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PREVENTIVE CONSERVATION OF CULTURAL HERITAGE

CONSERVAÇÃO PREVENTIVA DO PATRIMÔNIO CULTURAL

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ABSTRACT

Preventive conservation implies, amongst many other aspects, the characterization of the atmospheric environment around monuments or cultural heritage (CH) items, with the intention to improve the conditions and to contribute to the preservation. We have, over the last two decades, intensively used various forms of X-ray spectrometry and automated electron probe X-ray microanalysis, always together with ion chromatography, micro Raman analysis, on-line soot determinations, gravimetry, etc., to identify particle types and their sources in indoor environments, including museums, while also gaseous indoor pollutants were assessed. The cases studies outlined in the present paper concern the Wawel Castle, in Cracow, Poland, the Alhambra complex in Granada, Spain, and the Plantin-Moretus Printing Museum in Antwerp, Belgium. Some questions that are presently far from having been solved pertain to the deposition processes from the atmosphere to the CH items and the critical surface interactions that take place on the CH items.

Keywords: Preventive conservation, Cultural Heritage, X-ray spectrometry.

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RESUMO

Conservação preventiva implica, entre diversos outros aspectos, a caracterização do ambiente atmosférico ao redor de monumentos ou objetos de patrimônio cultural (PC), com a intenção de melhorar as condições e contribuir para a preservação. Nós temos, nas últimas duas décadas, utilizado várias formas de espectrometria de raios-x e sondas eletrônicas automatizadas com microanálise de raios-x, sempre em conjunto com a cromatografia iônica, análise micro Raman, detecção on-line de fuligem, gravimetria, etc., para identificar os tipos de partículas e suas fontes em ambientes internos, incluindo museus, onde também foram encontrados gases poluentes. Os estudos de caso do presente trabalho estão relacionados ao Castelo Wawel, na Cracóvia, Polônia, o Complexo Alhambra em Granada, Espanha e no Museu Plantin-Moretus na Antuérpia, Bélgica. Algumas questões aqui apresentadas que ainda estão longe de terem sido solucionadas, remetem aos processos de deposição da atmosfera para os itens do PC e as interações superficiais críticas que ocorrem nos objetos do PC.

Palavras-chave: Conservação preventiva, Patrimônio Cultural, Espectrometria de raios-x.

CONTEXT

Studying the environmental conditions (micro-climate, microbiology and chemical pollution) around a work of art, with the intention to improve them and to extend the object's lifetime, is one of the aspects of "preventive conservation". The idea of preventive conservation is, of course, much wider and it is defined by the AIC (American Institute for Conservation of Historical and Artistic Works) as: "The mitigation of deterioration and damage to cultural property through the formulation and implementation of policies and procedures for the following: appropriate environmental conditions; handling and maintenance procedures for storage, exhibition, packing, transport, and use; integrated pest management;

emergency preparedness and response; and reformatting/duplication" . This paper will only focus on the environmental (air pollution) aspects.

One of the first thorough studies regarding the effects of air pollution on historical buildings was performed at the Taj Mahal, in Agra, India, in the early 1970s. The marble of the Taj Mahal was found to react with SO_2, forming a crusted layer on top of this shining white stone. The same phenomenon was observed at many other buildings and statues in Europe. Today, this effect has been studied thoroughly, and a consensus has been reached regarding its mechanisms. Atmospheric SO_2 (mainly from S impurities in fossil fuels) transforms calcite ($CaCO_3$), the main mineral in marble, limestone and sandstone, into gypsum ($CaSO_4.2H_2O$). Compared to calcite, gypsum has a higher porosity and water-solubility. Consequently, the top-layer of the gypsum is washed away more easily by run-off rainwater, and, at sites protected from rainwater, the gypsum absorbs soot (emitted mainly from diesel cars) and atmospheric water vapour, resulting in a blackened crust which is more prone to frost damage in winter. In most developed countries, the atmospheric levels of SO_2 have been reduced significantly in the last three decades, e.g., by more than 60% in the European Union from 1980 to 2000 and by over 80% in Belgium. Therefore, in developed countries, the SO_2 attack on calcite bearing stones is considered to be a lesser problem. Nowadays, in Europe, the effect of SO_2 on buildings is no longer studied in terms of chemistry and physics, because the related processes of deterioration are rather well known, but rather in terms of aesthetics, public awareness and public acceptance, i.e. chemistry and physics studies are replaced by sociologic and economic concerns nowadays.

On the other hand, concentrations of other gaseous pollutants, like NO_x and O_3, have not been reduced so much in the meantime, nor those of natural and pollution particles. At present, preventive conservation in the context of air pollution is mostly concerned with particulate pollution, both in the outdoor and indoor environment. Also at the Taj Mahal, SO_2 and NO_x levels are acceptable nowadays; however, dust concentrations remain very high there, especially in the dry season.

Analytical chemistry plays an important role in cultural heritage (CH) research.[3] In view of its non-destructive nature, X-ray spectrometry (XRS) is one of the most relevant analytical techniques in the field of conservation. For the past decades, it has also been the primary technique for determining the inorganic composition of atmospheric aerosols. Bulk aerosols and individual aerosol particles are often studied with X-ray fluorescence (XRF) spectrometry and electron probe X-ray microanalysis (EPXMA), respectively. Aerosol loaded filters are ideal targets (e.g. thin, homogeneous) and XRS does not require the dissolution of aerosols of low solubility (e.g., silicates, oxides of transition metals), This is in contrast to the more popular and wide-spread atomic absorption spectrometry and inductively-coupled plasma atomic emission spectrometry and mass spectrometry, where the loaded filters have to be dissolved completely often in strong acids prior analysis.

Conservation and preservation of our CH is a main challenge in the European Union. Within the research group "Environmental Analysis" (University of Antwerp, Belgium) the effects of the indoor/outdoor environment on the cultural artefacts have been investigated extensively in the past. Some illustrative case studies are discussed in the present work.

SAMPLING AND ANALYSIS OF ATMOSPHERIC AEROSOLS AND RELEVANT GASEOUS POLLUTANTS

For characterizing indoor atmospheric particles and their sources, a wide set of (micro-) analytical techniques are applied: ion chromatography (IC) for the analysis of ionic species, gas chromatography coupled to mass spectrometry (GC-MS) for organics, aethalometry for the monitoring of soot, gravimetry for determining the total aerosol mass in the air, XRF for elemental analysis and EPXMA for individual micro-particle characterization.

The sampling of gaseous air pollutants for periods up to one week was performed with Radiello® passive samplers (Fondazione Salvatore Maugeri, Padova, Italy). For long-term gaseous sampling, passive samplers from Gradko International Ltd. (Winchester, England) were selected. The exposed NO_2 and SO_2 samplers were leached with ultra-pure Milli-Q water, and then the leachates were analysed for nitrite, sulphite and sulphate, with a DX-120 ion chromatograph equipped with an AS50 autosampler (Dionex, Sunnyvale, CA, USA). Ozone concentrations were obtained by a colorimetric method as recommended by Radiello.

Particulate matter (PM) was sampled totally on Nuclepore filters by means of a Sartorius (Göttingen, Germany) polycarbonate filter holder, fitted with a tube (18 cm long, 6 cm diameter) to ensure homogeneous deposition of aerosols. MS&T™ samplers (Air Diagnostics and Engineering Inc., Harrison, ME, USA) were used to collect size-segregated aerosol fractions with an equivalent aerodynamic diameter below 1 µm (PM_1), 2.5 µm ($PM_{2.5}$) and 10 µm (PM_{10}) on Teflon membrane filters (TK15-G3M 37 mm, Pall, Ann Arbor, MI, USA). The vacuum pumps for PM_1, $PM_{2.5}$ and PM_{10} sampling (Air Diagnostics and Engineering Inc.) were operated at flow-rates of 23, 10 and 10 L min^{-1}, respectively, which was checked daily with a calibrated rotameter. Total sampled air volumes were registered with standard gas-flow meters. In order to determine the aerosol mass concentrations in air, filters were conditioned and weighed at a constant temperature and relative humidity (20 ± 1 °C; 50 ± 5% RH) before and after sampling. Up to 20 elements were determined in the aerosol filter deposits by XRF analysis. An Epsilon-5 high-energy energy-dispersive XRF spectrometer from PANalytical (Almelo, The Netherlands) was used. The spectrometer has a powerful X-ray tube, 3D polarizing geometry, up to 15 secondary targets and a high-resolution HPGe-detector, which provide more favourable detection limits. MicroMatter Co. standards were used for calibration of spectrometer. These standards are thin (Mylar) film standards of elements prepared by vacuum deposition resulting in a highly uniform layer. A check of the calibration was made by analysing the standard CRM 2783 from NIST.

Size segregated sampling for eventual individual particle analysis was performed using a Berner or May type cascade impactor. Particles were collected on Si or Ag substrates. The size-segregated samples were analysed by means of a JEOL 733 electron probe micro-analyser equipped with a super-atmospheric thin-window energy-dispersive X-ray detector under the control of homemade software. This setup allows the analysis of low-Z elements, like carbon, nitrogen and oxygen, which are required for -rough- chemical speciation at the single particle level. About 100 and 300 particles were analysed in the manual (fine particles) and automatic mode (coarse particles), respectively. To avoid beam damage, the sample holder was continuously cooled by liquid nitrogen. The X-ray spectra were evaluated by a non-linear least squares fitting program. The semi-quantitative elemental composition in the particles was calculated with an iterative approximation method based on Monte Carlo simulations.[4] In the next step, the particles were classified by means of hierarchical cluster analysis (HCA), based on the elemental data obtained by the low-Z EPXMA. The HCA was performed using the Integrated Data Analysis System (IDAS) program.[5] All analysed particles were divided into different clusters (i.e. particle types) according to their elemental similarity, followed by the calculation of the average elemental weight concentrations, average diameters and relative abundances (%) of each particle type. Particles on the different impactor stages were all treated independently.

THREE ILLUSTRATIVE CASE STUDIES ON AIR POLLUTION IN EUROPEAN MUSEUMS

The Wawel Castle Museum in Cracow, Poland[6,7,8]

The Wawel Castle Museum in Cracow is a precious historical monument, well known for its Flemish tapestries and other priceless artworks from the whole world. In 1978, it was placed on the UNESCO List of the World's Cultural and Natural Heritage. This museum is open in summer and winter time, but most visitors are recorded in summer. The number of tourists has increased significantly in the last decades. Every year, nearly one million tourists visit the museum. Therefore, the indoor air quality should be monitored because such an intensive tourism flow is potentially dangerous for the CH objects present in the museum. It has been observed in the museum that some tapestries were getting stained recently by indoor pollutants. The influence of tourism on microclimate perturbations and indoor pollution was investigated. Samples of the PM and gaseous matter were collected inside and outside the Museum of the Castle, in winter and summer, and in different rooms at different floors.

Figure 1 illustrates the ratio of relative abundances of the particle types for days with and without tourists (the museum is closed on Mondays). The particles were analysed with EPXMA. A T/NT ratio (i.e. concentration ratio for days with tourists (T) and days without tourists (NT) when the museum is closed) of 1 means that there is no influence of the visitors. The ratio of the low-Z element particle abundances is independent of the presence of visitors, in both seasons and floors. Mostly carbon-rich compounds and soot were found in this low-Z fraction:

these enhance the potential threat regarding CH protection. Micro-Raman spectroscopy confirmed the presence of soot particles, in addition to $(NH_4)_2SO_4$, being a natural global background aerosol. It can be assumed that outdoor pollution is the main source of particles indoors. The very fine particle fraction can easily be transported indoors by air exchange through leaks in windows and doors. Therefore, based on this chemical analysis, a preventive conservation measure is to seal windows and doors with silicones to prevent the entering of soot particles. Knowing that these soot particles are released by diesel cars, an additional measure is to prevent car traffic in the neighbourhood of the museum.

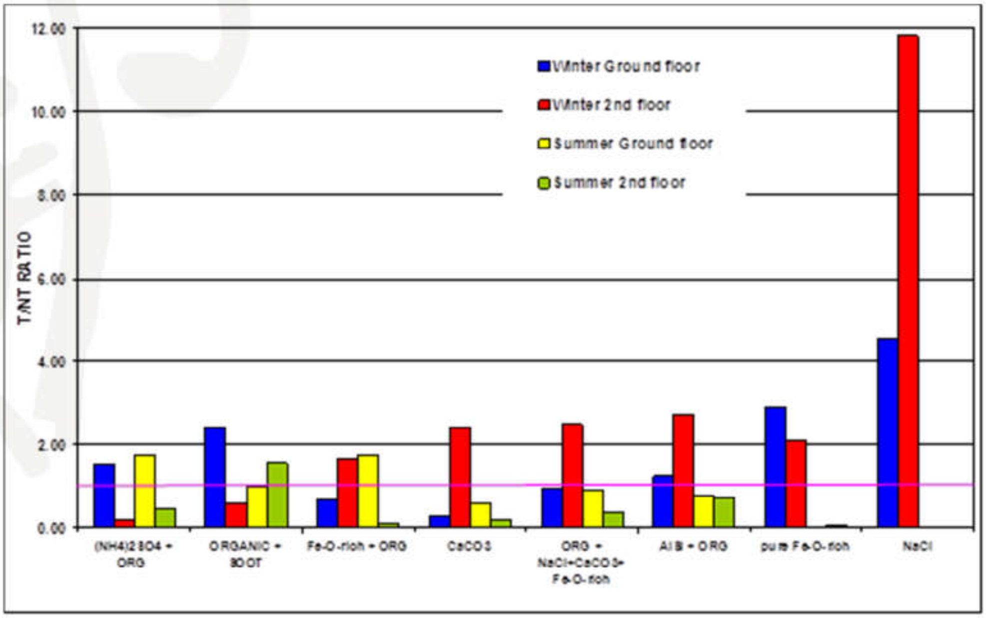

Figure 1: Ratios of the percentage of the individual particle types, for days with tourists to days without tourists, i.e. Mondays (T/NT) in the coarse PM fraction for the Wawel Castle, Cracow, Poland. A ratio of one implies that the visitors have no influence.

The elemental concentrations were determined by XRF (not shown). For Cl, a remarkable situation was observed. The T/NT-ratio was near 1 in summer, while in wintertime the airborne concentration of this element is much higher (ca. 20 times). Based on Figure 1, the same observation can be made. It appears that Cl is present as pure NaCl (although Cracow is over 500 km away from the sea) and NaCl conglomerates with Ca- and Fe-rich compounds. Probably, NaCl is brought in the museum by visitors due to street de-icing in winter. Therefore, it was advised to avoid de-icing with salt nearby the museum and to de-ice manually by using shovels instead.

The Alhambra Monument in Granada, Spain[9, 10, 11]

Every year, two million people visit the world-famous Alhambra monument in the South of Spain, listed as UNESCO world cultural heritage since 1984. The monument represents the most important and beautiful example of Islamic art and architecture from the Middle Ages in Europe. Granada city is situated in a natural basin, surrounded by mountains with altitudes up to 3500 m, about 50 km from the Mediterranean Sea. Due to this topography and the prevailing low wind speeds, in combination with traffic emissions, pollution-derived PM often accumulates in the urban air of Granada. Although it is closed for traffic, taxis are allowed to enter the monument. Public transport buses are scheduled every 10-15 minutes to shuttle the visitors between the city centre and the monument. The composition, sources and potential risks from atmospheric aerosols for conservation were investigated at the Alhambra monument, in a close cooperation with the research group of Carolina Cardell in the Department of Mineralogy and Petrology of the University of Granada.

The palaces at the Alhambra monument were originally built to maximally integrate the surrounding nature and environment and to provide a refreshment shelter from the hot and dry summer climate of Granada. The rooms of the Nasrid palaces consist of high, arch-like entries and many opened windows. Consequently, the indoor concentrations of PM_1 and PM_{10} were observed to be fairly high, and following closely the variations in outdoor air quality. The PM_{101} aerosols were mainly composed of soil dust, rich in calcite, dolomite and silicates, and containing considerable amounts of aged sea salts, especially $NaNO_3$. Indeed, it was found by single-particle analysis that sea-salt derived particles that all contain Na, were no longer NaCl in Granada, neither were they Na_2SO_4 after reaction with SO_2, but nearly all $NaNO_3$, after reaction with NO_x from traffic, on their way between the sea and the monument. $NaNO_3$ is very aggressive and more hygroscopic than NaCl; its hygroscopicity properties depend very much on the impurities present. The carbonate-rich soil originated mainly from suspension of local soil. However, also North African dust contributed to the mineral aerosol content in summer; during periods of up to a week, the local PM concentration could rise to nearly 100 µg/m³ in these periods. Although Sahara dust is chemically not very aggressive, some –unavoidable- erosion effects will result anyway. In the non-industrialized area of Granada, vehicular traffic was found to be the main source of PM_1, consisting mainly of ammonium sulphates and nitrates (the latter only during winter, because in the warm summer, ammonium nitrate will decompose more into gaseous ammonia and nitric acid) and black carbon (BC) or soot. Heavy metals were found to originate from diesel exhaust (V and Ni) and tire tread emissions (Cu, Cr, Pb and Zn).

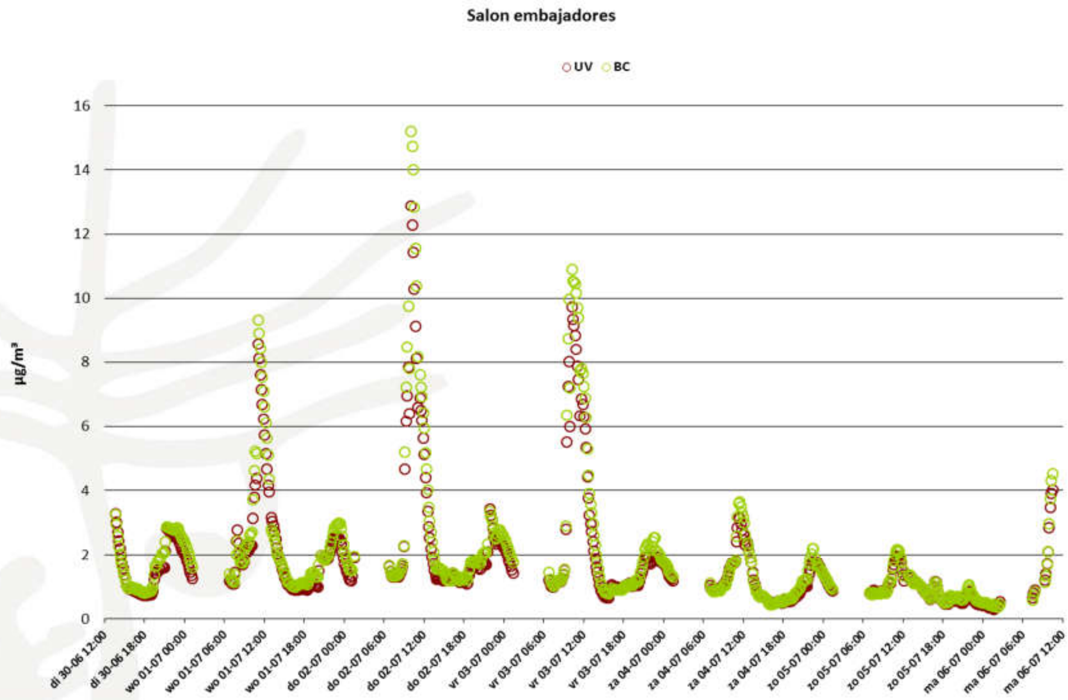

Figure 2: Concentration trends of black carbon (BC) and UV-absorbing aerosols (UV) recorded during summer inside the Nasrid palaces, The Alhambra, Granada, Spain.

Figure 2 shows a time series for the BC concentration recorded during summer inside the Nasrid palaces. In Granada, BC is expected to be mainly produced by vehicular emissions and could therefore be used to monitor the impact of car (diesel) exhaust on the Nasrid palaces. Daily BC concentrations accounted for about 19-40% of the total PM_1 fraction by mass. The highest concentrations are found on working days during morning traffic jams; however, concentrations also peaked at the beginning of the evening hours (especially in the weekends) when the life in the city is boosted after a long and warm summer day.

Although the Alhambra brings prosperity and economic benefits to the Granada region, it should also be protected from the pressure of mass tourism. Recently, the municipality government planned to help tourists with getting more easily to the monument, by allowing cars to drive through the "Gate of the Pomegranates" and the Alhambra park. At present, the BC concentration close to the Gate of the Pomegranates is around an average of 2 $\mu g\ m^{-3}$. However, when the street is opened for traffic in the future, the BC concentration is expected to rise up to 8 $\mu g\ m^{-3}$ or even higher, as found at a similarly steep street with dense traffic. This is well above the 2-3 $\mu g/m^3$ level, which is generally considered as acceptable near monuments. Such decisions could have a considerable impact on the levels of BC and other vehicle derived pollutants inside the Nasrid palaces, with major implications for their future conservation and the enjoyment of visitors to this famous monument.

The Plantin-Moretus printing museum in Antwerp, Belgium[12, 13]

Christopher Plantin (1520–1589) was the greatest printer-publisher of the second half of the 16th century and the museum is his printing plant and publishing house. In 1877, both the living quarters and the printing offices were opened to public. Today, one can visit the fascinating 16th and 17th century printing workshop, the letter foundry, the corrector's room and the bookshop, the library (more than 25,000 volumes from before 1800) and the office, all still in their original state. The collection contains more than 600 manuscripts from the 9th to the 16th century, including many atlases and bibles and 154 incunabula (such as the 36-line Bible from Gutenberg, made in 1461 at the latest), etc. Because the building is a historic monument, not originally built as a museum, right in the busy centre of the city, it is not easy to maintain good environmental conditions. The premises consist of a series of original houses and buildings connected to each other, with a central, late 16th century, enclosed garden/courtyard in the middle. Several doors open onto this garden and the visitor steps out from the rooms directly into the open air (and vice versa).

The recent research in the Plantin Moretus Museum focuses on the indoor air quality assessment in terms of seasonal changes of outdoor pollution levels. The main task was to characterize the most threatening air pollutants and to determine whether the show cases are protective enough. The conclusions made hereafter from these studies will be used in the future to ameliorate the way the collection will be presented to the public. For preventive conservation purposes, it is important to avoid noxious air pollutants indoors. The considered gases were SO_2, NO_2 and O_3. The concentrations of the gases were generally found to be the highest outside the museum, lower in the rooms and the lowest in the showcases, during all seasons. PM was differentiated into two fractions of bulk particulate matter ($PM_{2.5}$ and PM_{10}) and size segregated single particles. The indoor reduction of the coarse fraction of PM (cut-off diameter between 2.5 and 10 μm) indoors was higher in comparison to the fine fraction (cut-off diameter below 2.5 μm).

The Indoor/Outdoor ratio values are shown in Fig. 3. In case of aluminosilicates and calcites, an accumulation process of fine particles was observed, but only in the autumn and winter period. Sulphur-rich particles, potentially harmful for CH objects, were mainly associated with the fine fraction (more than 88% by mass) in both the indoor and outdoor environment. Since fine particles penetrate more easily to the indoor environment, indoor sulphur concentrations were found to be comparable to those in ambient air. Carbon-rich particles, the most dangerous from preventive conservation point of view, were particularly present also in the fine fraction and were equally distributed in the building. In the summer, they represented up to 80% of all particles.

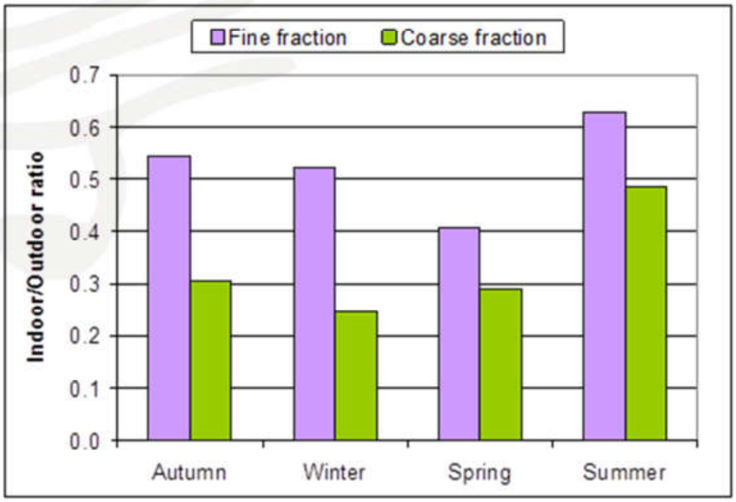

Figure 3: Indoor/Outdoor ratio values for fine and coarse fraction in different seasons in the Plantin-Moretus Museum, Antwerp, Belgium.

From a preventive conservation point of view, it is most important to keep the windows more closed in summer; also, the temperature and relative humidity variations and the light intensity appeared to be too high.

CONCLUSIONS

These case studies have shown that environmental factors are important for preventive conservation, even indoors. By using different analytical techniques, we try to find the reason for the deterioration of CH items. Moreover, we try to optimize their storage conditions in various indoor environments. Future studies are urgently needed concerning the deposition rates of atmospheric pollutants to CH items, and particularly concerning the interaction process of particles with the surface of CH items. Indeed, considerable work has already been done on the interaction of pollution gases with CH items, but except for sea salt, hardly any research has been carried out and published on the direct effects of atmospheric particles.

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