

# **RESEARCH ARTICLE**

**Open Access** 

# Indoor air pollution impact on cultural heritage in an urban and a rural location in Romania: the National military museum in Bucharest and the Tismana monastery in Gorj County

Terje Grøntoft<sup>1\*</sup> and Octaviana Marincas<sup>2</sup>

# **Abstract**

Assessment was performed of the air quality related risk to the conservation of cultural heritage objects in one urban and one rural indoor location in Romania, with expected different air quality related conservation challenges: the National military museum in Bucharest and the Tismana monastery in Gorj County. The work was performed within and subsequent to the EU-Memori project by applying Memori methodology, Memori®-EWO (Early warning organic) dosimeters and passive pollution badge samplers for acetic and formic acids. The measurements in the National military museum were performed in three rooms with different exposure situations, and inside protective enclosures in the rooms. The rooms had organic and inorganic objects on exhibition and in store. The observed risks were associated with photo-oxidizing impact probably due to traffic pollutants entering from outdoor, and/or light exposure and temperature. The risks were found to be moderate, generally comparable to typical European purpose built museum locations. The highest risk was observed in a more open exhibition room in the main museum building. It was indicated that some observable change might happen to sensitive pigments and paper within 3 years, and to lead, copper and sensitive glass within 30 years in this location. Risk for observable change to sensitive pigments, paper, lead and sensitive glass within 30 years, was indicated in the other locations. The lowest risk was observed in a warehouse. A reduction in photo-oxidizing risk was measured in two of the enclosures, but a slightly higher acidic impact was measured in all the three enclosures, as compared to the respective rooms. In the Tismana monastery, a high level of acetic plus formic acid was observed in the air in the storerooms for icons and textiles, and books. Damage risk within 3 years was indicated for lead objects and sensitive glass, and within 30 years for iron and varnish (Laropal A81, resin mastic and dammar). As organic acid attack increases significantly at higher air humidity (> ~ 60%), this would be especially important to avoid. Risk for photo-oxidizing damage to paper and sensitive pigments within 30 years was indicated.

**Keywords:** Air pollution, Conservation, National Military Museum in Bucharest, Tismana monastery in Gorj County, Memori

Full list of author information is available at the end of the article



<sup>\*</sup>Correspondence: teg@nilu.no

<sup>&</sup>lt;sup>1</sup> Norwegian Institute for Air Research (NILU), P.O.box 100, NO-2027 Kjeller, Norway

Grøntoft and Marincas Herit Sci (2018) 6:73 Page 2 of 12

# Introduction

This study assesses the main general air quality related risk for damage to cultural heritage objects in custody of the National Military Museum, Bucharest, and the Tismana monastery, Gorj County, in Romania. The Military Museum is located in the centre of Bucharest where air pollution, especially from local combustion sources in the city ("traffic and house heating pollutants") is a health issue, with transgression of recommended outdoor levels [1] such as the EU 2008 Air Quality Directive (AQD) presently in force [2]. This indicates possible transgression of levels suggested for exposure of cultural heritage objects located indoor [3, 4]. The Tismana monastery is located in a forested part of the countryside with generally much less traffic pollutants than in Bucharest. A possible damage risk and preservation challenge for objects stored indoor in relatively closed rooms in the monastery, partly constructed with and containing organic materials, may be due to off-gassing of acidic components.

Air pollution measurements were implemented in this work to evaluate these possible risks.

The measurements were performed within the EU-Memori project [5]. Air quality was measured in selected indoor locations at the sites, and the evaluation system and results reporting developed in Memori was applied. Memori® air quality measurements and risk evaluation system for cultural heritage is described on the Memori technology web pages, where measurement results are also reported to users on assigned pages [6]. A Memori assessment takes into account the most common photo-oxidizing and acidic damage risks to cultural heritage materials observed indoor due to exposure to gaseous air pollutants.

The most prevalent and aggressive gaseous air pollutants, coming from the outdoors, and commonly observed indoors, are the oxidants nitrogen dioxide (NO<sub>2</sub>) and ozone (O<sub>3</sub>). NO<sub>2</sub> can react to form nitric acid (HNO<sub>3</sub>). NO<sub>2</sub> and O<sub>3</sub> are usually emitted from outdoor combustion sources, mostly traffic, house heating and industry. Indoor sources for these pollutants, which could be for example kitchens with gas stoves, open fireplaces, or electrical appliances that produce ozone, are uncommon in cultural heritage buildings. Many building and object materials do however emit volatile organic compounds (VOCs). The types and manufacturing processes of building materials are very diverse. It is therefore not surprising that very many different species of VOCs have been observed in indoor air [7-9]. This includes the low molecular mass formic and acetic acids, which can damage some materials [10-14]. Damage due to exposure to formaldehyde has been reported, with the additional information that this effect may be due to oxidation to formic acid [4, 15]. In addition, various organic pesticides have historically been used in many collections [16–18]. Damage to cultural heritage objects due to exposure to heavier (than formic and acetic acid) weight VOCs seems to be uncommon. Such compounds could be involved in the degradation mechanisms of polymeric materials [19]. Retained and emitted organic solvents may have damaging effects on materials such as varnishes [20].

Air pollution is only one of many risk factors, and it is often a lesser one. Heritage objects can be threatened by dramatic events such as war, fire, earthquakes or flooding. Exposure to water in its different phases is often a serious risk. This includes effects of indoor air humidity and its fluctuations [21]. Ongoing climate change is affecting degradation rates and risks [22]. Damage due to air pollution typically develops in synergy with light and humidity exposure, which is easier to observe [23, 24]. Air pollution can be a critical factor in some situations. A typical example is the outdoor formation of black crusts on calcareous stone due to acidic-sulfuric impact and soot deposition [25, 26]. Tarnishing and corrosion of metal surfaces and accumulation of dust are commonly observed indoor [27–30]. Damage to objects from oxidizing and acidic air pollutants may be less obvious. Typical damage effects are fading of dyes and colour changes, and loss of strength in paper and textiles. Sensitive wooden objects such as musical instruments or inlays can be affected [6, 27, 28].

A general risk evaluation should be performed before implementing environmental measurements. The evaluation should consider possible air pollution species that could be present in damaging concentrations. Many different techniques can be applied to measure air pollution. It has been most common to measure single parameters. Passive sampling with subsequent analysis in the laboratory and continuous online monitoring are two main general methods. Several dosimeter methods have been developed to measure generic effects of the air pollution on materials. Passive sampling, either of single parameters or with dosimeters, is usually much less expensive and thus more accessible to most cultural heritage users [31]. Application of Memori dosimeters gives values for the most common indoor photo-oxidizing and acidic air pollution risks. Other air pollutants that may have a damaging presence in some situations, such as sulfur dioxide (SO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), dust and particles including chloride [27], must be measured with different methods.

Memori measurements have been performed in many studies in many indoor locations to assess and compare air quality for cultural heritage [32–34]. It is a well-suited method for general assessment of the main common damage risks related to gaseous air pollution. Diagnosis is performed by the separation between photo-oxidizing

Grøntoft and Marincas Herit Sci (2018) 6:73 Page 3 of 12

impact (which is usually due to outdoor sources) and the acidic impact (which is usually due to indoor sources). This allows determination of the probable reason(s) for observed air quality related damage risk, and to suggest mitigation measures, which could be implemented to protect vulnerable objects against the exposure.

# Methods/experimental

# **Measurement locations**

To perform the air quality risk assessment, related to the preventive conservation of the objects in the National military museum and the Tismana monastery, air quality measurements were carried out over a 3 months period, from July to October in the year 2012, in locations of interest at the two sites. The measurements were performed in locations with significant objects on exhibit or in store, and which were expected to offer different degrees of protection against external and internally emitted air pollutants.

The measurements in the National military museum were performed in three rooms and inside a protective enclosure in each room: (1a) In the warehouse for foreign uniforms, and (1b) in a melamine fibreboard storage wardrobe in the warehouse; (2a) in the probative objects storage room, and (2b) in a wooden historic storage chest in the storage room; and (3a) in a contemporary history room in the main museum building, and (3b) in a display showcase in this room. Figure 1 shows five of the six locations. A photo of the measurement samplers located outside of the wooden chest in the probative objects storage room was not available.

Cultural heritage objects on exhibit or in store at these locations were woollen blankets, silk dresses, different types of military uniforms made from wool and cotton, swords, medals, military decorations, rifles, a binocular, a military casket, and different types of weapons and metals. The majority of the objects were composite objects consisting of inorganic and organic materials, some with specific coatings. Figure 1 shows some of the objects.

In the Tismana monastery, (Fig. 2) the measurements were performed in an icons and textile storeroom and in a book store room, and just outside of the rooms in a corridor. Figure 2 shows the Tismana monastery, and its iconostasis. Photos of the exact measurement locations were not available.

# Measurement methods

A Memori risk evaluation can be based either on measurements with generic dosimeters and/or on parameter measurements of the considered photo-oxidizing (NO<sub>2</sub> and O<sub>3</sub>) and acidic (acetic and formic acid) pollutant gases. Memori was developed with the use of Memori-EWO (PPO) (Early Warning Organic



**Fig. 1** The measurement locations in the National Military Museum. **1a** In the warehouse for foreign uniforms, **1b** in a melamine fibreboard storage wardrobe in the warehouse, **2b** in a wooden historic storage chest in the probative objects storage room, **3a** in a contemporary history room in the main museum building, and **3b** in a display showcase in the contemporary history room. No photo was available of the samplers at location **2a** in the probative objects storage room

(Polyphenylenoxide)) synthetic polymer dosimeters to measure photo-oxidizing impact, and a specially designed sensitive glass dosimeter (GSD) to measure acidic impact [6]. The translucent dosimeter materials react with the atmosphere and become more opaque due to exposure in the heritage locations.

When dosimeters are used for the air quality measurements, the results are reported as change in light absorption due to the exposures, as "delta absorption values", for the relevant wavelengths in the ultraviolet (the Memori-EWO) and the infrared (the GSD) region. This change observed in the dosimeter material due to the exposure, corresponds with the air pollution load and thus with the risk. In The EU-Propaint project [9, 23] dose-response equations were developed, which correlated the values for the influencing environmental parameters and the dosimeter responses, based on statistical treatment of a large database of measurements. In the indoor museum locations, the concentrations in air of NO<sub>2</sub> and O<sub>3</sub> ("traffic pollutants"), and the uv (ultraviolet)-light exposure were found to influence the EWO response at rates depending on the temperature, whereas the concentration in air of acetic acid was found to influence to GSD response.

It was a major task in the EU-Memori project to further correlate the dosimeter response with the expected impact on different cultural heritage materials [6], for the application in risk assessment, as reported below. The

Grøntoft and Marincas Herit Sci (2018) 6:73 Page 4 of 12



**Fig. 2** The Tismana monastery in Gori County, Romania, and its iconostasis. Photos of the exact measurement locations in the icons and textiles, and book, rooms were not available. Photo courtesy: Tismana monastery

dose-response equations from the EU-Propaint project and additional available information about the sensitivity of cultural heritage materials to photo-oxidizing and acidic air pollutants, was the basic information used for this assessment. As a strong statistical correlation was found between the GSD response and the measured concentration of acetic acid indoor in museums [23], the GSD absorption values reported by default in Memori evaluations, can also be approximated by calculation from measured concentration values of acetic acid. The applied correlation equation is [23]:

$$GSD(app) = 0.2 \cdot [HAc + FA]/1000$$
 (1)

where GSD (app)=Approximated Memori-GSD value (absorption units). [HAc+FA]=the sum of measured concentrations of acetic and formic acids ( $\mu g/m^3$ ). This equation was used for the reporting in this work of the acidic effects as GSD values, or the concentration values of acetic plus formic acid are reported. Similarly, a doseresponse equation for the influence of NO<sub>2</sub> and O<sub>3</sub> on the EWO dosimeter has been developed [23]. Thus, the photo-oxidizing impact can optionally be reported as EWO values calculated from measured concentration values of NO<sub>2</sub> and O<sub>3</sub>, or as the concentration values of NO<sub>2</sub> and O<sub>3</sub>. Some further considerations related to the application of either dosimeter or parameter measurements, and their conversion by Eq. (1) are discussed in the "Discussion" chapter.

For the measurement in the National military museum and the Tismana monastery, Memori-EWO (PPO) dosimeters were used to measure the photo-oxidizing effect and passive pollution badge samplers [35] for acetic and formic acids were used to measure the acidic effect (Fig. 1).

The Memori-EWO dosimeter is a small piece of quartz glass, of dimension 1.5  $\cdot$  0.7  $\cdot$  0.1 cm. A thin synthetic

organic polymer film is spin coated on the glass surface. The glass piece is mounted in an aluminium holder (Fig. 3). The dosimeter should be exposed for 3 months in the indoor atmosphere. The results measurements can be performed in a purpose built small portable instrument [6] or with a laboratory uv/visible spectrophotometer. The detection limit has been found to be equivalent to approximately  $4 \mu g/m^3 NO_2 + O_3$  [32].

The results evaluation of the dosimeters is calibrated for a typical museum indoor temperature of 20 °C and relative humidity (RH) of 50%. The dosimeter is normally mounted in upright position. The holder then gives some sheltering against dust deposition. In indoor cultural heritage locations, the effect of dust during the recommended 3 months exposure has been found to be low. The explanatory power of the dose-response equation, which does not include dust impact, was about  $R^2$ =0.7 [23]. If the presence of dust is high or the dosimeter is exposed in horizontal position, lying down, dust can however accumulate on the dosimeter and affect the response.

In an indoor situation with a temperature (T) significantly different from 20 °C or RH significantly different from 50%, or with much dust, the dosimeter will respond to these factors and measure a higher risk value, and/or the object sensitivity may be different from that applied for the Memori traffic light evaluation (see below). The materials damage risk assessment was not calibrated towards these impacts. Thus, the occurrence and influence of such variations in environmental factors (T, RH and dust) on the dosimeter response, and on the risk evaluation, must be evaluated separately.

The acetic and formic acids were measured with passive pollution badge samplers. The gases diffuse though the net into the badge sampler (Fig. 3) and are absorbed

Grøntoft and Marincas Herit Sci (2018) 6:73 Page 5 of 12

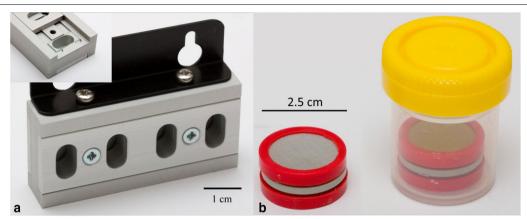


Fig. 3 a The Memori-EWO (PPO) synthetic polymer dosimeter in an aluminium holder. Four dosimeters can optionally be mounted in the holder for simultaneous parallel measurements. **b** A passive pollution IVL (Swedish environmental institute) type badge sampler, as was used to measure acetic and formic acids. In Fig. 1, the dosimeters and samplers are seen placed at the measurement locations

from the air on an alkaline filter located at its base. Subsequent laboratory analysis gave the values for the concentrations of the acids in air. The detection limit has been found to be  $0.5 \, \mu g/m^3 \, [23]$ .

The Memori assessment includes a "traffic light evaluation" of the measurement results, with indication of risk for degradation of 22 cultural heritage materials. The risk is described as the probable time before observable damage occurs and conservation is needed, with: "red" = within 3 years, "yellow" = from 3 to 30 years, and "green" = more than 30 years. General risk levels for cultural heritage, given as response values from measurements with the EWO and GSD, which are unrelated to the MEMORI "traffic light evaluation", exist from pre MEMORI work. For the EWO these are described as different typical European indoor museum environments [23, 28]. For the GSD they are based on overall evaluation of results from dosimeter development and application [36]. These GSD levels can be approximated as acetic plus formic acid concentrations by Eq. (1).

#### Results

The values for the air quality measured in the locations in the National military museum and Tismana monastery are given in Table 1.

Much higher values of photo-oxidizing impact was measured in the contemporary history room in the main museum building of the National military museum than in the other locations. Much higher values of acetic and formic acids were measured in the storage rooms with the organic objects (icons and textiles, and books) in the Tismana monastery, than in the corridor outside of

these rooms and in all the measurement locations in the National military museum. This is seen in Figs. 4 and 5.

A summary of the risk indications shown in the diagrams in Figs. 4 and 5, as provided by the Memori evaluation (see "Methods" section), for the measurement locations in the National military museum and the Tismana monastery are given in Table 2.

A comparison was then made in Fig. 6 with values measured in four seasons in 20 indoor museum locations (80 data points) over 1 year in the EU MASTER project, and arranged as "typical locations" in five categories (1 to 5) with decreasing air quality. For further description of the basis for this comparison, see [23].

The air quality risks in the National military museum were found to be moderate, generally comparable to typical European purpose built museum locations. The highest damage risk, more comparable to a historic house museum, was observed in the more open contemporary history exhibition room in the main museum building. The best situation was observed in a wardrobe in the warehouse for foreign uniforms, similar to a typical archive, storeroom or enclosure. A reduction in photo-oxidizing risk was measured in two of the enclosures, but a slightly higher level of acetic plus formic acidic was measured in all the three enclosures, as compared to the respective rooms. It was indicated that some observable change might happen to sensitive pigments and paper within 3 years, and to lead, copper and sensitive glass within 30 years, in the contemporary history exhibition room and showcase. Risk for observable change within 30 years, was indicated for lead, sensitive glass, sensitive pigments and

Grøntoft and Marincas Herit Sci (2018) 6:73 Page 6 of 12

Table 1 The values for the air quality measured with EWO-PPO dosimeters and the passive badge samplers for acetic and formic acid, in the locations in the National military museum and the Tismana monastery

Locations	EWO value, ΔE (uv-absorption value at 340 nm)	Acetic acid (μg/m³)	Formic acid (µg/ m³)	
National military museum				
1. Warehouse for foreign uniforms				
(a) In room	0.0070	100	40	
(b) In wardrobe	0.0056	140	50	
2. Storage room				
(a) In room	0.0082	100	50	
(b) In wooden chest	0.0114	290	100	
3. Main museum building, contemporary	history room			
(a) In room	0.0238	14	15	
(b) In showcase	0.0188	20	19	
Tismana monastery				
Icons and textile room	0.0090	1500	800	
Book room	0.0073	1100	520	
In corridor outside of rooms	_	170	50	

(See figure on next page.)

Fig. 4 The measurement results for the locations in the National military museum and the Tismana monastery presented in the seven (out of 22) Memori material risk evaluation diagrams, where some risk (red or yellow) were indicated are given in this figure and in Fig. 5. In the top diagram, for lead, the measurement locations are described by the circular results point markers. The circular point markers give the measurement results for the EWO (photo-oxidizing effect) on the horizontal axis, and the results for the acetic + formic acid measurements, represented by the GSD (Glass slide dosimeter) values (see "Methods" section), on the vertical axis. The locations are repeated for all the materials diagrams below the first diagram for lead. For the location outside of the rooms in the Tismana monastery, "T-in corridor outside of rooms", the EWO dosimeter value (photo-oxidizing effect) was not measured (Table 1), and the value on the x-axis is therefore not determined (see Table 1). "Green" indicates that, within the constraints of present knowledge, it is unlikely that the materials will change significantly within a period of perhaps 30 years. 'Red' indicates that damage is likely to occur to objects within 3 years and that damage will require active conservation. 'Yellow' indicates a situation in between

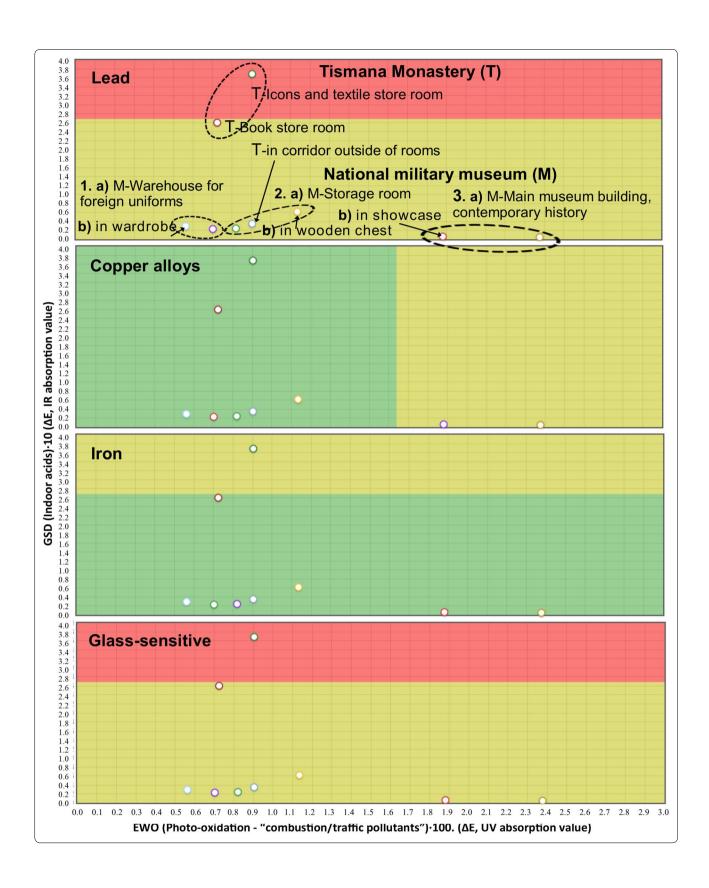
paper in the other locations in the National military museum.

Relatively high concentrations of acetic and formic acids were measured in the air in the store rooms for icons and textiles, and books, in the Tismana monastery. The highest damage risk was found in the icons and textile room, where it was indicated that observable damage, which would require active conservation, was likely to occur to lead and sensitive glass within 3 years ("red"). For iron objects, sensitive pigments, varnish (Laropal A81, resin mastic and dammar) and paper, it was indicated that observable damage would take longer to develop in both locations, between three and about 30 years ("yellow"). The risk to paper and sensitive pigments was due to photo-oxidation rather than acidic impact. No lower threshold was identified by Memori for photo-oxidative impact on sensitive pigments, so this risk could probably not be totally avoided [<del>6</del>].

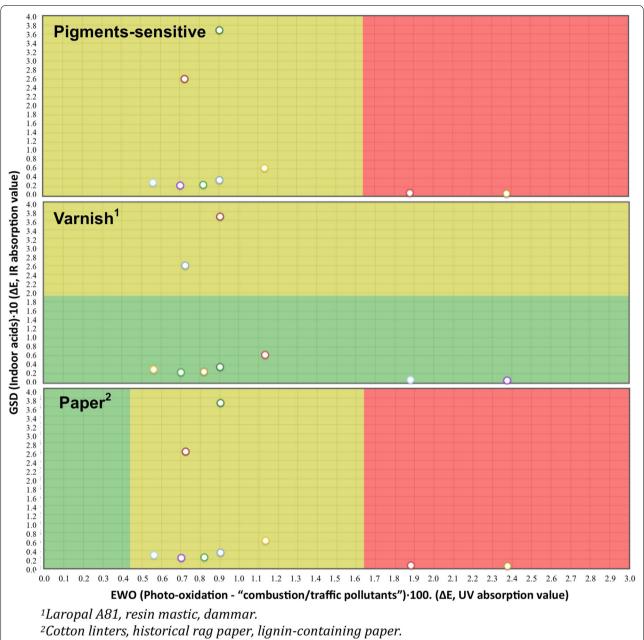
### Discussion

# Memori reporting based on dosimeter and/or parameter measurement methods

Differently from Eq. (1), the original statistical doseresponse equation for the GSD dosimeter does not, include formic acid [23]. Formic acid is however a stronger acid than acetic acid and is known to have degrading impacts [4, 37]. In museum locations the presence of formic acid typically correlates with that of acetic acid, with a concentration of about 25% that of acetic acid, but with large variation [9, 11, 12]. Thus, in statistical treatments it is a risk that the formic acid effect is hidden by that of acetic acid, by co-correlation. The optional reporting in this work of Memori results with GSD values calculated from measured concentration values by Eq. (1), or directly with concentration values of acetic plus formic acid, rather than by the measured GSD dosimeter values, should give a closely similar evaluation, but it is not a direct parallel. Dosimetry of generic pollutant effects and parameter measurements are different Grøntoft and Marincas Herit Sci (2018) 6:73 Page 7 of 12



Grøntoft and Marincas Herit Sci (2018) 6:73 Page 8 of 12



**Fig. 5** The measurement results for the locations in the National military museum and the Tismana monastery presented in the three remaining of seven (out of 22) Memori material risk evaluation diagrams, where some risk (red or yellow) were indicated (see the Fig. 4 caption)

approaches to risk assessment, with different qualities. The choice of measurement method could influence results, for example in situations with high temperature, humidity or dust levels. Dosimetry has the advantage of simultaneously assessing the combined impact of several environmental factors, whereas parameter measurements provide values for the concentrations in air of single air pollutants. The environmental degradation of complex objects is usually complex, and the sensitivities of the

object and its materials are often uncertain. A Memori risk evaluation is therefore a risk indication, which usually needs further evaluation, specification and diagnosis if risk is identified (i.e. indicated).

# Risk evaluation for the National Military museum and the Tismana monastery

The EWO-Memori dosimeter results indicated some damage risks to objects in the National military museum

Grøntoft and Marincas Herit Sci (2018) 6:73 Page 9 of 12

Table 2 Memori risks results summary diagram for the measurement locations in the National military museum and Tismana monastery

Location	Risk indication (see also "Methods" chapter)	
	Red	Yellow
National military museum	Material damage	
Warehouse for foreign uniforms, room and wardrobe, and 2. storage room and wooden chest		Lead (A <sup>a</sup> ) Sensitive glass (A) Sensitive pigments (PO <sup>a</sup> ) Paper (PO)
3. Main museum building, contemporary history room, in showcase and room	Sensitive pigments (PO) Paper (PO)	Lead (A) Sensitive glass (A) Copper (PO)
Tismana monastery		
Icons and textile room	Lead (A) Sensitive glass (A)	Iron (A) Sensitive pigments (PO) Varnish <sup>b</sup> (PO) Paper <sup>c</sup> (PO)
Book room		Lead (A) Sensitive glass (A) Sensitive pigments (PO) Varnish <sup>b</sup> (PO) Paper <sup>c</sup> (PO)
Outside of rooms		Lead (A) Sensitive glass (A)

Based on Figs. 4 and 5. "Red" indicates that damage is likely to occur to objects within 3 years and that the damage will require active conservation. "Yellow" indicates a situation in between "Red" and "Green" ("Green" indicates that within the constraints of present knowledge, it is unlikely that the materials will change significantly within a period of perhaps 30 years)

in Bucharest, due to exposure to combustion pollutants, most likely  $\mathrm{NO}_2$  and  $\mathrm{O}_3$  ventilated indoor from traffic, and/or uv-light exposure and high temperature. This is very typical for central European city locations, as for example identified in a recent study with Memori measurements in cultural heritage locations centrally in London [32].

Still, all the measurement locations in the National military museum were found to be similar or better than typical European "historic house museums". The observed reduction in the photo-oxidizing load and risk inside the enclosures in the Warehouse for foreign uniforms (1) and the contemporary history room in the main museum building (3) was an expected protective effect of the enclosures. The higher measured photo-oxidizing impact inside the wooden chest in the probative storage room (2) than in this room itself was thus surprising. This could be due to some unidentified oxidation impact, but probably more likely due to dust accumulation on the dosimeter glass, as the dosimeter was positioned horizontally besides rough textile materials (see Fig. 1, position 2b). Although dust accumulation was probably not a risk for the objects in this case, this points to the possible damage risks that may occur when co-locating sensitive objects with objects or materials which off-gas or release harmful substances. The slightly higher acidic impact measured inside all the enclosures than in the respective rooms in the National military museum is typical. It is well known that the levels of gaseous organic compounds are usually higher inside than outside of enclosures [9, 12, 38]. This is due to the larger emitting surfaces as compared to the volumes and usually lower ventilation rates of enclosures as compared to rooms. The small differences between the measured acidic impact in the enclosures and the rooms in the National military museum indicated little risk related to organic acid off gassing in the enclosures. This may be due to relatively low emitting materials and/or ventilation effects in the enclosures. The emission from materials is typically reduced as they age, and the aging of enclosures contribute to lower internal off gassing.

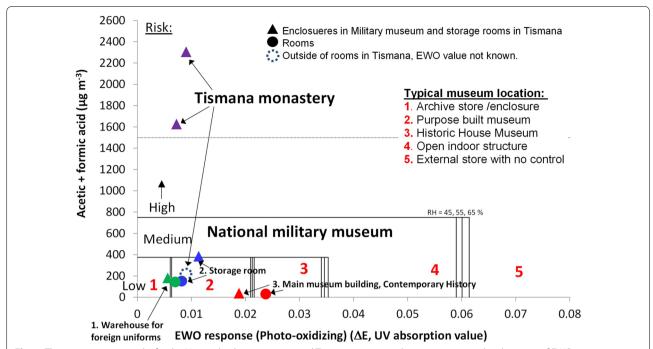
It seems that the most likely damages to develop in the National military museum in the short term (a few years) would be fading and colour change of pigments and surfaces, and embrittlement of paper. In the longer term (more than a few years), surface corrosion of metals could be expected. In this evaluation, it should be considered that surface corrosion of metal is very humidity dependent and that corrosion damage could appear

a Risk due to: A: acetic and formic acid; PO: photo-oxidation (Ozone, nitrogen dioxide and/or uv-light and temperature)

<sup>&</sup>lt;sup>b</sup> Laropal A81, resin mastic, dammar

<sup>&</sup>lt;sup>c</sup> Cotton linters, historical rag paper, lignin containing paper

Grøntoft and Marincas Herit Sci (2018) 6:73 Page 10 of 12



**Fig. 6** The measurement results for the National military museum and Tismana monastery locations compared with ranges of EWO response for five categories (1 to 5) of "typical museum locations" as found in the EU MASTER project [23, 28], and with approximate risk levels for the formic + acetic acid concentration (see "Methods" chapter). For the location outside of the rooms in the Tismana monastery the EWO dosimeter measurement was not performed

faster at higher than 50% relative humidity. The museum has many objects with such materials in exhibition and in store. Improved protection from exposure to air from outdoor and the consequent photo-oxidation could potentially extend conservation intervals and reduce conservation costs for such objects. The present use of showcases and enclosures has this protective purpose, which effect was verified by the measurements. Generally, some possible mitigation measures to reduce this exposure risk are: the moving of sensitive objects away from locations most influenced by the outdoors such as entrances and windows; avoiding exposure to light from outdoor; using showcases for sensitive objects; keeping sensitive objects in well closed and possibly conditioned store rooms; and avoiding high and fluctuating temperature and humidity conditions.

The indicated risk for acidic damage to metallic materials and sensitive (medieval) glass, and moderate risk for varnishes, in rooms in the Tismana monastery, due to exposure to acetic and formic acids, is expected in relatively closed rooms with low ventilation and significant emission especially from wood. The acidic atmospheres could initiate and accelerate surface corrosion on for example glass paintings and metallic objects. One could consider if such objects should be moved from the rooms. It would be beneficial to keep the rooms cool, and

ventilate the rooms under good (dry, cool) outdoor conditions without producing dramatic climatic fluctuations. As organic acid attack increases significantly at higher air humidity (>  $\sim 60\%$ ), this would be especially important to avoid [37, 39–41]. To most organic objects the acidic atmospheres would be of little risk [6, 14]. A moderate photo-oxidation risk was indicated for paper and sensitive pigments. Such materials would be present in objects in the icons and textile and the bookstore rooms. For preservation in the long term additional protection of such objects against exposure to light and outdoor air would be beneficial, by similar methods as suggested for the National military museum, for example by using showcase or protective enclosures.

It is important to note that, in many cases, the sensitivity of specific cultural heritage materials and objects would be different from that applied in the MEMORI assessment. Objects and surfaces are often complex mixtures of materials that have already been subject to change by environmental exposure. The exposure may have produced damages and additional vulnerability, or protective surface patinas. MEMORI is a tool, which supplies an evaluation and ranking of air pollution risks. It can give added information to conservators and assist in efforts to improve the preventive protection of objects in the most efficient way. Air quality measurements and

Grøntoft and Marincas Herit Sci (2018) 6:73 Page 11 of 12

risk evaluation can lead the attention to situations of concern where further investigation of damages and damage processes should be performed. They do not replace the essential understanding of single objects, their materials and their vulnerability, which the conservators needs to apply.

# **Conclusions**

Air quality measurements and risk assessment for cultural heritage materials were performed in the National military museum and the Tismana monastery in Gorj County in Romania, by applying Memori® methodology, dosimetry and passive pollution parameter sampling. Some risk was indicated for photo-oxidising damage to some types of sensitive materials in the National military museum in Bucharest. The highest risk for observable damage, which would need active conservation within 3 years, was found in a contemporary history exhibition room in the main museum building. The photooxidising damage risk in the room was evaluated to be similar to a typical European historic house. A moderate risk for observable damage, which would need active conservation within 30 years, was found in a warehouse, a storeroom and inside enclosures used in the museum, comparable to typical European purpose built museum locations. The materials most at risk were found to be sensitive pigments and paper. Some risk for damage to copper, lead, and sensitive glass was indicated. The risk could be reduced by measures to protect the objects against exposure to outdoor city air ventilated into the building, and against possible excessive light exposure and high and fluctuating temperature and humidity. The present use of protective enclosures has these functions.

Significant risk for damage to some types of sensitive materials, due to exposure to an acidic atmosphere, was observed in the icons and textile room and book store room in the Tismana monastery. Materials at risk were found to be especially lead and sensitive glass, with some risk also for iron objects and varnish (Laropal A81, resin mastic, dammar). Some risk for photo-oxidation of paper and sensitive pigments was found. Sensitive objects could be moved out of rooms with high acid emissions, probably mostly from wood materials. It would be especially important to avoid high humidity situations with RH above ~ 60%, which accelerate corrosion. It would be beneficial to keep rooms cool. Rooms could be ventilated when the outdoor air is good (clean, dry and cool). Paper and objects with sensitive pigments could be moved into showcases or protective enclosures, or moved away from exposure to outdoor air and light.

#### **Abbreviations**

A: acidic; AQD: Air Quality Directive; EWO: early warning organic dosimeter; FA: formic acid; GSD: glass slide dosimeter; HAc: acetic acid; M: national military museum; PO: photo oxidizing; PPO: polyphenylenoxide; RH: relative humidity; T: Tismana monastery; VOC: volatile organic compound.

#### Authors' contributions

OM did the measurement work, reporting from location and initial description of measurement locations. TG did the laboratory dosimeter preparation, laboratory measurements, organizing of the delivery of passive samplers and their analysis from the NILU laboratory, results data analysis, interpretation and development of the manuscript. Both authors contributed to finalizing the manuscript. Both authors read and approved the final manuscript.

#### **Author details**

<sup>1</sup> Norwegian Institute for Air Research (NILU), P.O.box 100, NO-2027 Kjeller, Norway. <sup>2</sup> The Romanian Ministry of Research and Innovation (MCI), Str. Mendeleev nr. 21-25, 010362 Bucureşti, Romania.

#### Acknowledgements

We would like to acknowledge the leadership of the "Ferdinand I" National military museum and the Abbess of Tismana monastery who accepted to cooperate within the Memori project as beneficiary partners and gave the permission to publish the obtained results. This research was made possible through the generous contribution of the conservators Ms. Gabriela Tuas from the National military museum and Sister Maria from the Tismana monastery who have assisted the performed measurements. We want to thank Håvard Vika Røen at NILU who did the programing of the MEMORI technology web pages.

#### **Competing interests**

The authors declare that they have no competing interests.

#### Availability of data and materials

All equations and data necessary to calculate the model are given either in the text or in the cited references.

#### Funding

This work has been funded by the EU- Memori project (Grant Agreement No. 265132) and by NILU-Norwegian Institute for Air Research.

# **Publisher's Note**

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Received: 29 October 2018 Accepted: 29 November 2018 Published online: 10 December 2018

#### References

- Lorga G, Raicu CB, Stefan S. Annual air pollution level of major primary pollutants in Greater Area of Bucharest. Atmos Pollut Res. 2015;6:824–34.
- Guerreiro C, González A, de Leeuw F. Air quality in Europe—2017 report. EEA report No 13, 2017. https://www.eea.europa.eu/publications/air-quality-in-europe-2017. Accessed Oct 2018.
- American Society of Heating, Refrigerating and Air-Conditioning Engineers. Museums, libraries, and archives (chapter 21). ASHRAE Applications Handbook (SI Edition), ASHRAE, Atlanta, 2007.
- Tétreault J. Airborne pollutants in museums, galleries, and archives: risk assessment, control strategies and preservation management. Ottawa: Canadian Conservation Institute: 2003.
- Dahlin E, Grøntoft T, Wittstadt K, Drda-Kühn K, Colombini M-P, Bonaduce I, Vandenabeele P, Larsen R, Potthast A, Marincas O, Schieweck A, Thicket D, Odlyha M, Andrade G, Hackney S, McDonagh C, Ackerman JJ. EU Project MEMORI. Final report. Measurement, effect assessment and mitigation of pollutant impact on movable cultural assets. Innovative research for market transfer. NILU OR 15/2014. http://www.Memori.fraunhofer.de/. Accessed Oct 2018.

- The Memori technology. Innovation for conservation. http://Memori.nilu. no/. Accessed Oct 2018.
- Schieweck A, Salthammer T. Emissions from construction and decoration materials for museum showcases. Stud Conserv. 2009;54:218–35.
- 8. Schieweck A, Salthammer T. Indoor air quality in passive-type museum showcases. J Cult Herit. 2011;12:205–13.
- Dahlin E. (ed.) EU Project PROPAINT. Final report. Improved protection of paintings during exhibition, storage and transit. NILU OR, 42/2010. http:// propaint.nilu.no/. Accessed Oct 2018.
- Grøntoft T, Lankester P, Thickett D. Reduction of acidic pollutant gases inside showcases by the use of activated carbon adsorbers. e-PS. 2015;12:28–37.
- Grøntoft T. Performance evaluation for museum enclosures. Measurement, modelling and mitigation of pollutant impact on objects in museum enclosures. ePreserv Sci. 2012;9:36–46.
- Grøntoft T, López-Aparicio S, Scharff M, Ryhl-Svendsen M, Andrade G, Obarzanowski M, Thickett D. Impact loads of air pollutants on paintings: performance evaluation by modeling for microclimate frames. J Am Inst Conserv. 2011;50(2):105–22.
- Salthammer T, Siwinski N, Vogtenrath W, Schieweck A. Occurrence of formaldehyde and organic acids in the museum environment. HB 2006—Healthy buildings: creating a healthy indoor environment for people, proceedings 2006:2:283–286.
- Ligterink F, Di Pietro G. The limited impact of acetic acid in archives and libraries. Herit Sci 2018;6:59, https://doi.org/10.1186/s40494-018-0225-y Accessed Nov 2018.
- Grzywacz CM. Monitoring for gaseous pollutants in museum environments: Tools in conservation. Los Angeles: The Getty Conservation Institute; 2006.
- Marcottea S, Este L, Leboucherc S, Minchinc S. Occurrence of organic biocides in the air and dust at the Natural History Museum of Rouen, France. J Cult Herit. 2014;15:68–72.
- Schieweck A, Delius W, Siwinski N, Vogtenrath W, Genning C, Salthammer T. Occurrence of organic and inorganic biocides in the museum environment. Atmos Environ. 2007;41(15):3266–75.
- Glastrup J. Insecticide analysis by gas chromatography in the stores of the Danish National Museum's Ethnographic collection. Stud Conserv. 1987:37:59

  –64
- Shashoua Y. Conservation of plastics: materials science. Elsevier/Butterworth-Heinemann: Degradation and Preservation; 2008.
- Bonaduce I, Odlyha M, Di Girolamo F, Lopez-Aparicio S, Grøntoft T, Colombini MP. The role of organic and inorganic indoor pollutants in museum environments in the degradation of dammar varnish. Analyst. 2013;138:487–500. https://doi.org/10.1039/C2AN36259G.
- EN 15757:2010. Conservation of cultural property—specifications for temperature and relative humidity to limit climate-induced mechanical damage in organic hygroscopic materials. Brussels: European Committee for Standardisation 2010.
- Sabbioni C, Brimblecombe P, Cassar M. (eds.). The atlas of climate change impact on European cultural heritage: scientific analysis and management strategies anthem environmental studies. Anthem Press, 2010.
- Grøntoft T, Odlyha M, Mottner P, Dahlin E, Lopez-Aparicio S, Jakiela S, Scharff M, Andrade G, Obarzanowski M, Ryhl-Svendsen M, Thickett D, Hackney S, Wadum J. Pollution monitoring by dosimetry and passive diffusion sampling for evaluation of environmental conditions for paintings in microclimate frames. J Cult Herit. 2010;11:411–9.
- Bacci M, Cucci C. The role of light. In: Camuffo D, Fassina F, Havermans J. (eds.) Basic environmental mechanisms affecting cultural heritage. Understanding deterioration mechanisms for conservation purposes. COST action D42, Nardini editore. Firenze; 2010, p. 115–146.
- Brimblecombe P. (ed.). The effects of air pollution on the built environment. Imperial College Press, London 2004. https://ia800200.us.archive.org/10/ items/PeterBrimblecombeTheEffectsOfAirPollutionOnTheBluit/%5BPeter\_ Brimblecombe%5D\_The%20effects%20of%20air%20pollution%20on%20 the%20bluit.pdf. Accessed Oct 2015.
- Grøntoft T. Conservation-restoration costs for limestone façades due to air pollution in Krakow, Poland, meeting European target values and expected climate change. Sustain Cities Soc. 2017;29:169–77.

- Blades N, Oreszczyn T, Bordass B, Cassar M. Guidelines on pollution control in museum buildings, Museums Association, London 2000. In: Martin D. (ed.) UNSPECIFIED Museums Association: London. http://discovery.ucl. ac.uk/2443/1/2443.pdf. Accessed Oct 2018.
- Dahlin E. (ed.) EU project MASTER. Final report. "Preventive Conservation Strategies for Protection of Organic Objects in Museums, Historic Buildings and Archives". NILU OR 76/2010. https://www.nilu.no/master/76-2010-emdteq-MASTER.pdf. Accessed Oct 2018.
- 29. Lithgow K, Lloyd H, Brimblecombe P, Yoon YH, Thickett, D. Managing dust in historic houses: the visitor/conservatory interface. ICOM Committee for Conservation, 14th Triannual Meeting. 2005;662–669. https://www.english-heritage.org.uk/siteassets/home/learn/conservation/collections-advice-quidance/icom14dust.pdf. Accessed Oct 2018.
- Thickett D, Costa V. The effect of particulate pollution on the corrosion of metals in heritage locations. In Bridgland J. (ed.) ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15–19 September 2014; art. 0907;8 pp. Paris: International Council of Museums. (ISBN 978-92-9012-410-8). https:// www.icom-cc-publications-online.org/PublicationDetail.aspx?cid=16931 9ff-c184-4851-a20e-c3c90f1 fabbd. Accessed Oct 2018.
- Rosenberg E, De Santis F, Kontozova-Deutsch V, Odlyha M, van Grieken R, Vichi F. Measuring gaseous and particulate pollutants. Instruments and instrumental methods. In: Camuffo D, Fassina F, Havermans J. (eds.) Basic environmental mechanisms affecting cultural heritage. Understanding deterioration mechanisms for conservation purposes. COST action D42, Nardini editore. Firenze; 2010, p. 115–146.
- Grøntoft T, Thickett D, Lankester P, Hackney S, Townsend JH, Ramsholt K, Garrido M. Assessment of indoor air quality and risk for damage to cultural heritage objects with Memori<sup>®</sup> dosimetry. Studies in Conservation March 2016;61;70–82. Issue sup1, The Indoor Environment, Taylor & Francis. http:// www.tandfonline.com/doi/full/10.1080/00393630.2015.1131477. Accessed Oct 2018.
- 33. Grøntoft T, Dahlin E, Håland S, Vika Røen H, Heltne T, Thicket D, Lankester P, Schieweck A. The "Memori system; measurement, effect assessment and mitigation of pollutant impact on movable cultural assets. Innovative Research for Market Transfer. In Troi A, Lucchi E. (Eds.) Cultural Heritage Preservation. EWCHP-2013. Proceedings of the 3rd European Workshop on Cultural Heritage Preservation. Bozen/Bolzano, Italy, 16th to 18th September, 2013;23–28. European Academy of Bozen/Bolzano (EURAC).
- Lopez-Aparicio S, Grøntoft T, Dahlin E. Air quality assessment in cultural heritage institutions using EWO dosimeters. ePreserv Sci. 2010;7:96–101.
- 35. Ferm M. A sensitive diffusional sampler (IVL), B–1020. Swedish Environmental Research Institute Publication 1991.
- 36. Mottner P. Early warning dosimeters for monitoring indoor museum climate: environmental impact sensors and LightCheckTM. In: Argyropoulos V, Hein A, Harith MA, editors. Strategies for saving our cultural heritage: papers presented at the International conference on conservation strategies for saving indoor metallic collections, Cairo, 25 February 1 March 2007. Athen: TEI of Athens; 2007. p. 53–7.
- Hackney S. Colour measurement of acid-detector strips for the quantification of volatile organic acids in storage conditions, Studies in Conservation 2016;61:sup1;k 55–69, https://doi.org/10.1080/00393630.2016.1140935. https://www.tandfonline.com/doi/pdf/10.1080/00393630.2016.1140935. Accessed Oct 2018
- Thickett D, Stanley B, Booth K. Retrofitting old display cases. Preprints of the 15th Triennial Meeting of the ICOM Committee for Conservation, New Delhi. New Delhi: Allied Publishers Pvt Ltd Vol II;2008:775–782. (AP).
- Cano E, Bastidas JM. Effect of relative humidity on copper corrosion by acetic and formic acid vapours. Can Metall Q. 2002;41(3):327–36.
- 40. Tétreault J, Sirois J, Stamatopoulou E. Studies of lead corrosion in acetic acid environments. Stud Conserv. 1998;43(1):17–32.
- Strlič M, Thickett D, Taylor J, Cassar M. Damage functions in heritage science. Stud Conserv. 2013;58(2):80–7. https://doi.org/10.1179/2047058412 Y.0000000073.