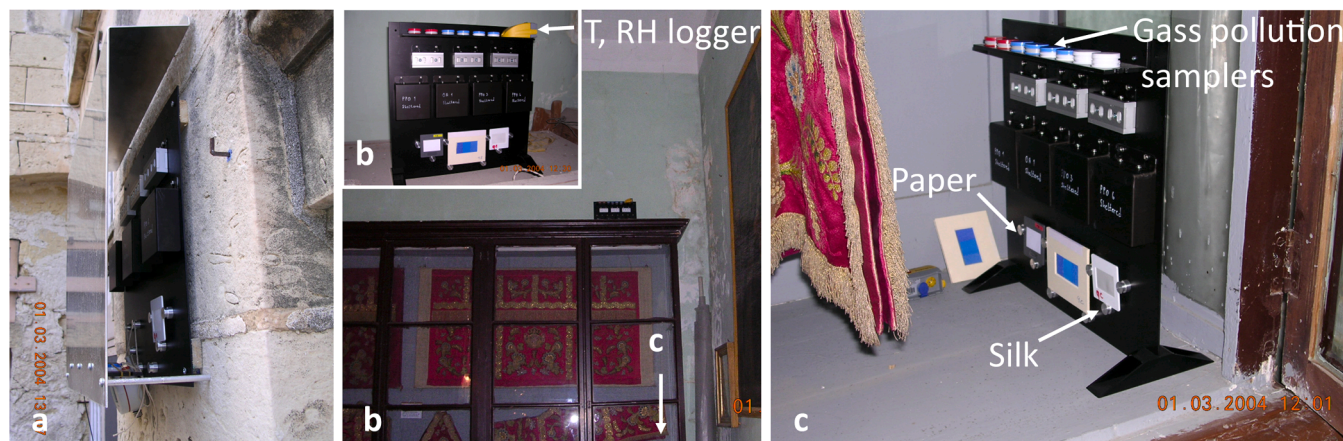


Fig. 1. The exposure racks outdoors (a), in the gallery (b) and in the enclosure (c) in site no.9, Wignacourt Collegiate Museum, Malta. The paper and silk samples are seen mounted on the racks. Duplicate passive samplers of four gaseous pollutants are seen on the top of the racks: From the left to right: SO₂, NO₂, O₃, and then acetic acid and formic acid that were collected on the same sampler. Aluminum (Al)-holders of so called EWOs (Early Warning Dosimeters), are seen below the passive samplers. Blue Wool dosimeters can be seen between the silk and paper samples.

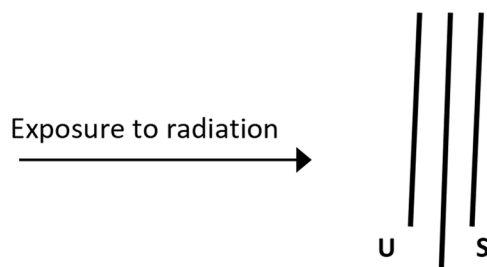


Fig. 2. A schematic of the paper slide. U = unshielded, S = shielded.

use at each location (a, b, and c) at each site (1–10, Table 1). The monthly time series of the recorded data and/or averages of these were reported and the annual averages were calculated. The exposure doses of visible light (Vlh, Luxh d⁻¹) and UV radiation (UVh, kWhm⁻² d⁻¹) were approximated from the reported average values of the VI and UV measured with electronic meters at the indoor locations (b and c) at 12.00 pm in the three months from March to May 2004. The reported radiation data from the indoor locations (b and c) is given in Table A.1 in the Appendix. Luxbug stand-alone (location 4), and Elsec and Hobo (locations 7 and 8), loggers were used at three of the locations. These seem quite representative of loggers used at the time. Unfortunately, we do not now have the full information about the used loggers and their technical data, such as detection limits. In this context it should however be considered that the effects of the indoor UVh on the silk and paper deterioration was found to be due to relatively high doses in a few locations (see below). The diurnal doses over those three months were assessed from the reported presence of only artificial lighting (A), only natural light (N), or a mix of artificial and natural light (A + N) in the locations by Eqs. (1)–(3):

$$D_A = R_{I, 12PM} \times L_{A,h} \quad (1)$$

$$D_N = R_{I, 12PM} \times 4h \quad (2)$$

$$D_{A+N} = [(R_{I, 12PM} \times L_{A,h}) + (L_{I, 12PM} \times 4h)] \times 0.5 \quad (3)$$

where D_A , D_N and D_{N+A} are the artificial (A), natural (N) and mixed artificial and natural (A + N) visible light or UV radiation doses, $R_{I, 12PM}$ is the measured radiation intensity at 12 noon (Lux for VI and mWm⁻² for UV) assessed at the exposure locations to represent the situation over the three months from March to May, and $L_{A,h}$ is the daily hours of

artificial light. It was thus assumed that four hours of constant natural radiation intensity equal to that at midday (12 noon) would approximately correspond to the radiation exposure during the longer time of increasing radiation (light) from the morning until noon and then decreasing radiation (light) towards the evening. In the cases with mixed artificial and natural radiation (light) it was assumed that half of the radiation intensity was represented by the natural light, and the other half by the artificial radiation dose over the time the light was turned on. The outdoor radiation exposure would be low due to the shielding, but it was expected to vary depending on the different geolocations, mounting locations and directions, and the atmospheric conditions during the year. A simplified/tentative estimation of the outdoor UVh (mWhm² d⁻¹) exposure of the samples was used in the dose-response analysis. The average outdoor (a) UVh was suggested to have been five times that in the galleries (b). This average was then distributed between the outdoor locations proportionally to the different annual average Global Horizontal Irradiation (GHI, kWhm⁻²) at the sites [17]. The UVh was measured to be zero in five of the ten galleries, and the UVh estimated by these procedures in one gallery, 4b, only, was higher than those estimated in the shielded locations outdoors (see Fig. 3). Location 4b was reported to have a short peak of direct sun exposure in the early day. Due to partial measurements of RH, T, VI and UV, little available information about the loggers used, and the method of assessing the annual doses the UVh and Vlh, a higher uncertainty was expected in these parameters than in the values of the pollution parameters. It was unfortunately not possible to quantify this uncertainty by the available measured data.

To ascertain the realism of the UVh values, they were correlated with the BW cumulative exposure (kLuxy⁻¹) values, and the significance of their inclusion in DRFs was checked by substitution with the BW values in the DRFs. Positive and significant correlations with the BW values should confirm a valid overall ranking of the calculated UVh between the locations. We acknowledge, still, that the random errors in the calculated UVh loads may be large and that there may be systematic errors due to, for example, incorrect weighing between the natural and artificial light or of the seasonal loads. Based on the available data, this uncertainty was unavoidable. For the regression-outlier analysis that was performed it was most important that the calculations distinguished correctly between the locations with the lowest and highest radiation doses. A possible systematic error seemed less critical as it would mainly affect the values of the regression coefficients and less their significance. As will be discussed, the values of the regression slopes from the performed regression-outlier analysis with the few data should probably not, in any case, be applied to other data without controls. On this basis, we preferred to do the main analysis with the inclusion of the

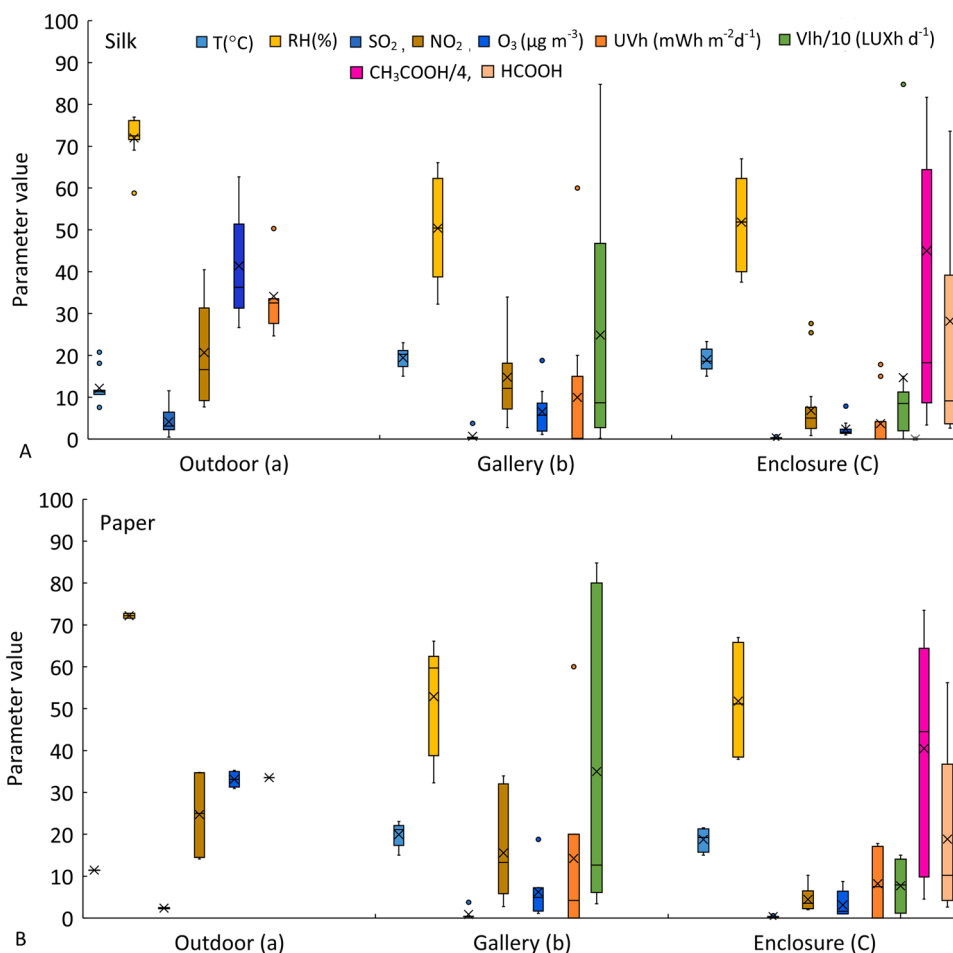


Fig. 3. The environmental parameter values at the exposure locations of the silk, and paper with a $\Delta dP > dl$. The boxes represent the 1st and 3rd quartile of the data points, the “x” is the average, and the horizontal line in the boxes is the median. The whiskers extend up from the top of the boxes to the largest value less than or equal to 1.5 times the interquartile range (IQR) and down from the bottom of the box to the smallest value larger than 1.5 times the IQR. Outliers beyond this range are represented by small filled-in circles. The ranges of some parameter values, UVh, Vlh and SO₂, extend down to zero when their presence was not measured in some location.

fundamental variables of the UVh and Vlh, rather than the BW results. Due to the many uncertainties related to the UV and VL measurements and dose-assessment the inclusion of UVh in three of the seven reported DRFs should probably be considered more as well-founded, we think, hypothesis than verified correlations.

2.2. The silk and paper samples and their analysis

The silk samples were prepared by Historic Royal Palaces in London, UK, of a modern silk textile (*Bombyx mori*). The samples were cut from the centre of the light-exposed side of one uniform piece of the textile and were expected to have the same molecular weight distribution at the start of the exposures. In the analysis, 1.5 mg of each silk sample was dissolved in 0.4 ml concentrated lithium thiocyanate (LiSCN) solution. The LiSCN solvent dissolves silk by disrupting hydrogen bonds holding together the protein structure, but without causing polymer degradation. Gentle agitation at room temperature was used to complete the dissolution. The samples were filtered to fiber lengths $<0.45 \mu\text{m}$ by centrifuge micro-filtration. 20 μl of the silk solution was injected to the Size-Exclusion Chromatography (SEC) system, using a flow rate of 0.3 ml/min, and a total run time of 30 min per sample. The mobile phase was 8 M urea, which denatures (uncoils) the protein in solution, run at a constant temperature of 30 °C. The column used was a Phenomenex BIOSEP S-4000 column with Security Guard Cartridge System. The column was calibrated using protein narrow standard calibration

markers, meaning the results should be considered as relative, rather than absolute molecular weights. After running the series of narrow standards, a linear fit was performed, and a log Mw (weight-average Molecular weight (atomic mass units, a.m.u)) vs. retention time calibration curve was plotted. Three replicate injections were carried out for each dissolved silk sample. The results are reported as the mean (average) value of their mean molecular weights (Mw) from the fitting to the curve of the standards. The error is expressed as the standard deviation (SD) of the three replicate injections. The Mw is biased towards larger molecules. This is different from the measure of the number-average molecular weight (Mn) which is biased towards molecular weights with high frequency (the mode). These measures usually share the same trends, but it is reported in the literature that Mw relates most closely to the tensile strength [2,18]. Mw is also the most reproducible factor, and therefore the Mw was used in this work. Smaller Mw (or Mn) numbers indicate shorter average silk polymer chains, and a decrease in molecular weight is indicative of polymer degradation. The Mw data are shown in Table A.2 in the Appendix.

The paper samples were prepared by University College London, UK, of a test paper based on a late nineteenth century recipe for poor quality, acidic paper. This was as changes could not be expected to occur to stable papers in one year, while more acidic papers deteriorate at a faster rate. The paper was manufactured by the University of Manchester. The analysis was of the average change in the degree of polymerization (dP) [19] of the three exposed duplicates from before to after the exposure

(ΔdP). The uncertainty (\pm) was reported as one standard deviation. The analysis was carried out using a standard viscometry method (ISO 5351-1-1981, now replaced with ISO 5351:2010 [20]) at the University of Ljubljana in Slovenia. The ΔdP was calculated by subtracting the dP scores from the value of $dP = 1407 \pm 50$ of a reference sample and converting to a positive value. The reference sample had been stored in a freezer during the test period of one year at one of the exposure locations (no. 9). The ΔdP results above a detection limit (dl) of one standard deviation of the reference sample: $dP_{dl} = 1407 - 50 = 1357$ were included in the dose-response analysis. The ΔdP data are shown in Table A.3 in the Appendix. The environmental parameters, and silk and paper deterioration parameters, are written below by their abbreviations.

2.3. Dose-response regression analysis

The Mw and ΔdP were the dependent variables in the dose-response analysis and determination of significant DRFs. The annual averages in the 30 locations of each of the duplicate values of the pollutant gases, and of the T, RH, Vlh, and UVh, were the independent variables. This gave a total duplicate set of 60 data points, with 20 data points outdoors for the silk and 4 data points outdoors for the paper, and with 20 data points in the galleries and 20 data points in the enclosures for both the paper and the silk. The standard deviation in the duplicate values of the pollution measurements averaged over the year and all the locations were ($\mu\text{g m}^{-3}$): 0.3 for SO_2 , 0.8 for NO_2 , 1.1 for O_3 , 16.0 for FoAc and 48.5 for AcAc.

The multiple linear regression analysis was performed by including all the independent variables from the start, then by backward elimination of variables that were not significant on a 95 % level (two sided) in steps until only a set of significant additive explanatory variables remained. In cases where no significant explanations were found the dose-response hypothesis was discarded. All further notations of statistical significance reference to this level of 95 %. In cases where several independent variables were found to have significant effects, their possible multicollinearity was checked by regressing each of them with all the other significant variables. If statistically significant interdependencies were found it was concluded that multicollinearity was affecting the results. The model was then reformulated by multiplication of the interacting variables to single combined effect variables. The analysis by backward elimination was then iterated as described above with the inclusion of the combined variables from the start, until the final equation with only significant effects was obtained. The solutions were again checked by regression of the dependent variables against each single independent variable and then forward addition of one to three additional variables, while keeping only the significant variables in each step. The possible multicollinearity was checked as described above. If a different, significant explanation (DRF) of more of the variation was found (that is with a higher R^2) this was chosen. To investigate the effects of notable outliers, the full analysis was repeated without the outliers. The significant DRFs with and without outliers are reported. If the best DRF could not be uniquely determined the alternatives are discussed. The analysis was made separately with all the outdoor and indoor locations included (a + b + c), with the indoor locations (b + c), and with the enclosure locations (c), and separately for the paper samples in the unshielded and shielded positions. The analysis was performed in XLSTAT. The normality of the distributions needed for the significance notations in XLSTAT to be valid, were checked with the Shapiro-Wilks equation [21], which defines normality as a calculated p-value > 0.05. The correlations that were found from the regression analysis will mainly be called “effects” through the paper. The uncertainty in generalizing these effects beyond the sample sets was clearly larger in the cases of the fewer paper samples ($n \leq 13$) with larger triplicate variation, than the silk samples ($n = 30$).

2.4. Recommended levels

The responses in the derived DRFs were compared with ASHRAE (The American Society of Heating, Refrigerating, and Air-Conditioning Engineers) museum average recommended one-year doses of $10 \mu\text{g m}^{-3} \text{ a}^{-1}$ of NO_2 [24], SO_2 and O_3 [22], and a recommended level in general collections of $78 \mu\text{g m}^{-3}$ of FoAc [23]. The ASHRAE 2007 guidelines [23] suggests lower levels for general collections, of $1 \mu\text{g m}^{-3}$ of NO_2 and $0.4 \mu\text{g m}^{-3}$ of SO_2 without specifying this as a dose over several years. This still seems to mirror the 10 years levels of $1 \mu\text{g m}^{-3}$ in the ASHRAE 2003 levels [22]. The background and development of these guidelines were described and discussed by Tetreault [25]. Regarding exposure to UV radiation, it has been stated that “there is no rational basis for recommending that museum objects may be subjected to any level of ultraviolet exposure, and elimination of UV is recommended” [26]. As an illustration of expected increasing deterioration of sensitive materials by increasing exposure to UV radiation, a comparison is still presented of the observed UV dose-response effects on the silk and paper. This was based on an advice that the UV exposure should be below $10 \mu\text{W/lm}$, but up to a maximum of $75 \mu\text{W/lm}$ [27]. These UV limits seem to be based on a recommendation in the now withdrawn standard BS5454:2000 [28], that the UV radiation should be in the range from 0 to 0.5 mWm^{-2} up to 3.75 mWm^{-2} , at exposures below 50 Lux (lm/m^2), of medium sensitive materials up to 8 hd^{-1} and of highly sensitive materials up to 1 hd^{-1} [26]. These levels correspond to UV energies of $2 \text{ mWhm}^{-2} \text{ d}^{-1}$ up to $17 \text{ mWhm}^{-2} \text{ d}^{-1}$, at the mean daily equivalent maximum exposures of 4.5 h of artificial or natural lighting, that was reported for the 10 sites (b, c). The effect of given NO_2 , SO_2 and O_3 doses would, generally, be observed over longer times at proportionally lower concentrations of the gases [22]. The concentration of $78 \mu\text{g m}^{-3}$ FoAc acid should probably be considered as an adverse effect level under which deterioration is seldom observed (a NOAEL) [29,30]. Thus, if assuming constantly increasing dose-responses, the comparison of the observed reductions in the Mw and ΔdP with the recommended maximum doses of the NO_2 and O_3 , and with doses of FoAc at a concentration $\geq 78 \mu\text{g m}^{-3}$, are independent of the exposure times. The deterioration of the silk and paper described by the DRFs in environments above the recommended limits are in the following termed, “intolerable”.

3. Results

3.1. The environments

Fig. 3 shows the ranges of the environmental parameter values at the exposure locations of the silk, and paper with a $\Delta dP > \text{dl}$.

Fig. 3A shows the notable outliers in the silk analysis of the assessed UVh in location 4b, and of Vlh in locations 10b and 10c. Possible significant correlations with these parameters were thus expected to depend mainly, and possibly solely, on the high assessed UVh and/or Vlh exposures at these locations. Fig. 4 shows the correlation between the reported values of the BW (Table A.4 in the Appendix) and the assessed UVh and Vlh. Fig. 4 shows the correlation between the Blue Wool response (BW) and assessed UVh (A) and Vlh (B) doses.

Fig. 4A shows a positive correlation between the BW response and the assessed UVh that depended mainly on the location 4b outlier. The correlation was also present when this outlier, 4b, was removed, but was weaker and depended then wholly on locations 3b and 7c. The correlation in the sites with the paper $\Delta dP > \text{dl}$ was similar for the both the UVh ($y = 0.015x + 3.3$, $R^2 = 0.31$) and Vlh ($y = 0.033x + 218$, $R^2 = 0.069$). The less good overall correlation with the Vlh (B) than with UVh was mainly due to three outliers, 3b, 10b and 10c, that were better explained by the assessed UVh (Fig. 4A). It could be expected that the BW would respond mainly to the UVh where this was present. The correlations in Fig. 4A seemed to confirm that the calculated UVh could be used to assess the radiation effect in the regression-outlier analysis of

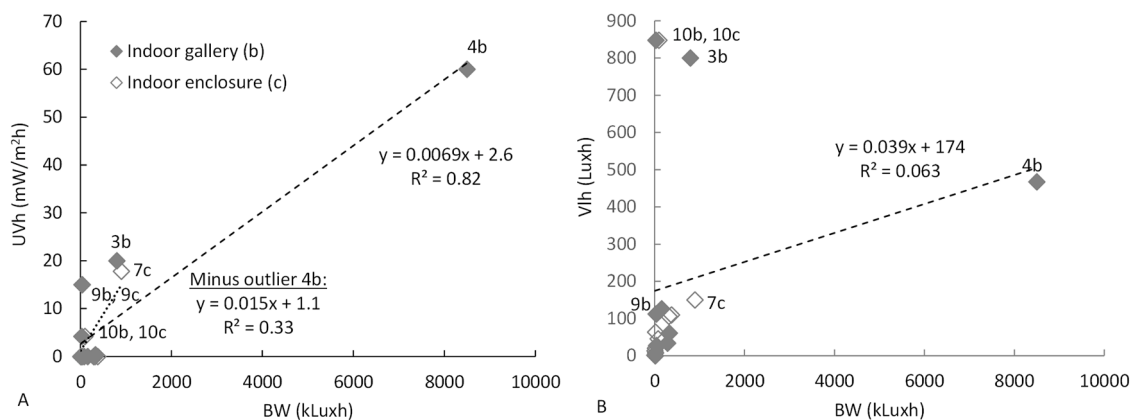


Fig. 4. Correlation between the Blue Wool response (BW) and assessed UVh (A) and Vlh (B) doses in all the indoor locations.

the silk and paper. As will be shown below, a significant influence on the deterioration of the silk and paper were in some instances found of the UVh, but never of the Vlh. The low BW response in location 9b indicated more uncertainty in the assessed UVh in this location. This will be discussed where relevant in the derivation of the DRFs.

3.2. The silk and paper deterioration

Fig. 5 shows the distribution of the average molecular weight of the silk and change in the degree of polymerization of the paper samples after the exposures.

The silk samples were cut from the same material and there was very little variation in the Mw between the silk triplicates (Fig. 5A). The observed variation between the locations was thus an effect of the exposures. Eleven of the unshielded paper samples (55 %), and five of the shielded paper samples (25 %), had ΔdP values that were over the detection limit of one standard deviation. The differentiation between

these variations.

3.3. Dose-response functions (DRFs)

The significant DRFs from regression analysis for the silk, and paper in the unshielded (U) or shielded (S) positions, in the number (n) of locations outdoors and indoors (a + b + c), indoors (b + c), or in the enclosures (c) are given below. The standardized coefficients of the DRFs are given in Table 2. DRF5_{BW} was added as a supporting equation to DRF5 with substitution of the UVh parameter with the BW exposure. The substitution of UVh with BW in DRF7 was not significant and is therefore not shown. This is discussed in Section 4. The parameter units were given in Fig. 3.

DRF1 : Silk (1.a + b + c, n = 30)

$$Mw = 79000 (\pm 2000) - 42 (\pm 4) \times NO_2 \times O_3, R^2 = 0.68 \quad (4)$$

$$DRF2 : \text{Silk } (2.a + b + c, n = 30): Mw = 77000 (\pm 2000) - 1.1 (\pm 0.1) \times NO_2 \times O_3 \times UVh, R^2 = 0.66 \quad (5)$$

the paper samples, and with the reference ΔdP , was relatively small in one year. The ΔdPs of some of the paper samples were close to the detection limit and should be considered more uncertain, especially of samples 4cU, 5bU, 9cS and 9bS (Fig. 5B). The ΔdP of some paper samples were spread across a range and in some cases one measurement differed from the others. The larger inhomogeneity of the sensitive paper, than of purer less sensitive papers, may have been a reason for

DRF3 : Paper (U, a + b + c, n = 13)

$$DdP = 60 (\pm 4) + 0.254 (\pm 0.005) \times NO_2 \times O_3 \times SO_2, R^2 = 0.99 \quad (6)$$

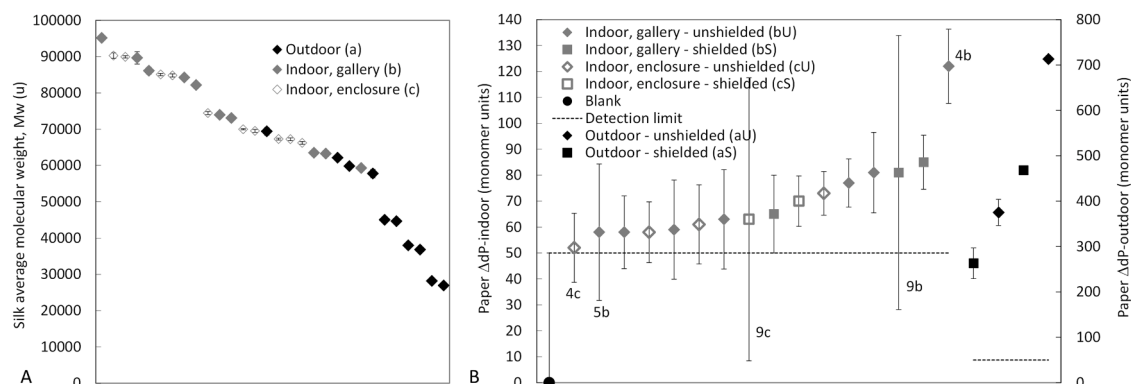


Fig. 5. Ranked values of the average molecular weight (Mw) of the silk samples after exposure, and of the change in the $\Delta dP > dl$ of the paper samples. The error bars represent the standard deviation of three replicates.

Table 2

Standardized regression coefficients and significance of the independent environmental parameters in the DRFs. nn = non-normal distribution of the residuals according to the Shapiro-Wilks test.

DRF no.	NO ₂ × O ₃ × UVh	NO ₂ × O ₃ × SO ₂	NO ₂ × O ₃	UVh	HCOOH	O ₃	SO ₂	NO ₂	RH × UVh
1 ^a			-0.83, nn,						
2 ^a	-0.81								
3 ^a		1.00							
4 ^a			1.00						
5 ^a				0.89					
6 ^b					1.15	0.56			
7 ^b							0.45	0.55	-0.52

^a A parameter significance ≥99.99 % indicated domination by clusters or outliers.

^b The parameter significance was ≥99.5 % and <99.99 % due to outliers and/or few data points (n ≤ 5).

DRF4 : Paper (S, a + b + c, n = 7)

$$: \text{DdP} = 66 (\pm 3) + 0.369 (\pm 0.007) \times \text{NO}_2 \times \text{O}_3, R^2 = 0.96 \quad (7)$$

DRF5 : Paper (U, b + c, n = 11): DdP = 57 (±2)+1.0 (±0.1)

$$\times \text{UVh}, R^2 = 0.80 \quad (8)$$

DRF5_{BW}: Paper (U, b + c, n = 11): DdP = 62 (±2)+0.007 (±0.001)

$$\times \text{BW}, R^2 = 0.80 \quad (8, \text{BW})$$

DRF6 : Paper (U, c, n = 4)

$$: \text{DdP} = 47 (\pm 2) + 0.47 (\pm 5) \times \text{HCOOH} + 1.4 (\pm 0.3) \times \text{O}_3, R^2 = 0.95 \quad (9)$$

DRF7 : Paper (S, b + c, n = 5) : DdP = 64 (±3)+2.7 (±0.8) × SO₂+2.5 (±0.2) × NO₂-0.008 (±0.002) × RH × UVh, R² = 0.93

(10)

4. Discussion

The explanation power, R², is shown for all the significant trends in this section. Trends shown without the R² were not significant.

4.1. Silk

Fig. 6 shows the regressions of DRF1 and DRF2.

Three clusters along a linear trend of lower Mw with higher environmental loads can be observed. The clustering was amplified, but the spread increased somewhat, in the regression with NO₂ × O₃ × UVh as compared to NO₂ × O₃. The regression slope was then only affected by the outdoor UVh, except slightly by the UVh in location 4b. The regressions with only the outdoor locations (a) were significant. The slight dichotomization by the clustering would have contributed to this, but less of the variation was still explained (R² = 0.57 and R² = 0.31) due to the relative increase in the spread of the data. The explanation by DRF2 indoors (b + c, Fig. 6B), depended solely on the UVh outlier 4b and was better with only UVh included as the independent variable in the regression (R² = 0.16). The indication of deterioration of the exposed silk by the indoor environment was thus only due to the assessed much higher UVh in one of the galleries, which did correspond to the effect observed outdoors. A hypothetical increase in the used multiplication

factor, of the outdoor as compared to indoor UVh exposure, from 5 to 10, gave a similarly good explanation (R² = 0.65). If assuming that the outdoor UVh exposure was on average similar as indoors, which implied a multiplication factor of 1, DRF2 was still significant, but with relatively more influence of the indoor locations, and a lower explanation power (R² = 0.46). Overall, this analysis seemed to show a possible additional, but small, significant influence on the deterioration of the outdoor exposed silk, of also other environmental factors than air

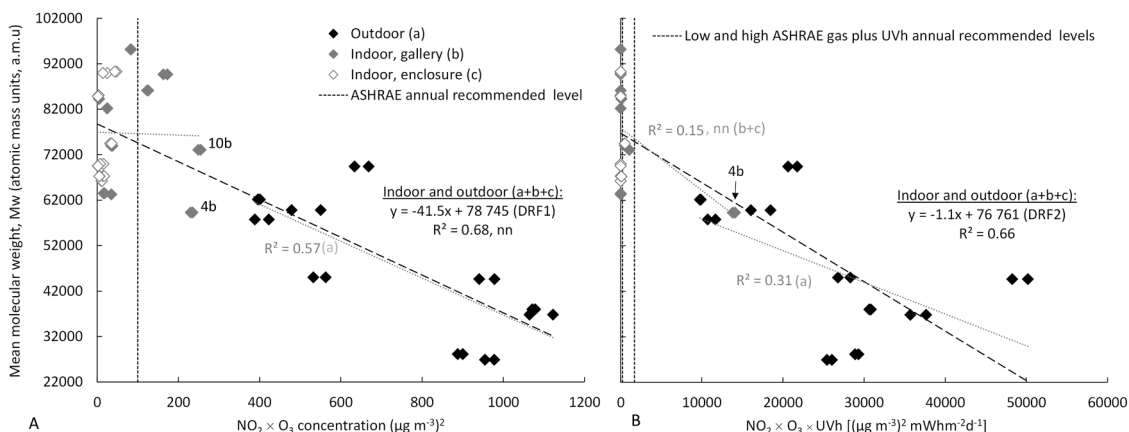


Fig. 6. Regressions of the average molecular weight (Mw) of exposed silk samples against NO₂ × O₃ (A) and NO₂ × O₃ × UVh (B).

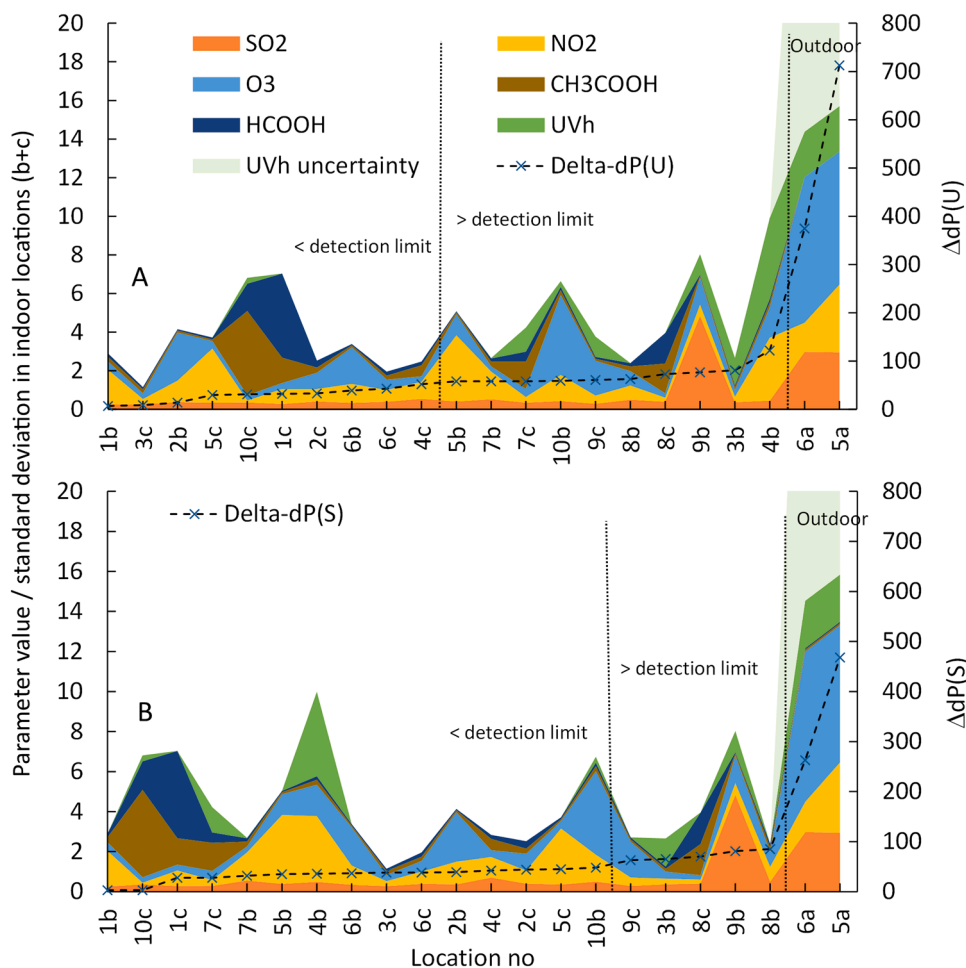


Fig. 7. Comparison of normalized values of the air pollution and UVh at the locations ranked by the ΔdP in the unshielded (A) and shielded (B) positions.

pollution (NO_2 , SO_2). We hypothesized that this might be UVh exposure that was suggested to have been approximately 5 times or higher than the average indoor UVh exposure.

No effects were found of the environments inside the enclosures on the silk Mw. Although the spread was large, the DRFs, environments, and Mws of the gallery samples (b) indicated that doses over the recommended levels would result in increasing deterioration of the silk, and that this was observed in one gallery location (10b) due to oxidation by NO_2 and O_3 , and in another gallery location (4b) also in combination with UVh. If the DRFs are linear with time over several years one would expect the Mw of silk in the equivalent indoor environments to

transgress the tolerable levels represented by the DRFs in more of the locations in a few years. If the outdoor average UVh was lower, or higher, than five times the average indoors, then the absolute value of the coefficient in DRF2 would be respectively higher (steeper) or lower (slighter). This would however not change the value of the standardized coefficient or explanation of the variation (R^2).

4.2. Paper

Fig. 7 compares the values of the air pollution, UVh, and ΔdP of the paper in all the locations where the paper was exposed. The T was not

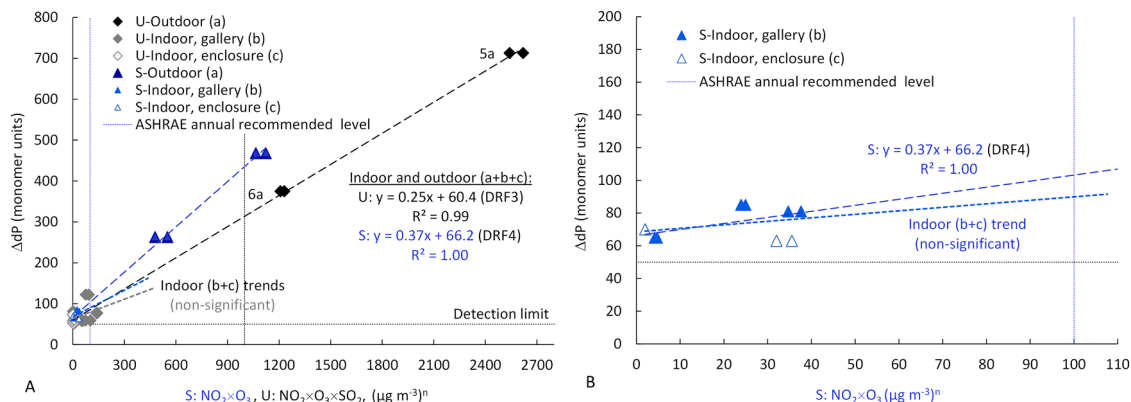


Fig. 8. The significant regressions of the unshielded (U) and shielded (S) paper in all the locations (a + b + c).

included due to its small variation between the indoor locations. The RH was not included as only a negative effect was found of RH, in one DRF. The VI was not included as only the UVh was estimated outdoors and the radiation effects that were found were due to UVh.

There was notable variation in the air pollution and UV radiation between the locations. The total pollution and UVh loads on the unshielded samples with a $\Delta dP(U) > dl$, were often higher than, or comparable to, those with a $\Delta dP < dl$. This indicated an effect from the measured environment on the ΔdP . Exceptions were locations 1c and 10c that had the highest [FoAc] and [AcAc]. The total pollution and UVh loads on the shielded samples with a $\Delta dP(S) < dl$, were more often higher than on those with a $\Delta dP > dl$. This indicated a lesser or less general effect of the environment on the ΔdP of the shielded samples. In both cases, of the unshielded and shielded samples, Fig. 7 shows a need to discuss the effects of outliers. The regression analysis of the paper ΔdP responded mainly to these outliers and then returned a high explanation (R^2) of the variation in the ΔdP . The analysis should thus mainly be considered as an outlier analysis that indicated effects of relative higher environmental doses in some locations. Fig. 8A shows the regressions of the DRFs of the unshielded and shielded paper in all the locations (a + b + c). Fig. 8B focuses on the low values of the $\Delta dP(S)$ indoors (b-c).

In the case of the unshielded samples in Fig. 8A, O_3 provided the highest single separate variable explanation with an $R^2 = 0.68$. A notable improvement, to an R^2 of 0.93 was obtained by the combination of O_3 with NO_2 , and then the smaller improvement to the $R^2 = 0.99$, observed in Fig. 8A, by again combining with SO_2 . The indoor (b + c) trends were positive but not significant. In the case of the shielded samples, the separate single effect of NO_2 explained most of the variation with an $R^2 = 0.97$. The combination with O_3 then gave the $R^2 = 0.995$. The further multiplication with SO_2 was also significant, but SO_2 did not have a separate significant effect or additive or combined effect with either NO_2 and, or O_3 . The SO_2 added minimally to the explanation in Fig. 8 and was omitted. The high explanations, of R^2 0.99 and 1, clearly depended on the inclusion of the outdoor samples (5a and 6a) and the consequent linear trend of the indoor cluster and two outdoor locations. The indoor first year $\Delta dP(U)$ s due to effect of the pollution gases were clearly tolerable, whereas the indoor $\Delta dP(S)$ were nearer the intolerable response. This somewhat surprising evaluation was due to the inclusion of SO_2 in the DRF for the $\Delta dP(U)$ s but not for the $\Delta dP(S)$ s, and much lower measured values of SO_2 than NO_2 and O_3 , compared to the recommended levels (Fig. 3). The combination of the pollutants in the DRFs were not made to be mechanistically correct, and the correlation of the concentrations of the pollutants does not show mechanistic interaction between them in the reactions with the paper. Still, this difference in the evaluation depending on the inclusion of SO_2 , seems to show the importance of possible interdependent effects of

environmental parameters, versus the comparison with recommended levels of single parameters. If the deterioration depended on the presence of several interacting pollutants, or other environmental parameters, it would not be strictly correct to assess the tolerability relative to the values of the separate pollutants—although this may be what is practically possible.

Fig. 9 shows the regressions of the DRFs of the unshielded samples in the indoor locations (b + c) only.

The explanation in this case of the responses $< dl$ (with the $\Delta dP(dl) = 50$) seemed to be that all the unshielded indoor samples (U, b + c) with a $\Delta dP < dl$ had $UVh = 0$, except location 10c (Figs. 7A and 10C) that had a low UVh like the gallery (10b, Fig. 9A). Location 10b had however the highest load of the oxidizing pollutants $NO_2 + O_3$ (Fig. 7A), and the second highest indoor temperature of all the locations. The combined $NO_2 \times O_3 \times SO_2$ parameter had a positive near significant (92.5 %) effect on the ΔdP , that mainly depended on the NO_2 (single correlation significance = 91.4 %). Location 10c had high AcAc and FoAc (Fig. 7), but the separate, additive, and combined effects of the AcAc and FoAc were negative or ~ 0 in the indoor unshielded locations.

When the high UVh outlier 4b (Fig. 9A) was removed, the UV effect was still significant, but it explained much less of the increased variation ($R^2 = 0.24$) relative to the UVh range. A separate barely significant effect was in this case also found due to the high SO_2 outlier 9b (Fig. 9B). This high $[SO_2]$ was probably explained by SO_2 emissions from a bakery chimney across the street from the sampling site. The residual distribution was, however, in this case non-normal, and the notable outliers, 3b and 8c, also showed the weakness of this explanation. Fig. 9B was still included to illustrate how the difference in the ΔdP of samples 3b and 9b, was more likely explained by the UVh (Fig. 9A). By comparison with the BW response, it was found that the assessed UVh in locations 9b and 9c may be a less certain high value outliers. A possible lower UVh in these locations would not significantly affect the positive correlation and explanation. The high ΔdP of sample 8c was probably explained by the highest [FoAc] in this enclosure (Figs. 3B and 10A). DRF5 indicated an intolerable deterioration due to UVh , especially in location 4b, but also in locations 3b and 9b, and probably due to SO_2 in location 9b before c. 2.5 years, although it seemed that the UVh exposure in this location was more critical.

Fig. 10 shows the regressions (correlations) of the DRFs of the unshielded paper in the four enclosures (c) with a $\Delta dP > dl$, and a comparison with the samples with a $\Delta dP < dl$.

The separate correlation with FoAc was strong but depended on one location with much higher concentrations (8c, Fig. 10A). The separate correlation with O_3 was weak (Fig. 10B), but the addition of O_3 to the regression notably improved the explanation of the ΔdP (Fig. 10C). This improvement was especially due to an adjustment of the prediction of

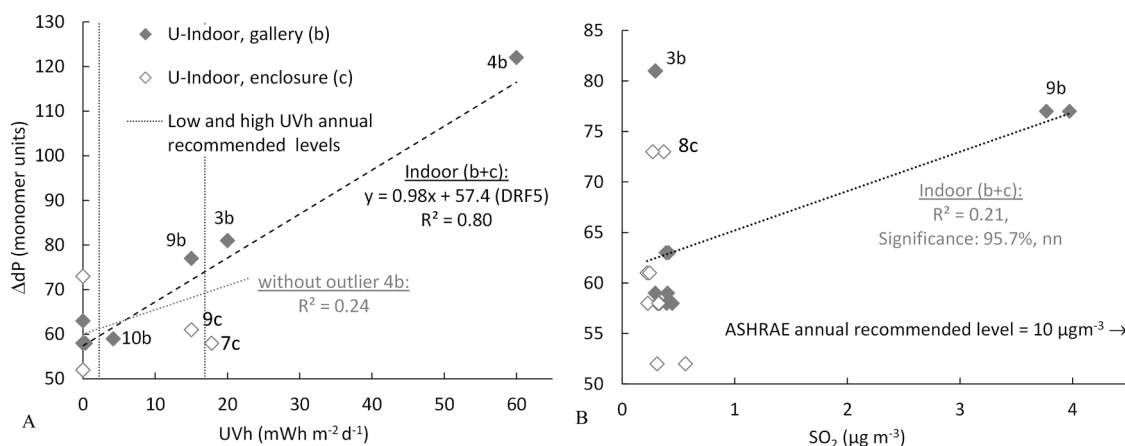


Fig. 9. The significant regressions of the unshielded paper (U) in the indoor locations (b + c) including (A) and excluding (B) the location 4b outlier. The legend of both A and B is given in A. nn = non-normal distribution of residuals.

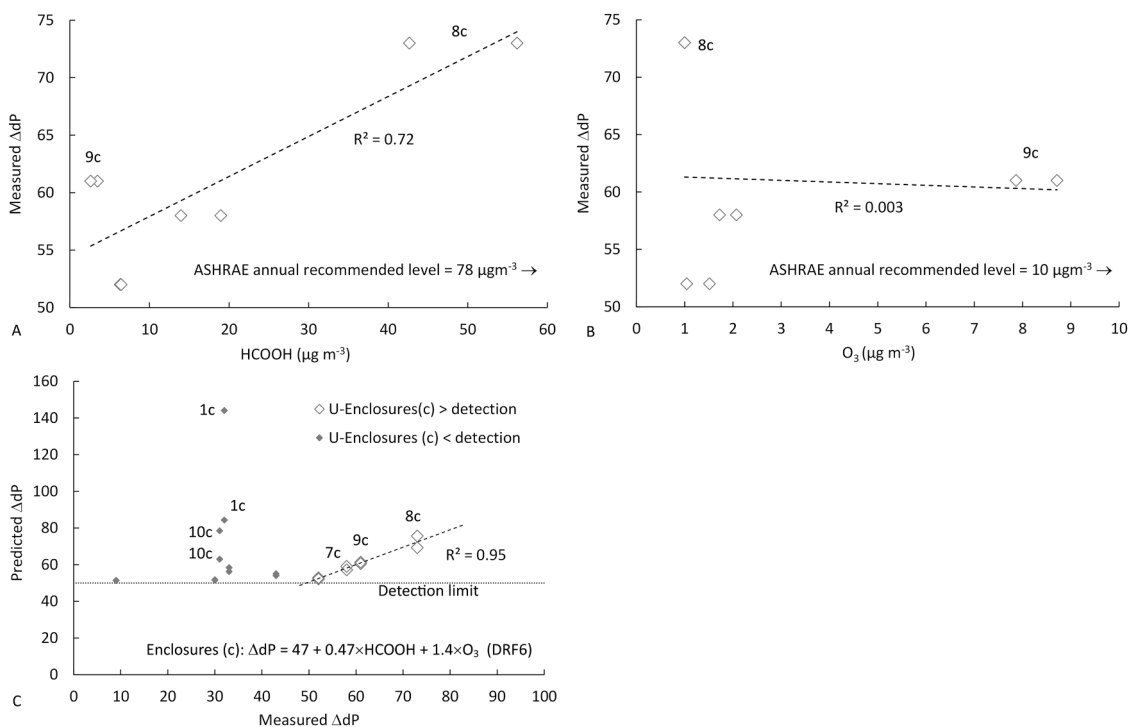


Fig. 10. The significant regressions of the unshielded paper (U) in the enclosures (c). The legend of all (A, B and C) is given in C.

the ΔdP in location 9c (Fig. 10A) by the high value of O_3 in this location (Fig. 10b).

Among the locations with a $\Delta dP < dl$ in Fig. 10, location 1c and 10c stand out with markedly higher predicted values than the other locations, due mainly to higher [FoAc] in these locations (Fig. 7). The explanation of the $\Delta dP < dl$ in location 1c was probably that it had the lowest annual RH of all the enclosures (Fig. 3B). The deposition of

pollutant gases like ozone [31], and emissions of [30] and deterioration by organic acids typically decrease [7,32] with decreasing RH. Only locations 9c, 7c, and 10c reported $UVh > 0$, with the UVh in 10c being c.25 % of that in 9c and 7c. A positive but non-significant additive effect was found of the UVh together with FoAc. The degrees of freedom in the analysis did, however, not allow a possible addition of the UVh to DRF6.

Significant negative correlations were however found in this case of

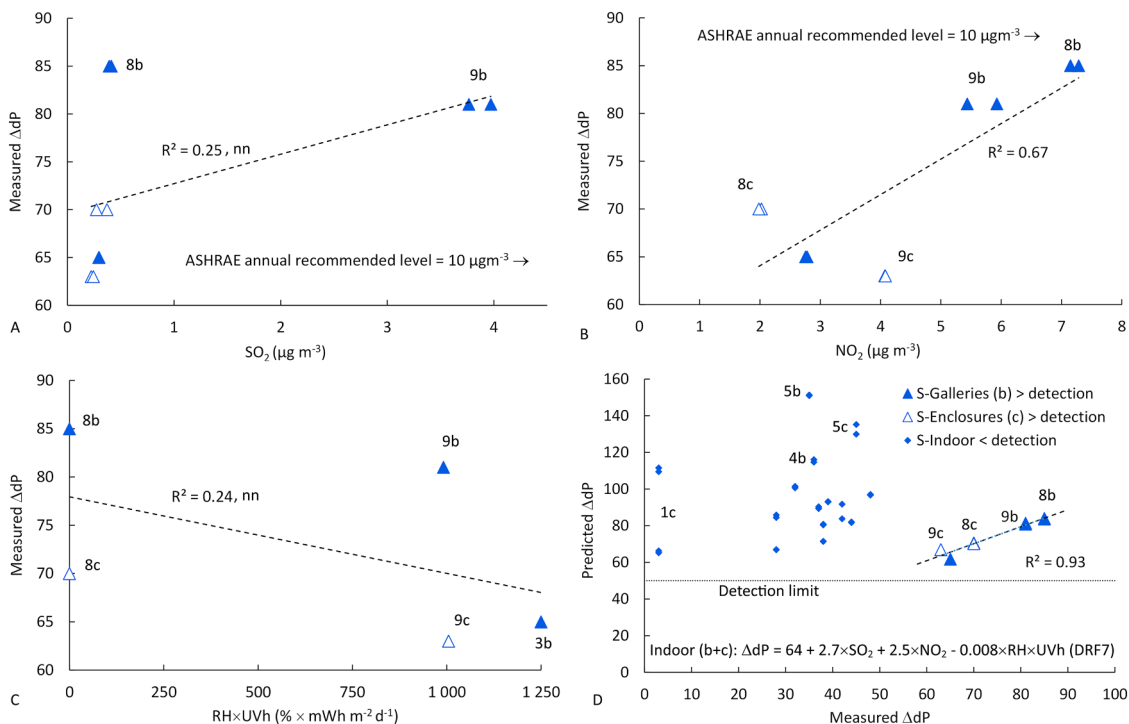


Fig. 11. The significant regressions of the shielded (S) paper in the indoor locations (b + c). The legend of all (A, B, C and D) is given in D. nn = non-normal distribution of the residuals.

the ΔdP with NO_2 alone and together with the radiation (UVh or Vlh). This effect is also not included in DRF6 (Fig. 10) as the degrees of freedom were not sufficient. It seemed also to be an indirect effect on the environment rather than a direct effect on the ΔdP . When the correlation with either UVh or Vlh was added to that of NO_2 , the negative standardized coefficient of NO_2 became more negative. The addition of NO_2 to FoAc, in DRF6, reduced the significant effect of the FoAc, whereas the addition of either of UVh or Vlh increased the significant effect of FoAc at the same time as the effects of the UVh and Vlh turned to be positive and larger (but still insignificant). The negative effect of the NO_2 , and combined with the UVh and Luxh, seemed to be due to increased ventilation of the enclosures at higher values of these parameters. The ventilation increased the $[\text{NO}_2]$ and reduced the $[\text{FoAc}]$ in the enclosures, and thus the effect of the FoAc on the ΔdP . The correlation coefficients in the enclosures (c) between the FoAc and NO_2 , UVh, and Vlh were: -0.6 , -0.12 , and -0.06 . Location 9c (Fig. 10) had a ratio of NO_2 inside to outside of the enclosure that was ~ 3 times that of the three other enclosures with a $\Delta dP > dl$, which is a strong indication of higher ventilation of this enclosure, and contribution to the observed high $[\text{O}_3]$ and low $[\text{FoAc}]$ (Fig. 10). The increased effect of FoAc with the addition of the UVh or Vlh and positive correlation of these parameters with the ΔdP when added with FoAc rather than with the NO_2 , still showed the probable/possible small effect of the UVh that was present in the enclosures in increasing the ΔdP . The observed first year effects were tolerable but would, if DRF6 was linear over longer time, become intolerable in the next year in location 9c due to the $[\text{O}_3]$ and in location 8c due to the $[\text{FoAc}]$.

Fig. 11 shows DRF7 of the regressions (correlations) of the five shielded samples with a $\Delta dP > dl$ in the indoor locations (b + c), and a comparison with the samples with a $\Delta dP < dl$.

DRF7 includes an additive correlation with SO_2 , NO_2 , and $\text{RH} \times \text{UVh}$. The NO_2 correlation was significant by itself ($R^2 = 0.66$). The additional explanation was only provided with both SO_2 and $\text{RH} \times \text{UVh}$. The addition of RH by itself, rather than $\text{RH} \times \text{UVh}$, explained more of the total variation ($R^2 = 0.98$), but the correlations with, and between, RH and UVh were significant, and DRF7 with the $\text{RH} \times \text{UVh}$ parameter is therefore reported (Fig. 11). The minor adjustments of the correlation of the ΔdP with the NO_2 , that was obtained by the addition of SO_2 and $\text{RH} \times \text{UVh}$, is illustrated in Fig. 11 by the opposite high and low values in locations 8b and 9b, of NO_2 (Fig. 11B) versus SO_2 and $\text{RH} \times \text{UVh}$ (Fig. 11A and C), and then improved explanation with all the variables included (Fig. 11D). As was explained above location 9b may be a less certain high UVh outlier, but this would not significantly affect the positive correlations or explanations here. Only two shielded samples with $\Delta dP > dl$ were located inside enclosures (8c and 9c). The ΔdP of these samples were well explained by DRF7, due to the presence of UVh, with its negative effect, in location 9c (Fig. 11c) that had double the $[\text{NO}_2]$ of that in location 8c (Fig. 11B). When the SO_2 outlier 9b was removed the remaining significant additive correlation was of NO_2 (positive) and RH (negative) with an $R^2 = 0.98$. The NO_2 and RH also provided separate significant explanations, but with lower R^2 .

It seemed, in this case of DRF7, that the presence of UVh increased the deterioration effect of the measured $[\text{NO}_2]$ by reducing a protective effect of RH, but that the UVh at the same time, oppositely via the RH, reduced the deterioration effect of the $[\text{SO}_2]$. Together, this still resulted in the negative effect of $\text{RH} \times \text{UVh}$. The reasoning behind this assessment was that: In a regression of the ΔdP with NO_2 and SO_2 , only, the standardized coefficients of both were positive (0.73 and 0.23) but that of SO_2 was insignificant. When adding RH to the regression its coefficient was negative (-0.64), that of NO_2 became smaller (0.46) and that of SO_2 larger (0.59) and significant. The RH thus seemed to decrease the effect of NO_2 and increase the effect of SO_2 . When the RH was exchanged with the combined $\text{RH} \times \text{UVh}$ parameter (DRF7) the standardized coefficient of the $\text{RH} \times \text{UVh}$ increased to -0.5 compared to that of -0.64 of only RH, the NO_2 coefficient became larger (0.55) and the SO_2 coefficient smaller (0.45). The effect was the same but stronger when the

UVh parameter was replaced with the BW parameter, resulting in this case in a small and insignificant negative $\text{RH} \times \text{UVh}$ coefficient (-0.06) and small insignificant positive SO_2 coefficient (0.22), but a larger NO_2 coefficient (0.71). It seemed thus like the UVh decreased the first mentioned effect of RH, directly and indirectly via the pollutants, by effects in the opposite direction as only the RH. This might be explained by the presence of adsorbed water on moist surfaces close to and of the paper samples, in amounts that depended on the air humidity (RH) and on the and light-radiation, and possibly on other factors that influenced the sorption rates.

There should be no direct UV exposure of the shielded samples, but the matt black mounting rack and unshielded sample fronts (Fig. 2) would be exposed. It could be hypothesized that deposition of gaseous pollutants to the moist black rack, sample holders, and other close sample surfaces, would lead to more deposition and then some depletion of the pollution gases in the air behind the shielded samples. By itself this would lead to less deterioration of the paper. However, the UV and light-radiation on these surfaces would lead to less moisture and depletion, and a reduction of this effect of the RH. UVh was significantly correlated with the Vlh in the indoor locations, and it could be expected that the visible light-radiation (Vlh) also played a role in this. The pollution concentrations that were measured on the top racks were thus often probably higher than behind the paper samples, and relatively higher in the "dark and humid" conditions with less UVh and higher RH. The diurnal humidity and temperature cycles may also have played a role.

At the same time, however, one would expect that the radiation could indirectly lead to some drying of the paper sample itself that would reduce the gaseous deposition and deterioration of the paper. The different directions in the changes of the effects of NO_2 and SO_2 on the ΔdP when including the UVh in DRF7 may indicate that the effect of NO_2 was relatively more sensitive to depletion in the air close to the shielded paper, whereas the effect of SO_2 was more sensitive to sample surface drying. This apparent difference between the NO_2 and SO_2 might be related to the reactivity of NO_2 with surface water [33] and higher water solubility of SO_2 , with a c. 2 orders of magnitude larger Henry constant than NO_2 [34,35], and possibly also to the higher concentrations of NO_2 than SO_2 (Fig. 3). The UV and light-radiation seemed thus both indirectly to increase the pollution exposure by reducing the humidity and gaseous deposition on close surfaces of the shielded paper samples, and to reduce the direct deposition of and deterioration of the shielded paper by the pollution gases, by drying the paper. As in the case of DRF6 the observed first year effect of DRF7 was tolerable, but would become intolerable in the next (NO_2) or few (SO_2) years if DRF7 was linear over longer time.

The deterioration of the paper by NO_2 , O_3 , and UVh seems to be in accordance with the results of Pastorelli et al. [8]. We did not find an

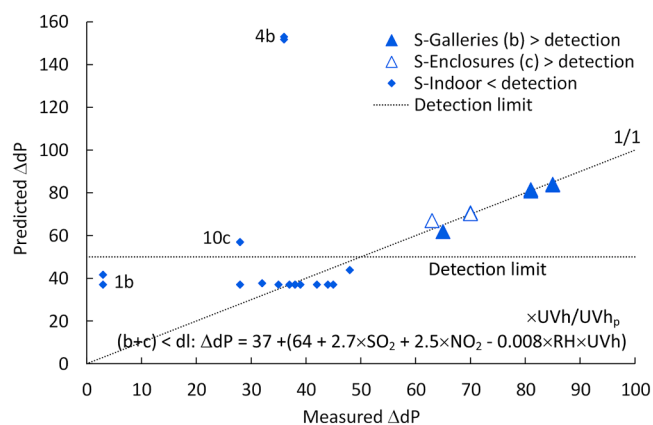


Fig. 12. Hypothesis of the prediction of the non-detection of ΔdP of shielded samples.

Table 3

Years until intolerable deterioration at linear effect according to DRFs, in galleries (b) and enclosures (c), and the fraction increased lifetime in the enclosures versus the galleries. It is generally considered that there should be no UV radiation in museums and the evaluation by lower and upper limits of UVh are only indicative.

Env. par:	$\text{NO}_2 \times \text{O}_3 \times \text{UVh}$	$\text{NO}_2 \times \text{O}_3 \times \text{SO}_2$	$\text{NO}_2 \times \text{O}_3$	UVh	HCOOH	O_3	SO_2	NO_2
DRF no	c (years) / b (years) = Fraction increased protection time in (c)							
1			6.8/1.0 = 6.8					
2	1.1–28 / 0.14–3.7 = 7.9–7.6							
3		257/18 = 14.3						
4			5.6/4.6 = 1.2					
5				1.2–2.1 / 0.16–0.27 = 7.5–7.8				
6					4.1/n.a. = n.a.	3.2/n.a. = n.a.		
7							36/6.6 = 5.5	3.3/1.9 = 1.7

effect of T, which may be due to the small indoor temperature variation, and a $T > 10$ °C in the two outdoor locations. Our analysis found, in addition, positive correlations of the paper deterioration indoors with UVh, and with FoAc and SO_2 due to high values in single locations, of $50 \mu\text{g m}^{-3}$ FoAc and $4 \mu\text{g m}^{-3}$ SO_2 . The negative effects of visible light dose and RH on the ΔdP , but antagonistic interaction between them, that was reported in the work of Pastorelli et al., may be for the same reason as that of UVh and RH on the shielded paper ΔdP suggested above.

Fig. 11 also showed that DRF7 predicted a higher than measured ΔdP of all the samples with $\Delta dP(S) < \text{dl}$. All except four of these locations had UVh = 0, and thus $\text{RH} \times \text{UVh} = 0$, and many of them had higher values of, especially, NO_2 than in the locations with a $\Delta dP > \text{dl}$ (Fig. 7). One would expect that the suggested effect of the UVh on the surface moisture, and then on the effects of the measured air pollution concentrations on the ΔdP , varied depending on location specific conditions. Still, a consideration of this tendency, and that 2/3 of the locations with a $\Delta dP < \text{dl}$ had UVh = 0, suggest that the pollution effect on these samples were less than predicted by DRF7. A simple hypothesis would then be that the $\Delta dP < \text{dl}$ could be predicted by multiplying DRF7 with the fraction of UVh in each location to a value of UVh_p where the pollution effect predicted by DRF7 would be present. Fig. 12 shows this prediction of the ΔdP , with the measured $\Delta dP < \text{dl}$ set equal to the median of $\Delta dP = 37$, and the UVh_p set equal to the highest UVh measured/estimated in the locations with a $\Delta dP < \text{dl}$, of $60 \text{ mWhm}^2 \text{ d}^{-1}$ (location 4b, Figs. 9A, 11). The inclusion or exclusion of the SO_2 term in DRF7 had a negligible effect on this assessment.

The prediction in Fig. 12 is clearly better than in Fig. 11D. Samples 4b, 10c and 1b are notable outliers. Location 4b had a much higher UVh than the other locations, location 10c had the highest UVh and some UVh, and location 1b had the lowest RH, of 34 %, of all the locations (Figs. 3 and 7). It may be that sample surface drying in these situations resulted in less deterioration of the paper despite the, possible, effect of reduced gaseous depletion by reduced humidity on surfaces close to the paper samples. In summary: it seemed that some radiation decreased the air pollution effect by drying close surfaces to the shielded paper samples, whereas more radiation or a very dry atmosphere reduced the pollution effect by also drying the sample surfaces.

Table 3 gives the years until intolerable deterioration of the silk and paper for the average of the indoor and enclosure locations, by the parameters in DRF1 to DRF7, according to the referenced recommended levels in Section 2.4. Linear effects were then assumed down to low indoor concentrations and to higher ΔdP than those measured in one year.

Table 3 shows that intolerable deterioration would probably happen before 7 years on average in the enclosures. This would be so except in the case of a combined pollution effect with low observed concentrations of SO_2 (DRF3), in which case the deterioration might be much slower. If considering only the observations inside the enclosures (DRF6), it would take 3–4 years for intolerable deterioration (ΔdP) to occur. The average increased protection in the enclosures compared with the galleries was 7 times for the silk (DRF1 and DRF2) and 6 times for the paper (DRF3–DRF5 and DRF7). The exposure locations in this work included a range of different modern and traditional showcases, and some special enclosures, that might realistically represent enclosures in use in Europe in 2004–2005, and possibly also today.

5. Uncertainty

The validity of linear regression analysis and its significance depends on presumptions of random scattering of the residuals around the regression prediction that do not vary depending on the value of x, that is non-homoscedastic, and are normally distributed. In addition, there should be absence of multicollinearity, outliers, linear relationships between the residuals and predictions that indicate missing explanatory variables, or curvilinearity in the residuals that indicate a better fit of a different non-linear model [36]. The residuals of the silk DRF1 and DRF2 (Fig. 6) were mainly meeting these presumptions, but showed a tendency to cluster in three areas that was accentuated to resemble correlation with three points in paper DRF3 and DRF4. Still, the spread and linearity between these clusters (silk) and points (paper) were good, showing high correlation and indicating strong effects. The remaining DRFs (5 to 7) should be considered outlier analysis or multiple parameter correlations with few data points. These correlations were all meeting the criteria of the degrees of freedom > 1 , implying that the number of data points were higher than the number independent variables plus one. These reported correlations/effects of few data points were significant and the most explaining ones among very many possible, usually insignificant correlations, and were thus clearly describing notable interdependencies in the data. Generalizations of these effects and their magnitudes from the few data points seem, however, uncertain.

6. Conclusion

Silk exposed during one year in external locations of ten European museums were notably more deteriorated than silk exposed in galleries

or enclosures. The five most deteriorated silk samples were exposed outdoors at urban locations. The indoors compared to outdoors deterioration of the silk correlated significantly with the differences in the outdoor and indoor environmental loads. The deterioration indoors was notably higher in one gallery location with higher environmental loads. 70 % of the observed reduction in the molecular weight of the indoors and outdoors exposed silk was explained by the combined exposure to NO₂ and O₃, and alternatively also in combination of these two pollutants with UVh.

The deterioration of unshielded paper was explained by a combination of the exposure to NO₂, O₃ and SO₂, and of shielded samples to NO₂ and O₃. The variation in the deterioration of the unshielded paper in only the indoor locations was due to differences in the exposure to UV radiation. Inside four enclosures the deterioration correlated with the exposure to FoAc and O₃. The deterioration of five indoors shielded samples correlated with the exposure to NO₂ and SO₂. An additional negative correlation was in this case found with the combination of RH and UVh. This was interpreted as an effect of pollution depletion by moist surfaces close to the samples, and drying of these close sample surfaces, and indirectly also of the sample surfaces themselves, by exposure to light and UV radiation. Due to the few samples, the large triplicate variation, and special shielding situation of the paper, one should be cautious in generalizing the DRFs beyond these experiments.

The result clearly showed outdoor deterioration of silk and sensitive paper by photo-oxidation, by NO₂, O₃ and UVh, and possibly acidic effects of NO₂. This deterioration of paper was in accordance with the results of Pastorelli et al. [8] In addition, the indoor deterioration of the paper correlated with the doses UVh, O₃, and/or NO₂, and also with SO₂ at a concentration of 4 µgm⁻³ and with FoAc at a concentration of 50 µgm⁻³. Close shielding was found to influence the environmental exposure by quite complex interactions between RH, probably T, the light and UV radiation, and the air pollutants. If the linear deterioration that was observed in one year outdoors, and in the galleries, also happened at lower doses and longer times in the enclosures, then the lifetime to intolerable deterioration of the paper and silk would be 6–7 times longer in the enclosures than in the galleries.

CRedit authorship contribution statement

Terje Grøntoft: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Kathryn Hallett:** Writing – review & editing, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation. **Nigel Blades:** Writing – review & editing, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

The average replica and variation data are available in the appendix of the paper

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Appendix

Table A.1

The radiation data reported from the MASTER indoor locations.

Site	Average measured radiation level at 12.00 noon from 1st March to 31st may 2004.		Type of lighting. A = Artificial, N = Natural = N, A + N = Mixed (if one is less contributing it is put in brackets)	Typical daily hours of artificial lighting. N.a. = Not available.
	Lux	UV (mW/m ²)		
Galleries (b)				
1	2	0	A	11.00–15.00
2	0.4	0	A	11.00–15.00
3	200	5	N	0
4	116.9	15	N.a.	N.a. Assessed to 4h
5	21.1	0	A	10.00–18.00
6	6.47	0	A + N	4.5 h
7	16.26	0.09	A+(N)	3–4 h
8	12.33	0	A + N	1–2 h
9	22.5	3	A	10.00–15.00
10	141.3	0.7	A	All day
Enclosures (C)				
1	16	0	A	11.00–15.00
2	3.4	0	A	11.00–15.00
3	5	0	N	None
4	0	0	N	0
5	17.7	0	A	10.00–18.00
6	25.82	0	A + (N)	4.5 h
7	40.01	4.75	A + (N)	3–4
8	16.69	0	A + N	1–2
9	22.5	3	A	10.00–15.00
10	141.3	0.7	A	All day

Table A.2

Silk post exposure Mw values. Mean of three replicas. SD = standard deviation.

Site	Outdoor (a)	±SD	Gallery (b)	±SD	Enclosure (c)	±SD
1	26,915	491	63,285	365	66,228	387
2	62,145	453	86,112	931	89,950	323
3	57,765	1169	84,247	171	85,073	329
4	37,991	752	59,281	397	69,982	173
5	36,810	238	89,666	1695	90,280	775
6	59,819	519	95,161	232	67,286	260
7	28,152	4	63,499	314	67,245	399
8	69,410	1053	82,181	476	84,824	406
9	45,024	464	73,966	882	74,455	406
10	44,647	255	73,071	638	69,543	386

Table A.3

Paper ΔdP values. Mean of three replicas. Bold figures are values above the 1-sigma detection limit. The variation (\pm) is given as $[(SD_m)^2 + (SD_r)^2]^{0.5}$, where SD_m and SD_r are the sample standard deviations of the three replicas of the exposed paper samples at the locations and reference paper samples.

Site	Outdoor unshielded (aU)	Outdoor shielded (aS)	Gallery unshielded (bU)	Gallery shielded (bS)	Enclosure unshielded (cU)	Enclosure shielded (cS)
1			7 ± 15	3 ± 11	32 ± 10	28 ± 7
2			14 ± 6	39 ± 9	33 ± 12	44 ± 15
3			81 ± 16	65 ± 15	9 ± 9	38 ± 9
4			122 ± 14	36 ± 22	52 ± 13	42 ± 8
5	713 ± 6	468 ± 34	58 ± 26	35 ± 5	30 ± 8	45 ± 8
6	375 ± 12	263 ± 4	39 ± 6	37 ± 25	43 ± 20	38 ± 11
7			58 ± 14	32 ± 12	58 ± 12	28 ± 11
8			63 ± 19	85 ± 10	73 ± 8	70 ± 10
9			77 ± 9	81 ± 53	61 ± 15	63 ± 55
10			59 ± 19	48 ± 20	31 ± 17	3 ± 14

Table A.4

Blue Wool (BW) cumulative exposure values (kLux h^{-1}) at the locations. Bold figures are locations with a $\Delta dp > dl$ of the unshielded and in some cases shielded paper.

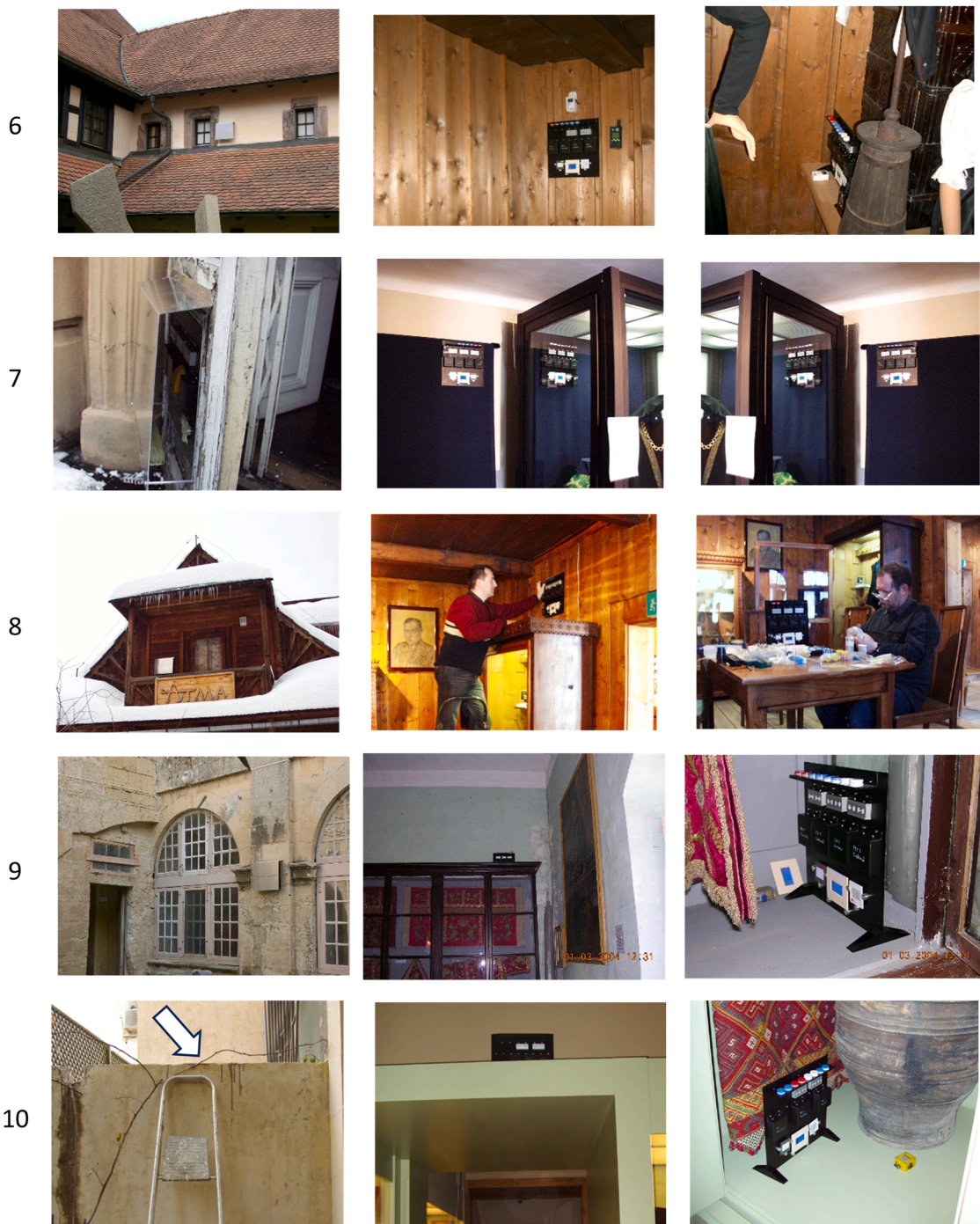
Station	Location. b = gallery, c = enclosure	Cumulative exposure (kLuxh)
1	b	25
	c	25
2	b	8
	c	9
3	b	800
	c	20
4	b	8500
	c	18
5	b	160
	c	320
6	b	45
	c	380
7	b	330
	c	900
8	b	290
	c	80
9	b	40
	c	35
10	b	30
	c	100

Table A.5
Location photographs.

Site	Outdoor (a)	Gallery (b)	Enclosure (c)
1			
2			
3			
4			
4 Oct.			
5			

(continued on next page)

Table A.5 (continued)



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