



# MEMORI



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## **MEASUREMENT, EFFECT ASSESSMENT AND MITIGATION OF POLLUTANT IMPACT ON MOVABLE CULTURAL ASSETS. – INNOVATIVE RESEARCH FOR MARKET TRANSFER**

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# Project Final Report

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## 1 Executive summary

The MEMORI project (Grant agreement 265132) was performed in the period 2010-2013. The project was coordinated by NILU-Norwegian Institute for Air Research and included 14 partners, four subcontractors and an advisory end-user group with 8 members. MEMORI aimed at providing the conservation market with innovative, non-destructive, and early warning technology for easy assessment of environmental impact on indoor cultural heritage. In addition a new web-based mitigation tool was developed.

A web based survey was performed at the start of MEMORI. The aim of the survey was an empirical study on the attitudes towards indoor air quality (IAQ) in European collections. The evaluation of the survey showed that many museums are not aware of the problems related to the objects in their collections, due to the IAQ.

The MEMORI technology consists of three parts; The *MEMORI dosimeter*, which is sensitive to indoor climate and light, and to the oxidizing and acidic air pollutants, commonly present in indoor locations. The handheld *MEMORI dosimeter reader*, designed for in-situ measurements, which will improve the functionality of the dosimeter by reducing the time for results evaluation and make the system more flexible. Finally, the *MEMORI webpage*, including PC software for easy reading and storage of the measurement results. The MEMORI web pages present guidelines and procedures, based on preventive conservation knowledge (<http://memori.nilu.no>).

In addition, damaging effects of organic acids on different types of organic materials were studied with accelerated ageing. The new samples were studied with advanced invasive analytical techniques and real objects with non invasive analytical techniques, to improve the scientific basis for recommendations of tolerable pollution levels.

Studies aimed at optimising the designs and regimes for control of enclosure environments were performed. They focused on the performance and applicability of pollutant adsorbents inside museum enclosures. Analyses of volatile organics inside the enclosures were performed both before and after installing adsorbents. A luminescence-based oxygen sensor for the detection of oxygen in anoxic enclosures was also developed.

Finally, an improved preventive conservation strategy was developed. All results from research were brought together in the MEMORI web pages. A decision support model was developed which identifies the risk of damage to collection materials, allowing individual end-users to consider their specific circumstances. Once risk is identified information about pollution measurement is provided, followed by assessment of results. This assessment includes the results from experiments carried out in MEMORI on the effects of air pollutants on selected materials. A comprehensive literature review on pollutant damage was made, resulting in the most up to date survey and presentation of pollutant damage on indoor cultural heritage. The decision support model allows end-users to input parameters about their own circumstances. The system provides various options and recommends the most successful potential mitigation technique, also considering initial cost outlay, ongoing cost and energy usage.

A detailed business and marketing plan was developed in cooperation with representatives of the end-user advisory group of the project. It is now the basic instrument for market transfer of the MEMORI technology.

## **2 The MEMORI project context and objectives**

### **2.1 Introduction**

The MEMORI project aims at providing the conservation market with innovative, non destructive and early warning technology for easy assessment of environmental impact on indoor cultural heritage. In addition the damaging effect of organic acids on different types of organic materials were studied with accelerated ageing and advanced non destructive analytical techniques. This provided an improved scientific basis for recommendations of tolerable pollution levels. Optimization of the use of mitigation measures, such as adsorbents, in protective enclosures was studied. Finally a preventive strategy to secure the conservation of movable cultural assets in protective enclosures was developed.

To achieve these aims, the following objectives were investigated:

- Integration of two dosimeter technologies from the previous EU projects AMECP and MASTER.
- Production of PC software and an interactive webpage for the users.
- Assessment of the damage impact of organic acids on cultural heritage objects.
- Optimizing of active and passive control regimes for protective enclosures.
- Facilitating the use of protective enclosures to save energy and mitigate climate change.
- Integrating results with existing preventive conservation strategies.
- Disseminating results and implementation of a business plan.

### **2.2 Development of the dosimeter technology and MEMORI webpage**

The development of the new MEMORI technology was performed by NILU and Fraunhofer ISC in close cooperation with an end-user advisory group. The output obtained from the discussions with the end-user advisory group was used as input to the development of the MEMORI dosimeter, reader and web pages.

The MEMORI dosimeter technology combine the advantages of the Early Warning dosimeter for Organic materials (EWO), developed by NILU within the EU-MASTER project (EVK4-CT-2002-00093) and the Glass Slide Dosimeter (GSD) developed by Fraunhofer ISC within the EU-AMECP project (EV5V-CT-92-0144). The new MEMORI dosimeter is sensitive to indoor climate and light, and to oxidizing and acidic air pollutants, which are commonly present in indoor locations. A prototype of a portable reader (the MEMORI dosimeter reader) for in-situ measurements and results' evaluation was developed and six instruments were built. PC software for easy reading and storage of the measurement results from the MEMORI dosimeter was developed together with the MEMORI technology web pages for uploading and presentation of results. The MEMORI web pages <http://memori.nilu.no> provide guidelines for performing MEMORI measurements. On the MEMORI web pages evaluation of measurement results in terms of damage risk to objects and of possible mitigation actions is performed, based on state of the art preventive conservation knowledge.

### 2.3 Assessment of the damage impact of organic acids

Previous research projects such as the FP5 IDAP project for improved damage assessment of parchment and the FP6 PROPAIN project which included studies on varnishes, demonstrated the lack of knowledge about the influence of organic acids on the materials investigated.

In MEMORI accelerated ageing exposures of organic materials; cellulosic material; varnish; pigment (organic and inorganic); parchment; textile and leather, to organic acids were performed in the laboratory. When through this report the investigation of “organic materials” in MEMORI is described in general, this includes also the investigations of the inorganic pigments. The main considered organic acids were acetic acid ( $\text{CH}_3\text{COOH}$ ) and formic acid ( $\text{HCOOH}$ ). The damage impacts were assessed by the use of advanced non-destructive analytical techniques.

The MEMORI partner University of Natural Resources and Life Sciences, in Vienna, who investigated cellulosic material, aged ten different species of papers naturally (at room temperature) and under accelerated conditions (at elevated temperature and, controlled humidity) in the presence of different concentrations of acetic and formic acid. The results showed accelerated cellulose degradation even at low concentration ( $>1.5 \text{ mg/m}^3$ ) levels of acetic and formic acid vapour.

The Department of Chemistry and Industrial Chemistry, University of Pisa, and the Thermal methods and Conservation Science Centre at Birkbeck, University of London investigated effects of organic acids on different varnishes, basing the work on methods and results obtained in the previous EU PROPAIN project (FP6 SSPI no 044254). The following varnishes were investigated; dammar, resin mastic, Regalrez 1094, Laropal A81 and dammar with a coating of Regalrez 1094. Chemical and physical changes to varying degree were observed for all the varnishes.

The Royal Danish Academy of Fine Arts, School of Architecture, Design and Conservation and the Thermal methods and Conservation Science Centre at Birkbeck, University of London, investigated the damaging effect of acetic and formic acids on parchment and vegetable tanned leather: two new vegetable tanned leathers (sumac and mimosa), one historical vegetable tanned leather, one modern parchment and one historical parchment. Changes with importance for appearance and state of conservation were observed.

The Ghent University, Belgium investigated in depth the effect of acetic acid on five pigments: lead white, red lead, lead tin yellow type I, malachite and sunfast orange (PO36). Experiments were carried out with no binder medium and no varnish layer, representing a worst case scenario, as both the binder medium and varnish would be expected to protect the pigment. Changes in color and luster were observed.

The University of Arts "George Enescu", Romania in cooperation with their subcontractor, The Institute of Macromolecular Chemistry “Petru Poni” Iasi, Romania, investigated the effect of acetic acid on wool and silk textiles and on metal threads woven into the textiles. Changes in the crystallinity of wool proteins increasing the fragility of wool fibers were observed.

## **2.4 Active and passive control regimes for protective enclosures.**

Current practical approaches for using enclosures were reviewed in the early stage of the project through consultation with different museum institutions, such as partners at Tate and English Heritage. The output from this process was used by Fraunhofer WKI as an input to both a laboratory and a field test program. The practical understanding and new results from testing were used to design best possible control regimes and mitigation measures, focusing on the application of adsorbing media to reduce the presence of organic acids in micro environments.

Directed studies were performed to determine the chemical and adsorption properties, adsorption rates and amounts of adsorbing materials that give the best effect, i.e. the highest adsorption capacity at the lowest cost. Laboratory studies were completed by subsequent analyses on-site at manufacturers for indoor enclosures and in museums. MEMORI used the available information from the research literature and producers of adsorbing materials to design innovative experiments testing their use and effect. The partner, Dublin City University, developed further a luminescence-based oxygen sensor for the detection of oxygen in anoxic enclosures. The sensor was tested at Tate.

This work in MEMORI provided improved practical recommendations for end-users about optimal strategies to reduce the presence and thus impact of degrading contaminants inside protective enclosures. It also considered factors such as initial cost outlay, ongoing cost and energy usage and selection of adsorbing materials which could contribute in the effort *to save energy and mitigate effects of climate change*.

## **2.5 Integrating results with existing preventive conservation strategies.**

An important part of the improved preventive conservation strategy supplied by MEMORI to end-users, was the integration of results from the investigation of the effect of organic acids on organic heritage materials. All this research was brought together by the partner, English Heritage. They also developed a decision support model for end-users, guiding them in performing measurements of air pollution, in evaluating the damage impact on objects and in deciding most effective mitigation strategies.

The decision support model identifies the risk of damage to collection materials, allowing individual end-users to consider their specific circumstances. Once risk has been identified, information about pollution measurement is provided, followed by assessment of results. This assessment includes the comprehensive literature review on pollutant damage on heritage materials including results from the MEMORI experiments carried out to understand the effects of organic acids on selected materials. If there is a risk of damage, mitigation techniques are required. The decision support model then allows end-users to input parameters about their own circumstances, and provides a number of tools to allow end-users to determine the inputs for the model. The most successful potential mitigation technique is recommended. A number of case studies are presented to help end-users understand the decision support model.

Guidelines have been developed to aid end-users in:

- Determining when to employ the MEMORI dosimeter, depending on their collection.
- How to deploy the MEMORI dosimeter including where in an enclosure and ideally at what time of year.
- How to interpret the MEMORI dosimeter response in terms of the relevance to their collection.

## **2.6 Disseminating results and implementation of a business plan.**

As an important part of the dissemination and marketing plan, a web based survey with the title, “The current situation and management of indoor air quality (IAQ) in European museums, archives and libraries“ was initiated. This survey was performed by the partner Fraunhofer ISC. The aim of the survey was to assess the extent of the application of IAQ measurements in European collections. The evaluation of the survey showed that many museums are not aware of IAQ risk to the objects in their collections.

Results from the MEMORI project have been disseminated extensively through the whole project period, in diverse publications and conferences, and a film, “New air for museums”, presenting the concept and results of the MEMORI project was produced by Euronews (in 12 languages) and broadcasted all over Europe.

A detailed business- and marketing plan was developed by the partners Association Culture & Work and NILU Innovation AS, in cooperation with representatives of the end-user advisory group of the project. It is now the basic instrument for market transfer of the MEMORI technology. From dissemination activities a “MEMORI community” of interested end-users (museums, art collections, art transportation services, conservation companies) was created as the future customers for the MEMORI technology and services.

### **3 Main S&T results/foregrounds in the MEMORI project**

#### **3.1 Introduction - How to manage risks from the environment?**

For all relevant end-users in museums and cultural heritage institutions it is important to understand when air pollutants and the indoor climate pose a significant risk to the collections in their care. A simple to use dosimeter technology and preventive evaluation methodology was developed within the MEMORI project to inform this decision.

While the focus of the research within MEMORI was on air pollution it was important to place this within the larger picture. Information has been provided in MEMORI for end-users to allow them to approach managing risk from the environment from an overall perspective.

It is well established that materials are at risk of damage from the environment. Controlling the environment to which an object is exposed reduces the need for interventive conservation and extends object lifetime. The main indoor environmental parameters that are known to cause damage to materials of importance to heritage are: Relative humidity (RH), light (UV and infra-red radiation), pollutants (both gases and dust) and temperature.

Each environmental parameter can be significant in different scenarios, and materials are often more sensitive to one parameter than another. In order to control the environment, thus reducing the risk of damage it is first important to monitor the environment. Temperature and relative humidity are often routinely monitored in larger heritage organisations. Light is also frequently monitored, but probably less so than temperature and relative humidity. Pollution is rarely monitored in comparison to the other parameters.

A number of materials off-gas (emit) pollutants, including objects themselves. Alternatively damaging pollutants can ingress from outdoors. The first step when considering indoor air pollution is to understand the materials that are likely to be affected by pollutants, and circumstances which can increase risk of damage by pollutants, for example the build up of internally generated pollutants within enclosures and higher RHs. The construction materials of an enclosure, for storage or display, or room, along with the air exchange rate will effect pollutant concentration. If an enclosure contains an emissive material, and the air exchange rate is low, the pollutant concentration can build up within an enclosure to damaging concentrations.

Enclosures that include wood or wood products, hardboard, MDF (medium density fibreboard, including E1 grades and ZF (zero formaldehyde)), chip board, particle board, OSB (orientated strand board) and plywood, in their structure, and have a low air exchange rate are likely to have high organic acid concentrations. Additionally the inclusion of woollen fabrics is likely to have problematic sulfide concentrations. Enclosures made from metal and glass, or other materials that have passed an environmental test, such as the Oddy test, can have very low levels of pollutants with low air exchange rates. The low air exchange rate will reduce externally generated pollutant ingress. This assumes the objects themselves are not emitting pollutants.

In a room it is possible that outdoor air pollutants can infiltrate, again the air exchange rate is important, and these pose the potential to cause damage.

The location of the building is important when considering outdoor generated pollutants. It may be beneficial to consult data on outdoor pollution levels, although some features such as busy roads can have a local impact.

Air pollutants can be classified into two groups, those generally generated indoors and those generally generated outdoors, as shown here:

- Indoor;
  - Volatile organic compounds (VOCs)/organic acids
  - Sulfides (also outdoor)
- Outdoor;
  - NO<sub>x</sub>
  - SO<sub>2</sub>
  - O<sub>3</sub>
  - Sulfides (also indoor)

It is important to consider the sensitivity of collections to the environment in general, as there may be other parameters of greater significance than pollution. A material damage table has been produced. This table allows end-users to identify risks to their collections from their environment (relative humidity, light and pollutants).

Where appropriate, focus upon the risk from indoor air pollution can be aided with the MEMORI dosimeter and the MEMORI dosimeter reader. In order to parameterise the MEMORI dosimeter it is important to understand the sensitivity of materials to the pollutants to which the dosimeter responds. For each material a table has been produced categorising its sensitivity to acetic acid (ethanoic acid, CH<sub>3</sub>COOH), formic acid (methanoic acid, HCOOH), ozone (O<sub>3</sub>) and nitrogen dioxide (NO<sub>2</sub>).

It was the aim of the work performed in MEMORI to understand the effect of a number of variables related to MEMORI dosimeter deployment on the measurement results obtained. The deployment location of the dosimeter can affect results, and the situations in which this can occur have been elucidated. The timing of dosimeter deployment has also been investigated, as pollutant emission can vary with time of year, due to variation in environmental conditions.

The MEMORI technology and web pages complements and adds to existing technology for assessment of risk for damage due to air pollution. Those commonly used are MEACO ([www.meaco.co.uk](http://www.meaco.co.uk)), Hanwell ([www.the-imcgroup.com](http://www.the-imcgroup.com)) and Eltek ([eltekdataloggers.co.uk](http://eltekdataloggers.co.uk)). Additionally a number of European projects have carried out research in this area, including MIMIC, MASTER, PROPAIN, MUSECORR, ERA (URL: [www.iaq.dk/mimic](http://www.iaq.dk/mimic), [www.nilu.no/master](http://www.nilu.no/master), [www.propaint.nilu.no](http://www.propaint.nilu.no), [www.Musecorr.eu](http://www.Musecorr.eu) and [www.era-project.eu](http://www.era-project.eu)). The MEMORI technology and web pages complements and adds to existing technology for assessment of risk for damage due to air pollution. It offers additional advantage by providing a system which allows in situ results measurements, basic diagnosis of the presence and sources for air pollution, risk assessment for objects and application of a decision support model to aid optimal mitigation action.

## 3.2 The MEMORI Technology

### 3.2.1 Introduction

The MEMORI technology is a system for measurement of air quality and evaluation of related risk for degradation of indoor cultural heritage. The combined air pollution and climate load in an indoor location is assessed by exposing the MEMORI dosimeter at a specific location for a period of time (usually 3 months), followed by measuring the level of change in the MEMORI dosimeter reader. The conservator or other responsible person in a museum, library, or an archive can expose dosimeters in their indoor locations and then by themselves measure the resulting values for the dosimeter with the MEMORI dosimeter reader, and assess the air quality using the MEMORI web results display and evaluation pages. This will provide them with an indication of risk for damage of selected heritage materials of interest.

The MEMORI technology provides a complete methodology for the evaluation of air quality risk to indoor heritage and suggested mitigation measures, guided by a decision support model. The methodology includes user guidelines and more detailed explanations of how the dosimeter response is related to air quality risk to the heritage materials.

### 3.2.2 The MEMORI measurement system

The MEMORI measurement system consists of a dosimeter (Figure 1), which is exposed on the cultural heritage location of interest for 3 months and a dosimeter reader (Figure 2), which measures the effect of the air environment on the dosimeter.



Figure 1: The MEMORI dosimeter, with the GSD (left) and EWO (right) glasses.



Figure 2: The MEMORI dosimeter reader.

The dosimeter holder, which is made of anodized aluminium, measures 90 mm x 25 mm x 4 mm. The holder includes two dosimeter pieces, a sensitive glass, the GSD (Glass Slide Dosimeter) developed by Fraunhofer ISC and a sensitive synthetic polymer EWO (Early Warning Organic) developed by NILU (Figure 1), which reacts to acidic and oxidizing air contaminants, respectively. In addition the dosimeter is sensitive to the climate factors, temperature, relative humidity and UV-light. The GSD typically measures the effect of organic acids from indoor sources where as the EWO measures effect usually mostly of “combustion pollutants” or “traffic pollutants” (nitrogen dioxide and ozone) that usually infiltrate from outdoor. Thus the dosimeter gives a response that represents the combined air pollution and climate load on the sensitive dosimeter materials. The MEMORI evaluation system correlates this measured effect with the degradation effect likely to be observed on different heritage materials, to indicate the degradation risk for cultural heritage objects.

Separate measurements and evaluations of indoor air quality by the exposure of the GSD and EWO and subsequent analysis in the laboratories have been performed in previous EU projects: FP5 AMECP, FP5 MASTER and FP6 PROPAIN. In the MEMORI project these two systems were integrated in one dosimeter with a portable reader instrument – the MEMORI dosimeter and reader (Figure 2) which was developed and built in order to measure the dosimeter in situ.

Important parts of the MEMORI technology are the user guidelines and the technical user manual which are available on the MEMORI technology web pages <http://memori.nilu.no>. These documents will give valuable information before starting to use the MEMORI technology.

The air quality is registered by the MEMORI dosimeter by measuring the dosimeter, before (the start point) and after exposure at the selected location, in the MEMORI dosimeter reader, which was developed by NILU (Figure 2). The MEMORI dosimeter reader is a portable selected wavelength instrument with the dimensions, 224 mm x 164 mm x 82 mm. The instrument enclosure is made of anodized aluminium. The reader has three diodes on the front panel (Figure 2) which informs the user about the measurement sequence (M), if the battery is charged or needs charging (B) and if the clock needs adjustment (C). The detailed procedure of exposure of dosimeters, operation of the reader and measurement sequence is explained in a short user guideline.

### **3.2.3 The MEMORI web pages**

The results values which are initially stored in the reader are uploaded to the MEMORI technology web pages (<http://memori.nilu.no>), by first connecting and downloading the measurement files to a PC, then logging into the web pages and applying the “uploading software”. The software and web pages were developed by NILU with contribution from all partners.

On the MEMORI web results pages the risk to heritage materials is represented by a simple “traffic light response” to the obtained measurement result. To get the traffic light response, the end measurement must have been performed and the user must write a location description and select a material for the evaluation. The material selection is

performed in the drop down menu and the selection can easily be changed to evaluate the situation for different materials or objects in the location.

The “Results pages” also give a more detailed evaluation by plotting the selected results in a two dimensional diagram, which shows the result for the part of the dosimeter sensitive to acids (GSD) and to oxidation (EWO) along the vertical and horizontal axis, respectively.

The diagram allows diagnosis if the likely reason for a high obtained result is indoor (most likely) sources of organic acids, which will give a high value on the vertical axis, or if it is photo-oxidation due to external influences and infiltration from outdoor (most likely) which will give a high value on the horizontal axis. The diagram will also show if a measured value is close to a different risk category, e.g. if an obtained “yellow” is close to a high risk “red” situation.

The traffic light colour indication of risk for the different selected materials is based on a correlation of the known environmental, air quality and climate, response of the dosimeter as compared with that of the materials. A material such as paper, for example, which is known to be quite sensitive to nitrogen dioxide, a response from the EWO part of the dosimeter, will signify a comparable risk for degradation in the measured environment.

However, although materials are sensitive to and degraded by some of the same influences from the air environment, the reaction mechanism for the degradation of different materials is different and there is some amount of uncertainty when the measured effect on the dosimeter is interpreted as a risk for degradation of a material. Increasing values obtained from MEMORI measurements should therefore be interpreted as a deteriorating environment for preservation of indoor cultural heritage with **indication** of different risk levels for different materials as shown by the traffic light evaluation.

### **3.3 Effects of organic acids on museum objects**

#### **3.3.1 Introduction**

The preservation of museum objects depends on their original condition, the type of materials they are made from, and on the quality of the environment where they are stored or displayed. In many indoor environments, and especially in less ventilated enclosures, concentrations of organic acids and Volatile Organic Compounds (VOCs) are often much higher than those of the inorganic gaseous pollutants.

More and more museums and institutions are using different kinds of protection enclosures, such as showcases, for different kinds of objects. In addition microclimate framing with front glass for paintings and storage boxes for archival materials are used to protect the objects from the impact of the environment.

Investigations were performed in the EU FP6 PROPAIN project about the environmental conditions inside enclosures that protect movable cultural heritage objects. Generally, the positive effects of enclosures are to reduce the effect of external humidity fluctuations, to decrease the negative influence of external pollutants, as well

as to offer protection against vandalism. However, little is known about the possible long term impacts of organic compounds, and particularly the organic acids, on the museum objects that are often protected by enclosures. The main organic acids to consider are acetic acid ( $\text{CH}_3\text{COOH}$ ) and formic acid ( $\text{HCOOH}$ ). Other organic acids, e.g. oxalic acid, may have degrading effects, but they are usually found in museum and archive enclosures at much lower concentrations than acetic and formic acid. The main indoor sources of organic acids are all wood species; with oak particularly emissive, and also wood composites.

A main objective for MEMORI has been to systematically study and assess the impact of organic compounds, and in particular the more aggressive organic acids, on movable cultural heritage objects made from cellulosic materials, leather/parchment, textiles, in addition to pigments and varnishes.

The following conclusions have been made from the extensive studies in MEMORI, assessing the effect of organic acids on the following materials.

### **3.3.2 Cellulosic materials**

The effect of exposure of acidic volatiles on paper degradation was explored in detail, by the University of Natural Resources and Life Sciences, Vienna, to finally generate practically valid guidelines for conservation of cultural heritage objects consisting of cellulose (Figure 3). In order to simulate cellulose degradation by acids, the conventional ageing in closed vessels had to be modified and a better understanding on how to perform an accelerated aging for paper has been established.

Ten different species of papers were aged naturally (room temperature) and under accelerated (elevated temperature) conditions in presence of different concentrations of acetic and formic acid.

Evaluation of paper degradation induced was carried out by measuring the molar mass distribution and keto/aldehyde contents using size-exclusion chromatography with MALLS/RI and selective fluorescence labeling – a special technique which is able to report even small changes to the cellulose molecule and hence able to judge the stability of the most important polymer in paper - cellulose. This approach allows to measure the velocity (speed) of cellulose degradation, i.e. how fast a cellulose chain is split under the conditions applied. The longer the cellulose chains on the molecular level are the stronger the overall polymer is. Chain length can hence be directly correlated to the stability of the paper or textile. The faster the cellulose molecules (polymer chains) are cleaved the faster the material deteriorates. Hence, the speed of degradation is an useful measure to analyze the stability in the presence of e.g. organic acids.

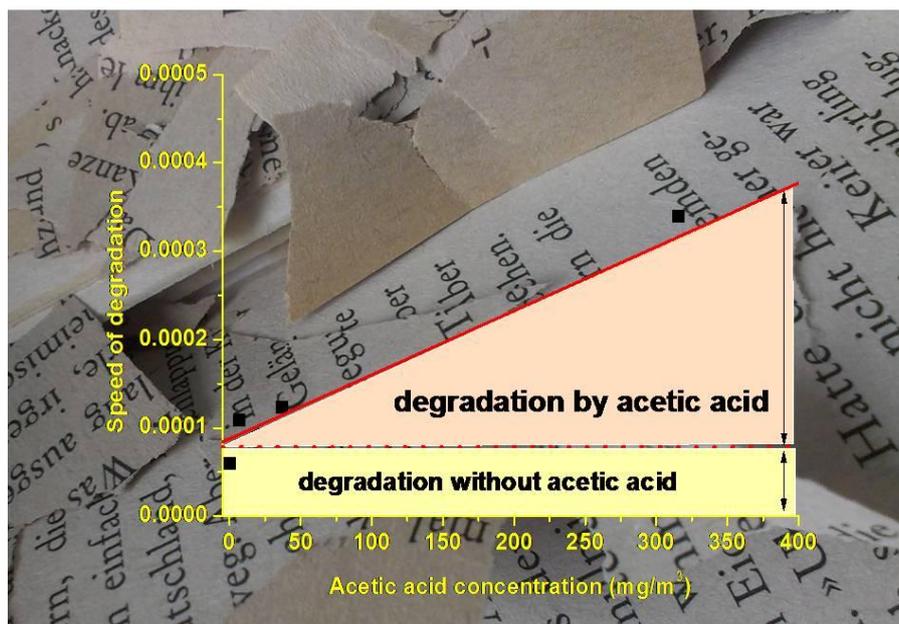


Figure 3: Schematic presentation of the effect of acetic acid on paper.

The rate of cellulose chain scission, as mentioned above a sensitive measure to analyze cellulose stability, could be determined as a function of acidic vapour concentration at different aging periods and different temperatures. The rate of degradation obtained is directly proportional to the concentration of acetic acid vapour – a parameter analyzed by the MEMORI dosimeter. Acetic and formic acid are able to accelerate cellulose degradation even at low concentration ( $>1.5 \text{ mg/m}^3$ ) levels of acid vapour.

The results from the different exposure types, tested in order to get reliable results, imply that hydrolysis of cellulose in presence of acidic vapour is not only dependent on the concentration of acid in the vapour, but also on the amount of acid in the paper after reaching an equilibrium between acidic vapour and acid within the paper.

Finally, kinetic studies of cellulose degradation at various temperatures and concentrations of acidic vapour allowed for the estimation of half-life degrees of polymerization of paper at different conditions and an extrapolation to room temperature. All relevant paper types, like the typical 19<sup>th</sup> century book paper, a rag paper, Whatman as a model paper and also lignin containing materials like a thermo mechanical pulp, relevant for newsprint, have been analyzed (Figure 4).

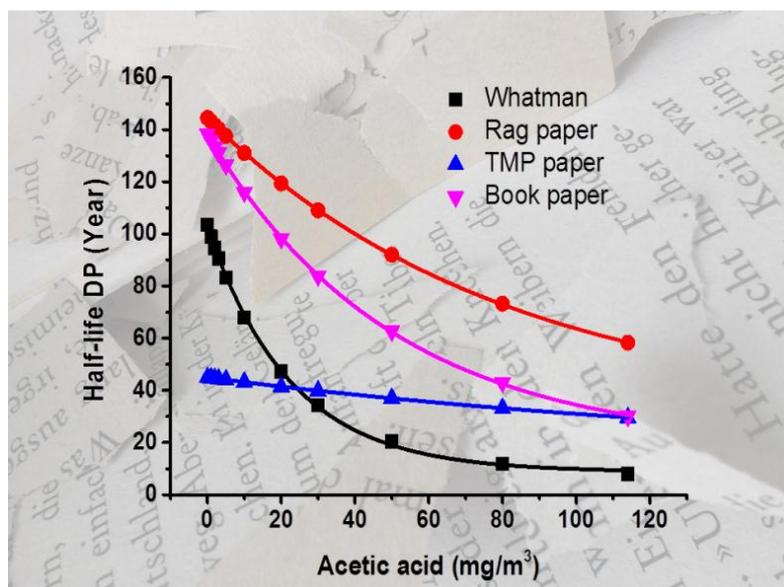


Figure 4: Effect of acetic acid on different paper types at ambient conditions.

In order to compare different paper types or cellulosic materials the concept of half-life DP (degree of polymerization) was applied. The half-life DP can be defined as the time needed to change the cellulose chain lengths to half of the original value. Cellulose usually contains many chains of different length, hence a chain lengths distribution exists. Based on the analytical techniques applied the chain length distribution, which is similar to the molar mass distribution, can be measured. For this distribution an average value for the chain length is calculated. The half-life DP is reached when the averaged value decreased to 50 % of the original value.

Based on the established dataset a relationship of the half-life DP as a comparable parameter in relation to different concentrations of acids, ie. acetic or formic acid at ambient conditions for different papers are now available.

The data at ambient conditions are finally necessary to reflect the situation at museums, libraries and archives. The results generated in this extensive study provide valuable data on the damage potential of organic acids for various paper types, such as rag paper, book paper, and lignin containing paper. This data matrices allow prediction of paper stability under real world conditions in a more reliable way. In addition, the data obtained can be transferred to other works of art containing cellulose, such as textiles made out of cotton, hemp or flax.

### 3.3.3 Leather/parchments

The Royal Danish Academy of Fine Arts, School of Architecture, Design and Conservation together with the Thermal Methods and Conservation Science Centre at Birkbeck, University of London, assessed the damaging effects of acetic and formic acids on parchment and vegetable tanned leather. The following materials were chosen: two new vegetable tanned leathers (sumac and mimosa), one historical vegetable tanned leather, one modern parchment (p) and one historical parchment (hp). The samples were exposed to acetic acid ( $c \leq 400 \text{ mg/m}^3$ ) and formic acid (3.3 vol. % -  $56.9 \text{ mg/m}^3$ ), a

mixture of the two, and then a blank with no acids for up to 16 weeks at 75% relative humidity (RH).

Exposure to acetic acid led to significant change from 0.3 to 0.9 pH units after one week of exposure for all three leathers and it stayed at the same level during the full ageing period. The same was the case for mimosa exposed to the mixed gases. However, with respect to the 3% HCOOH exposed samples, there seemed to be a tendency for increasing pH by exposure in case of historic and sumac and the opposite for mimosa. As expected, exposure to humidity alone did not lead to any significant changes in pH of any of the leathers.

Colour changes were observed on all leather samples including those exposed to moisture only. In particular, the data showed a significant change in colour for mimosa leather exposed to mixed acids compared to both the reference samples and the moisture treated mimosa samples.

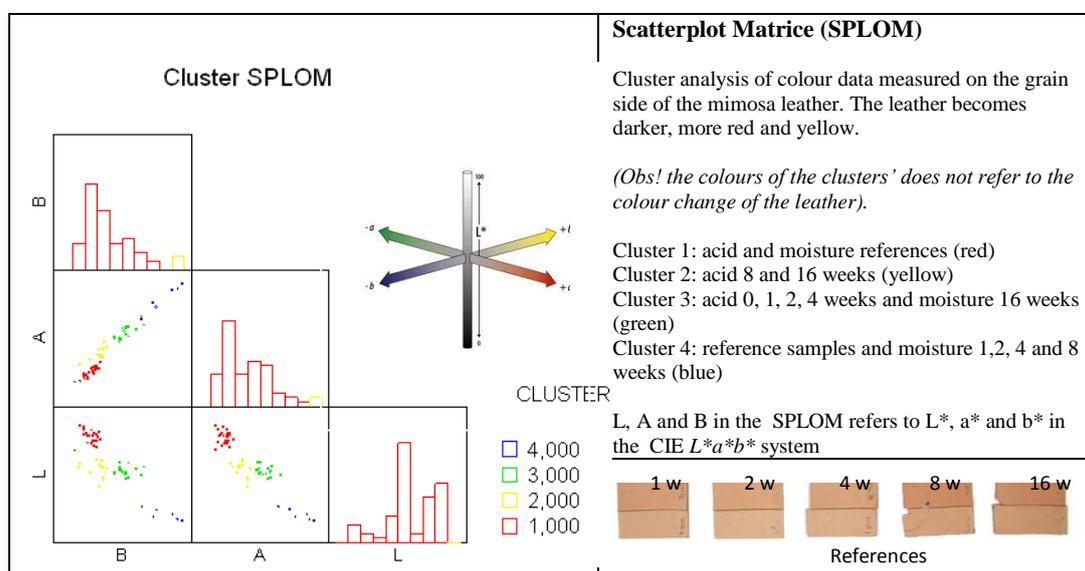


Figure 5: Scatterplot Matrice presenting a cluster analysis of colour data measured on the grain side of the mimosa leather.

The cluster analysis showed a significant separation of the 8 and 16 weeks acid exposed samples from all other samples (Figure 5). The colour change was a result of chemical modifications of the tannins which was accelerated by exposure to organic acids.

No significant changes in the hydrothermal stability of leather were observed. Atomic Force Microscopy (AFM) of mimosa leather showed changes in the morphology of the surface fibres. Surface gelatinisation occurred following 8 weeks of exposure to acetic acid (10%) at 75% RH. There was also a reduction in the elastic modulus of the sample.

With the mixture of acetic and formic acids at 75 % RH sumac leather showed a different response with respect to the individual reference samples after 1, 4 and 8 weeks of exposure. The measured differences were correlated to the extent of gelatinisation, already in the previous IDAP project. Differences of 3.8, 10.1 and 22.6% were observed by controlled environment Dynamic Mechanical Analysis (DMA). In

comparison thermal ageing at 120°C for 96 hours gave a value of % change of 9.5%. This measured the change in sample displacement with programmed increase in RH.

Preliminary measurements with controlled environment (DMA) for historical leather appeared to show that formic acid had an effect, more so than the sample exposed to 75% RH alone. Exposure to formic acid caused an increase in stiffness and an accompanying reduction in viscoelasticity, indicating that some hardening and cross linking of the leather had occurred.

For parchment, the effect of exposure to acetic acid ( $c \leq 400 \text{ mg/m}^3$ ) at 75% RH up to 16 weeks caused acid to be trapped inside the parchments; this was illustrated by a significant drop in the hydrothermal stability and by a significant drop in pH accompanied by swelling of the parchment structure. However, after a degassing period of at least two weeks only a slight but significant decrease in the hydrothermal stability could be detected in parchment. Although the hydrothermal stability of historical parchment seemed to be almost unaffected by the acid exposure, the drop in pH and swelling as well as shrinkage of its fibre structure during exposure were also significant.

Observed morphological changes of the fibres show that acetic acid exposure induced permanent damage to both parchments. This was confirmed by AFM and micro-thermal analysis which indicated that surface gelatinisation had occurred following 8 weeks of exposure to acetic acid (Figure 6a and Figure 6b). It should be noticed that our observations showed that a somewhat longer exposure to moisture alone led to similar morphological changes and similar changes in the hydrothermal stability of the fibres.

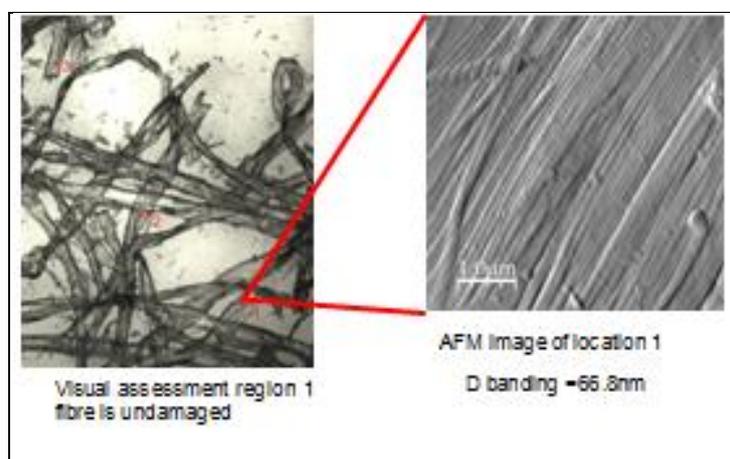


Figure 6 a: Shows location on undamaged parchment fibre from parchment P(053) before acid exposure and its AFM image with the regular banding pattern of collagen (67 nm spacing).

It can be concluded that the acetic acid exposure in 8 weeks had reduced the pH of both parchments from around 6.7 to around 4 for historic and 3.85 for modern parchments where the risk for extreme swelling in moist or humid condition was present for most parchments. Degassing only raised the pH less than one pH unit in both cases. Compared to samples exposed to 75% RH only, the swelling/de-swelling activity of the acid exposed samples were higher for both the modern and historical parchment.

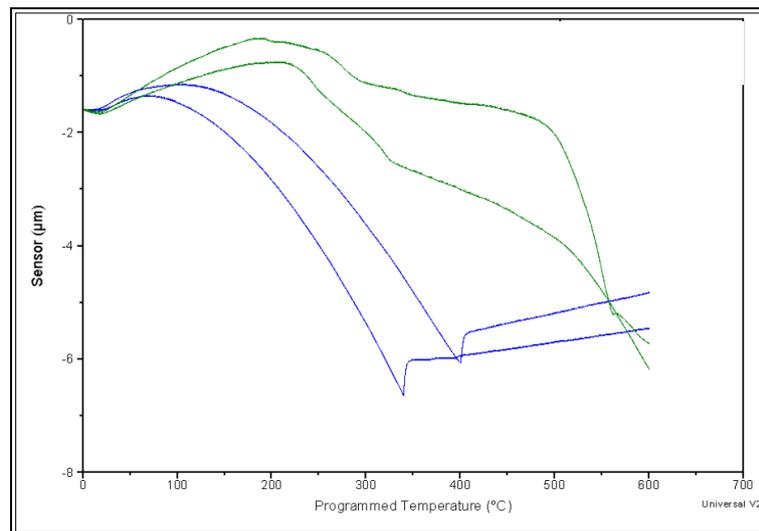


Figure 6 b: *Microthermal analysis which measures surface displacement ( $\mu\text{m}$ ) with temperature shows the effect of 8 weeks of exposure to acetic acid; blue curves (unexposed) and green (after exposure). The shift to higher temperature is evidence that surface gelatinisation has occurred.*

A two column t-test of the means of the measured thickness in mm (which represents a measure of the swelling/de-swelling) of the historical parchment samples before and after exposure showed that the thickness in average was significantly higher for the exposed samples (Figure 7a).

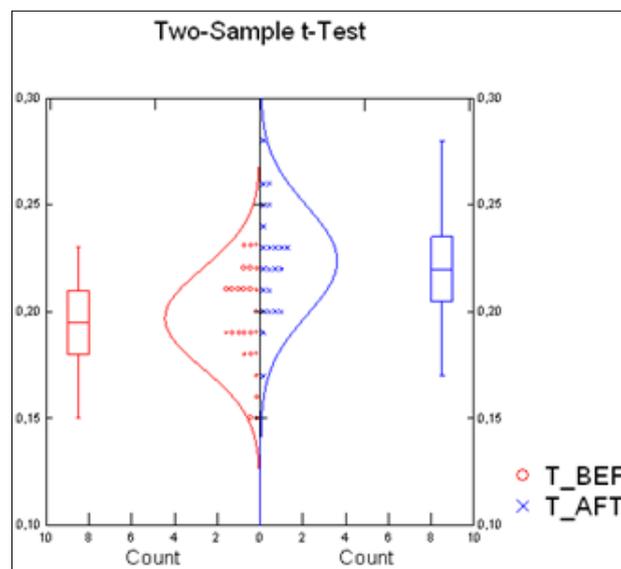


Figure 7 a: *Plot of the measured thickness in mm of historical parchment samples before ( $T_{\text{BEF}}$ ) and after ( $T_{\text{AFT}}$ ) 1, 2, 4, 8 and 16 weeks' of acid exposure. Curves show the t-distributions and bars and boxes the standard deviations and position of the sample averages, respectively.*



*Figure 7b: Historical parchments (origin unknown): Movement of the fibre network may cause the stiff ink layer crack and flake off.*

Despite the fact that no change in hydrothermal stability even after 16 weeks' of exposure was observed for the historical parchment, our results indicated that a degraded and weaker fibre network will be subjected to relative greater physical strain by swelling/de-swelling under the same storage conditions compared to a less degraded parchment. Therefore, we recommended examining if organic acid exposure in ambient doses over relative longer time may cause the same destructive lowering of pH and surface gelatinisation as this may lead to severe damage including loss of text and paint layers when the parchment structure swelled or contracted (Figure 7b).

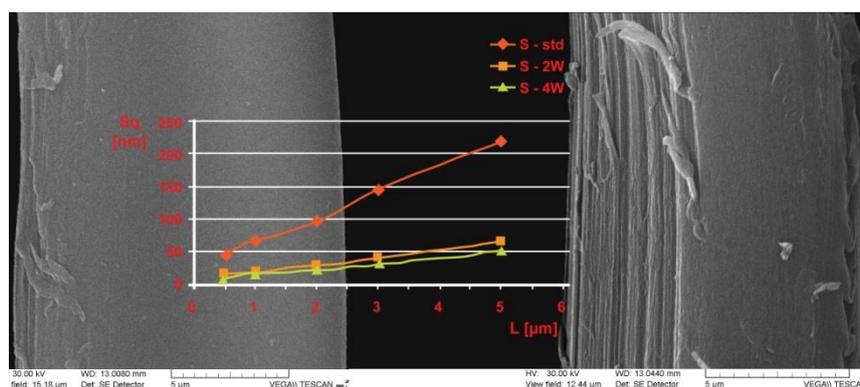
### **3.3.4 Textiles**

Laboratory experiments and studies to evaluate and quantify the risk for degradation of silk and wool materials due to exposure to organic acids, analyses of different textile samples subjected to accelerated acetic acid exposure and of textile object surfaces in situ were performed. Accelerated ageing of textile material has been performed to determine the chemical changes caused by exposure to the concentration levels of particularly organic pollutants observed indoors in cultural heritage collections and in protective enclosures for movable cultural heritage assets.

Scientific investigations of movable cultural heritage objects from medieval collections and historic samples from museums & galleries (from Tismana, Putna and Sucevita monasteries, and Romanian Military National Museum Bucharest) have been accomplished. The selected cultural heritage items for sampling are dated and were easy to handle due to a good state of conservation. The English Heritage partner collected historic woollen samples and delivered them to UAGE to analyze them. The historic textile materials, including wool, silk fibres and the golden threads have been visualised with the optical microscope – Polarised Light Microscopy, the elemental chemical composition have been analysed with EDX, while the threads analysis have been performed with micro-FTIR, and the micro-morphology have been investigated with SEM and AFM. Physical parameters of the materials have been determined, including the breaking strength, imaging fibre assessment, and colour changes. These techniques have been chosen to determine and monitor the process of degradation,

modifications of the molecular composition and physical properties, as an effect of ageing. Complementary analytical techniques have been used to understand and detect chemical alterations at the molecular level.

The evidence of changes during acid exposure of silk have been put into evidence by FTIR, SEM and optical microscopy analysis correlated with physical parameters of the materials as the breaking strength, fibre assessment and colour changes. The most visible impact of acidic environment have been observed on the raw (un-degummed) silk, on the outer layer of sericin. It was obvious that after two weeks of exposure at acetic acid, it becomes brittle and is detaching from the fibroin. Exposed at acetic acid the degummed silk started to deteriorate after two weeks and intensity of degradation processes intensifies alongside the increase of exposure time (see Figure 8).

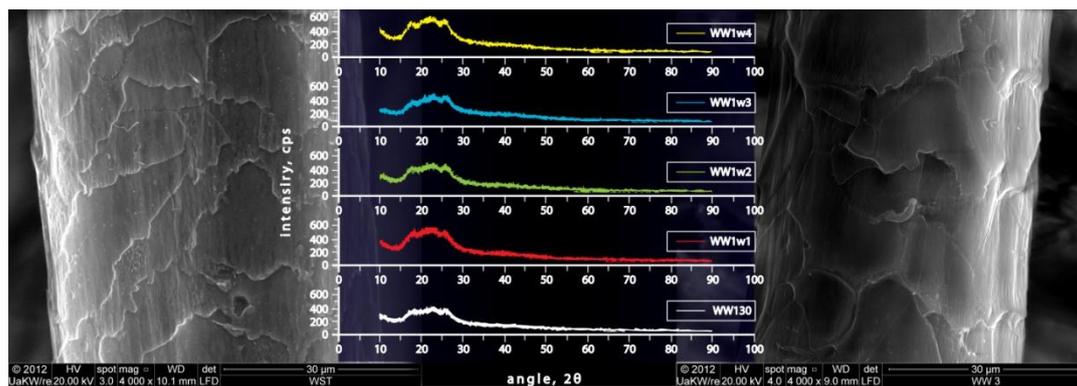


**Figure 8:** Evolution of the normal strain ( $\epsilon = Sq / L$ ) correlated with the dose of exposure; extreme deterioration process is visible using SEM (the degummed silk exposed at acetic acid starts to deteriorate after two weeks and extensive detachments that occurs after four weeks made the fibre very brittle).

Four stages of deterioration were recognized in the silk: (a) micro-fissures were observed in the fibre with the erosion of the surface, (b) the deterioration became greater and occurs mainly at the edges, (c) detachments along the axis of the fibre took place, in the form of fine strips of material peeling off the surface, (d) an extreme deterioration process was visible, an extensive detachments that made the fibre very brittle. The tensile test have been conducted on the silk fibres, a method of analysis that is characteristic of the properties of materials ( $\sigma$  and  $\epsilon$ ) rather than the dimensions or load ( $\delta$  and  $P$ ) of a particular specimen. The normal strain ( $\epsilon$ ) or extension strain expressed by the deformation ( $Sq$ ) and unit length ( $L$ ) shows that the mechanical properties of the aged silk are dramatically modified after two weeks and no major changes occurred during the third and the fourth weeks (Figure 8). This proves that the cracking patterns are similar for both accelerated and natural aged silk, mainly longitudinal micro – fissures, detachments and some transverse cracks in historic samples only. Specific and clear trends in change of the  $\Delta E$  values by exposure at both acetic and formic acid have been found. The silk from historic objects have suffered processes of hydrolysis and denaturation of the polypeptidic chain chain due to acetic acid exposure. The transformation of the polypeptidic chain results from processes of oxidation, hydrolysis and / or denaturation of the amidic structure. The (AI / AII) hydrolysis degree of the cultural heritage samples is 2 – 7 % higher than that of the reference and the hydrolysis degree considering the band from  $450 - 3300 \text{ cm}^{-1}$  is also higher than in the reference,

also the denaturation degree ( $\Delta v$ ) shows a 1 – 8 % increase. The hydrolysis degree of the cultural heritage samples is 2 – 7 % higher than that of the reference and the denaturation degree shows a 1 – 8 % increase.

The impact of accelerated acidic exposure of woollen samples was analysed by SEM, AFM, XRD and FTIR. The effect of formic acid on wool has a grater negative impact. The deterioration of scale tissue started after first week of exposure, during the second week detachments and loss of scale occurred, after three weeks the cuticle is severe damaged and detached, cracks alongside the fibres were formed and radical loss of it was visible after four weeks (Figure 9).



*Figure 9: XRD analyses are correlated with the imaging techniques SEM/EDS. Deterioration of the wool structure increase by chemical breakdown of disulfide bridges within structural units of the first layer and the exocuticle and matrix of the cortex.*

Two amino acids, components of wool, glycine and glutamic acid show a different degree of crystallinity. The acetic acid treatment agent generates crystallization of glycine and the increasing degree of crystallinity of glutamic acid. Cumulative diffractogram of XRD data for wool fabric samples, Figure 9, suggests that the crystallization of glycine was induced by treatment agent and glutamic acid degree of crystallinity was increased. At the base of cumulative diffractogram, reference diffractograms of cystine, glycine and glutamic acid (alfa and beta) were represented. Glycine: Peak from 14.64 deg. - was “increased” from samples no. WW1 to WW4 – the influence of treatment upon crystal consisted in formation of this structure. Peak from 25.26 deg. – was missing in the WW130, WW 1 and WW2, and appeared in WW3 and WW4, “slightly” derived from glycine growth crystals (it probably was a “weak altered” crystal). The peak from 25.26 was characteristic for (110) plane of glycine. In the case of apparition of characteristic peaks of glycine, most credible hypothesis was the crystallization of glycine induced by treatment agent. This induces increased fragility of wool fibres. The deterioration of the wool structure increase by chemical breakdown of disulfide bridges within structural units of the first layer and the exocuticle and matrix of the cortex and the establishment of new intra- and intermolecular cross-links via reaction of these carbonyl groups with protein amino groups within and between structural units. These reactions most likely led to a gradual increase in brittleness and a gradual loss of structural differentiation, as already have been illustrated by SEM/EDS analysis and micrographs that support these conclusions. For wool aged samples no clear trends in change of the  $\Delta E$  values by exposure at both acetic and formic acid have been found. Fibres from the historic samples showed a

granular / fibrillar fracture indicating moderate loss of interfibrillar cohesion that causes a break of rough surface appearance, defined by groups of morphological units. Most samples exhibited a variety of breaks including brittle, granular, fibrillar and multiple split ends. The most commonly found fractures were a combination of granular and fibrillar and were similar to the fractures found in aged wool. Acid attack on the peptides bond, salt linkages and secondary bonds of accessible keratin chains in the amorphous regions can change the structure of the wool. After photo-oxidation, the disulphide link may turn into a sulphonic acid side group, which can cause acid hydrolysis of neighbouring peptide bonds.

The impact doses have been observed but it has not yet been possible to establish threshold levels based on no observable adverse effects levels (NOAELS) and / or lowest observable adverse effects levels (LOAELS) for exposure of textile materials to organic acids.

Silks with remnant sericin gum coating the fibroin fibres would require different conservation protocol. A link of the scientific results at macromolecular level with the observed impact of acidic concentrations and doses at a visual level have been established. Optical microscopy visualisation could be correlated with scanning electron microscopy, FTIR microscopy as useful imaging techniques that put together information on observed state of conservation at macro level, micro level and molecular level. Evidence have been found for the degradation of wool and silk textile due to exposure to formic and acetic acid; however more research is needed to understand the level of risk. The new knowledge will make possible better assessment of the present environmental risk to the textiles due to air pollution and possible mitigation actions that can be implemented to reduce the risk.

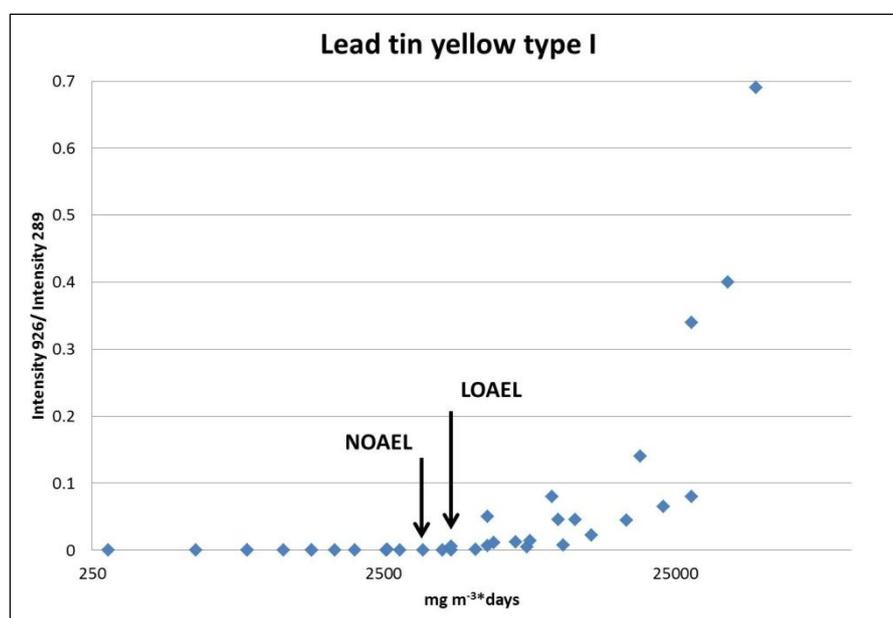
### 3.3.5 Pigments

The investigation of the effect of organic pollutants on pigments was carried out on model samples at Ghent University (Belgium) by means of non-destructive techniques. Five pigments were selected for in depth investigation: lead white, red lead, lead tin yellow type I, malachite and sunfast orange (PO36). Experiments were carried out with no binder medium and no varnish layer, representing a worst case scenario. Both the binder medium and varnish would be expected to protect the pigment.

Periodical investigation of pigments samples exposed to organic pollutants (different concentrations of acetic acid in the atmosphere, different length of exposure) was carried out with different techniques, as digital imaging and vibrational (Raman) spectroscopy, to evaluate both the on-going visual changes and molecular modifications. It is important to point out the availability of mobile/portable Raman instruments: in situ measurements are becoming more and more exploitable for the survey and monitoring of works of art inside their environment.

On exposure to acetic acid in the range ca. 280 mg m<sup>3</sup>\*days - 142000 mg m<sup>3</sup>\*days (1 week of exposure to 1% acetic acid at 75% RH and 7 weeks of exposure to 100% acetic acid at 75% RH, respectively), colour changes were observed for all pigments, but no specific trend could be defined. For the three lead based pigments, lead acetate was detected by means of Raman spectroscopy as the expected degradation product.

The combined effect of the concentration of acetic acid in the atmosphere and the length of the exposure is expressed through the *dose*. The relative intensity of the degradation product (i.e. the ratio between the Raman intensity of the degradation product band versus the Raman intensity of one characteristic band of the intact pigment) was then correlated with the acetic acid dose responsible for that change, as in Figure 10 for lead tin yellow type I. Alteration is likely to occur for doses above 4250 mg m<sup>3</sup>\*days (lowest observable adverse effect limit, LOAEL), while up to a dose of ca. 3400 mg m<sup>3</sup>\*days no changes in the sample can be detected: it means that the environment can be considered safe for that specific pigment. This latter value corresponds to NOAEL (no observable adverse effect limit) and is set at 20% lower values than LOAEL. Between these two values, the environment can be potentially harmful. The change in air quality is reflected in the formation of the expected degradation product. For red lead and lead white safe doses are below the NOAEL value of 2000 mg m<sup>3</sup>\*days, while those above 2500 mg m<sup>3</sup>\*days (LOAEL) are responsible for the formation of a detectable amount of lead acetate.



*Figure 10: Correlation of relative intensity of the degradation product's Raman band with the calculated dose of acetic acid. The lowest observable adverse effect limit (LOAEL) is the lower dose that produces a detectable amount of degradation product, while no observable adverse effect limit (NOAEL) is set at 20% lower dose. The environment is not expected to damage the material for doses below NOAEL, above LOAEL, on the other hand, it is likely to be harmful.*

No experimental work was carried out with formic acid and no research has been found in the literature. The risk categories have been assigned keeping in mind that the results come from a simplified model that results in a more aggressive attack of the investigated materials. This consideration implies the need of studying real paintings with a special focus on the identification of degradation products to better understand the behaviour of pigments under real-life exposure, as well as the confidence that the determined harmful doses are related to very extreme conditions, thus being safe under “normal” situations.

### 3.3.6 Varnish

Part of the MEMORI project has focused on investigating the effect of organic pollutants (acetic and formic acid) on varnishes. This investigation was performed by the Department of Chemistry and Industrial Chemistry, University of Pisa, and the Thermal Methods and Conservation Science Centre at Birkbeck, University of London. Experiments were based on the following varnishes, dammar, resin mastic, Regalrez 1094, Laropal A81 and dammar with a coating of Regalrez 1094.

For all the varnishes studied damage has been observed, from the chemical and physical point of view. Natural resins dammar and mastic showed oxidation under exposure to organic acids (Figure 11).

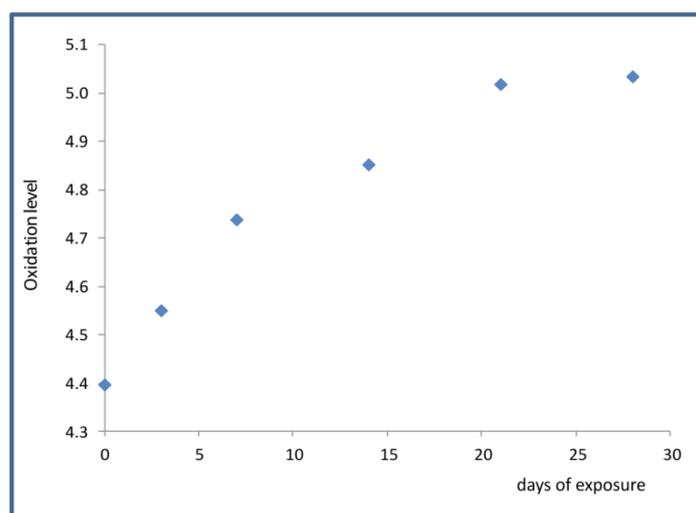


Figure 11: Oxidation level of dammarane compounds in dammar resin measured by gas chromatograph mass spectrometry (GC-MS) as a function of days of exposure to acetic acid 1%, 75% RH.

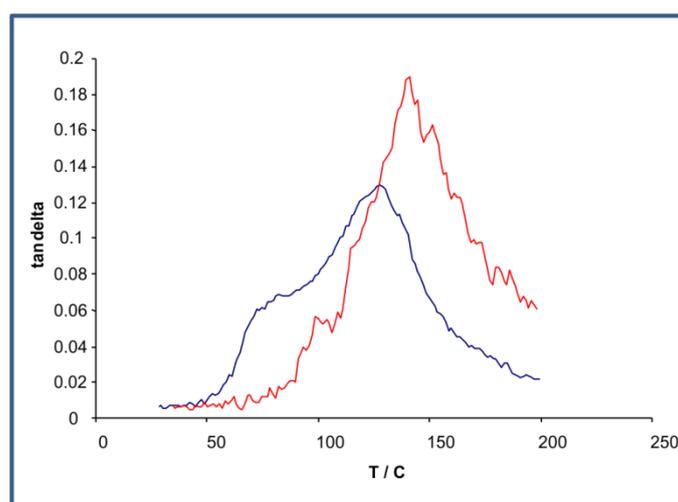
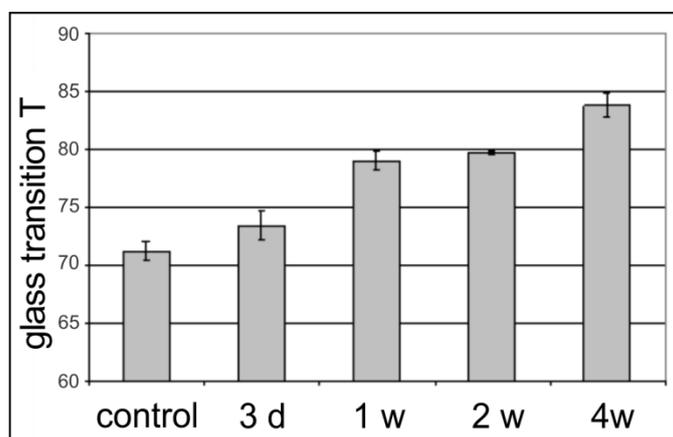


Figure 12: Effect of acetic acid on resin mastic measured by dynamic mechanical analysis (DMA): Control (dark blue) and mastic varnish exposed to acetic acid 1%, 75% RH for 4 weeks (red). The shift of the peak towards

*higher temperatures from blue to red to green indicates increased degradation of the resin.*

Molecular changes observed are responsible for changes in the physical properties of the varnish, both from the optical and mechanical point of view. An oxidised and cross-linked varnish is embrittled, less plastic, might result in worse optical performances and is thus destined to a shorter life. Moreover an oxidized and crosslinked varnish requires the use of polar solvents for solubilisation during conservation treatment, which would be aggressive to the paint layers underneath.

In general there is evidence that the synthetic varnishes, Regalrez 1094 and Laropal A81 are more resistant to organic acids than the natural triterpenoid resins. In particular for synthetic varnishes damage was observed mainly using surface techniques (3), but this is a precursor for further damage to the bulk of the varnish. Figure 13 shows that the glass transition temperature increases with acid exposure. This means that a higher temperature is required before the varnish softens.



*Figure 13: Increase of the surface glass transition temperature of Laropal A 81 on exposure to acetic acid 1%, 75% RH as a function of the days of exposure, measured by micro thermal analysis.*

Once proven that organic acids can cause damage to the paint varnish, it is important to understand the extent of this damage, in relation to other known sources of damage such as temperature and light. Experiments showed that thermal ageing caused much more damage than the ageing with acetic acid alone. Preliminary experiments were performed by exposing dammar model varnishes to acetic acid, formic acid, light and a combination of light and acetic acid. The analysis of these samples showed that acetic and formic acid cause cross-linking (and thus a loss of solubility), but the effect of light, alone and in combination with acetic acid was much more pronounced. This indicates that light ageing causes more damage than ageing with organic acids. The data also showed that the combination of light and acetic acid is the most damaging, highlighting a synergistic degrading effect.

These results are confirmed by the analysis of varnishes exposed at selected sites (Figure 14). Here the dynamic mechanical analysis (DMA) curve of a dammar control sample (blue line) is compared with those of dammar varnishes exposed at Tate (UK) in a transport packing case (red curve) and Chesters in a showcase (green curve). The

total dose of organic acids for both locations was the same ( $20 \text{ mg m}^{-3} \cdot \text{days}$ ). However, at Tate the varnish was kept in complete darkness, at Chesters the varnish was exposed to low light levels. Data show that varnish samples exposed within the packing case in Tate store were damaged as a result of their exposure to the level of organic acids present in the packing case. At Chesters where the varnish samples were exposed not only to similar levels of organic acids but also to light the damage was higher. Figure 14 shows the DMA curves. The shift of the peak towards higher temperatures from blue to red to green indicates increased degradation of the varnish.

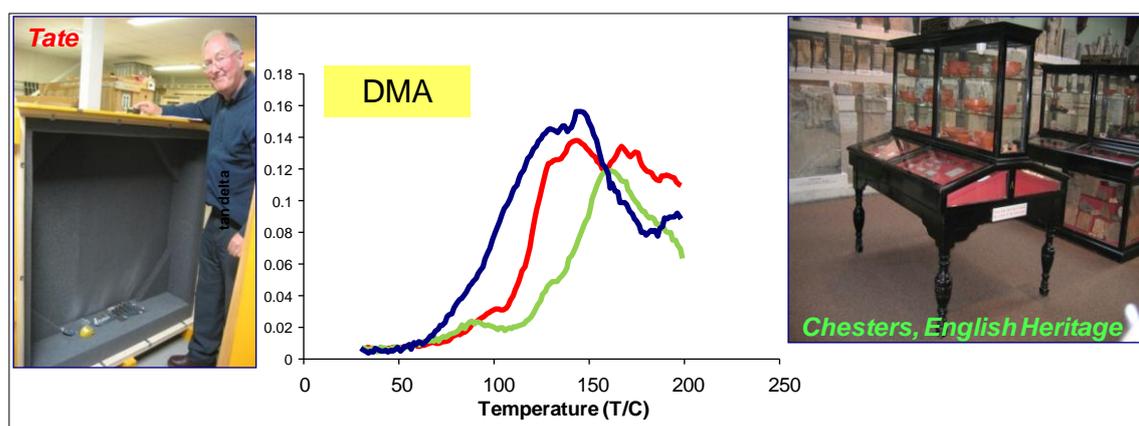


Figure 14: Effect of exposure to organic acids on site for dammar resin sample: DMA curves of control sample (blue line) a dammar varnish exposed at Tate (UK) in a transit frame (red line) and Chesters (UK) in a showcase (green line). In both locations the dose of organic acids was ( $20 \text{ mg m}^{-3} \cdot \text{days}$ ).

Although quantification of the lifetime of a varnish is in general not possible, as the combined effect of all possible environmental parameters cannot be known, these results clearly indicate that monitoring levels of organic acids is fundamental. If in fact levels are known to be high, it is possible to intervene to reduce as much as possible sources of damage.

### 3.4 Recommendations for mitigation of airborne pollutants in museum enclosures

#### 3.4.1 Introduction

The Fraunhofer WKI Institute (Germany) was responsible for the development of mitigation strategies for the sustainable improvement of air quality within museum enclosures, such as showcases, frames, transport crates and boxes. The work performed, with input from several of the MEMORI partners, targeted on the optimization of designs and regimes for control of enclosure environments in order to protect moveable cultural heritage objects. This objective was achieved by two approaches: (1) careful selection of materials for constructing and decorating enclosures, (2) installation of adsorbent media for the sustainable mitigation of pollutant levels.

#### 3.4.2 Main results

In a first step a literature study was performed to screen observed pollutant concentrations of organic acids (formic acid, acetic acid), formaldehyde and volatile organic compounds (VOCs) within museum enclosures used for exhibiting and storing movable assets. This research showed that there are still pollutant problems in showcases throughout Europe, as shown from the investigation done in the EU FP5 MASTER project, see Figure 15.

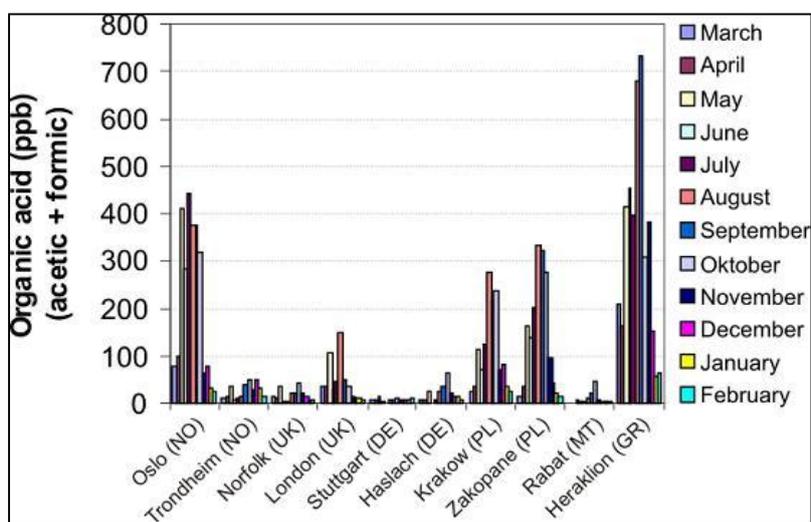


Figure 15: Sum values of formic acid and acetic acid obtained by diffusive passive sampling within showcases in different European museums. Information from the EU FP5 MASTER project.

Based on these results, a range of target substances which are characteristic for indoor air composition in museums as well as applicable adsorbent materials were selected for setting up experimental trials in the laboratory. Target substances were formaldehyde, formic acid, acetic acid, toluene and alpha-pinene. Adsorbing materials were included which are already used within museum environments and those which are especially designed for museum purposes, namely charcoal granulates, foams and cloths as well as zeolites. Some of these materials are very new and innovative and were provided by EMCEL, subcontractor within this task. The experimental studies have included the investigation of chemical and adsorbing properties and of the adsorption rate of the selected adsorbent materials for the target compounds under both active and passive conditions (with/without air flow). It was furthermore investigated if undesired fragmentation products might be generated by contaminant-adsorber interactions. In addition, desorption effects which have been tested as adsorbent materials, might act as secondary emission source, after adsorbing gaseous volatiles, which might be desorbed again at a later stage.

Activated charcoal materials were evaluated as the best performing adsorbent materials for the selected target substances. Both pure activated charcoals and alkaline impregnated charcoals showed a good or very good adsorption capacity. For this reason, the application of impregnated charcoal types, which are mostly more expensive, seems not to be necessary in order to mitigate pollution levels. Although zeolites performed well, no additional advantage was observed over activated charcoal media. As they are more difficult to purchase and might be of higher costs, they were

not recommended for field trials. Products which are especially designed for museum purposes had also no additional advantage according to the test results. Silica gels, which are already installed in most enclosures might have a slight filtering effect, but they are not really effective adsorbent media. Subsequently performed emission analysis of used adsorbent media gave strong indications that most of the materials off-gas toluene and alpha-pinene in a changed atmosphere. As some new substances occurred which could not be detected before performing exposure tests under active and passive conditions, it might be assumed that secondary or degradation products were generated.

Subsequently, adsorbent tests have continued with further investigations on-site in European museums within different kinds of enclosures selected by the project partners SIT (Spain), Tate (UK) and English Heritage (UK). Target compounds were measured before and during deployment of different activated charcoal adsorbents (see Figure 16). Results indicated that charcoal cloth was the most effective adsorbent, and that the new foam material produced by *EMCEL* was also effective, with granulate adsorbents less so. However, there are a number of important factors that could affect this, for example the surface to volume ratio of adsorbent material is very important, in general the granulate materials had a low ratio, where charcoal cloth and the foams had a high surface to volume ratio. In addition, practical considerations have been discussed, as this is often an important factor when working with collection materials. Typically it is easier to install a charcoal cloth, compared to granulate material, as facility trays or similar are required. Moreover, the filtration of target substances seems to be more effective within showcases than within microclimate-frames, perhaps due to the limited air space and air flow.



*Figure 16: Showcase at Aldborough, with the charcoal cloth deployed. Air sampling devices are visible in the bottom right corner.*

Furthermore, a modelling of contaminant impact fluxes was performed, which demonstrated that charcoal cloth was the most efficient adsorber tested during field trials.

In parallel to this work which is mainly focusing on adsorbent media and ways of application, the development and implementation of an optical oxygen sensing sensor for use in anoxic enclosures was successfully performed, in addition to the MEMORI dosimeter system. The optical oxygen sensing sensor developed by partner Dublin City

University, compared well to commercial systems (see Figure 17). The implementation of the sensor in both active and passive anoxic control regimes is moreover possible.

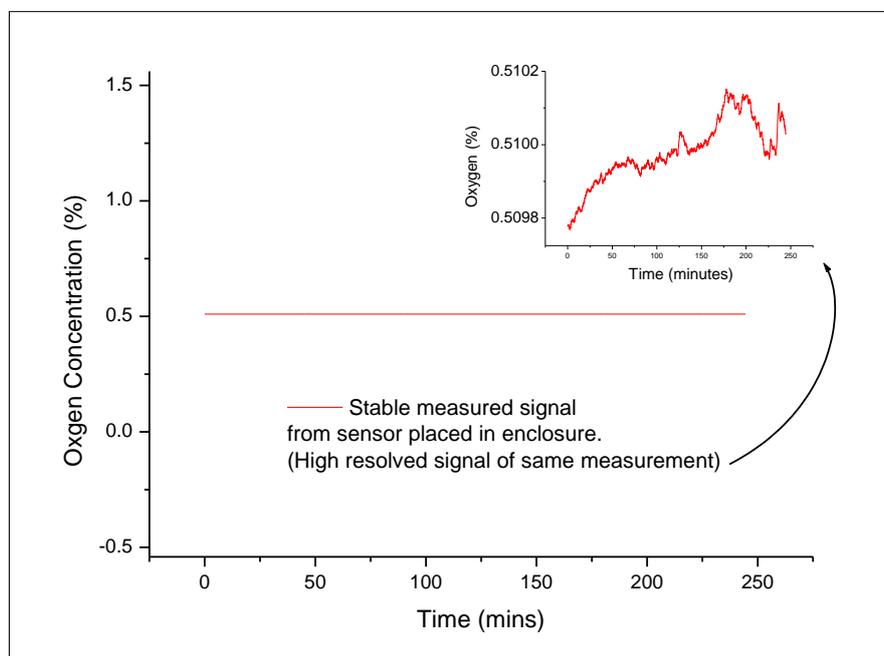


Figure 17: Oxygen measured in a sealed enclosure with use of the optical oxygen sensing sensor developed within MEMORI.

### 3.5 The MEMORI Guidelines for Preventive Conservation

#### 3.5.1 Introduction

The MEMORI user guidelines, which were developed by English Heritage in cooperation with all the partners, are available on the MEMORI web pages <http://memori.nilu.no>. The guidelines describe why, where and when to measure pollutants in general. In addition they describe the risk of damage from the environment due to the effect of humidity, light and air pollutants on a variety of organic and inorganic materials.

The guidelines are presented as the MEMORI technology web pages following feedback from the European museum survey and the first end-user workshop/meeting. The amount of background information has significantly been increased from that first envisaged as a result of feedback from the before mentioned activities. The guidelines also give an overview of the most likely emissions, e.g. organic or oxidising pollutants or sulfides, from different construction materials typically used in protective enclosures.

In addition more detailed information about the most common pollutants, their sources and to what materials they can degrade is presented. A number of tables are presented to allow end-users to quickly identify to which environmental parameters materials are

sensitive, with some consideration of the magnitude of sensitivity, and which materials emit pollutants. These will be used to determine when pollution measurements are appropriate, or if other measurements would be more beneficial as those parameters are likely to present a greater risk to materials present in the collections.

The guidelines give a short description of the types of methods that can be used to measure air pollutants. They discuss the selection of measurement locations that may give the most useful results and how the timing of measurements during the year may affect the measurement results. A tool is provided to determine the time period during the year when the maximum emission of acetic acid is expected. This can be used as a guide for when to measure organic pollutants, and to help understand how representative measurements are, when interpreting results and deciding if further measurements are required.

### **3.5.2 Decision support model**

A decision support model (Figure 18) with a focus on pollutants within enclosures is defined for the measurement, impact evaluation and most effective mitigation actions. This provides a number of tools for end-users to allow them to effectively carry out the process of deciding where to measure, assessing the result and employing mitigation strategies.

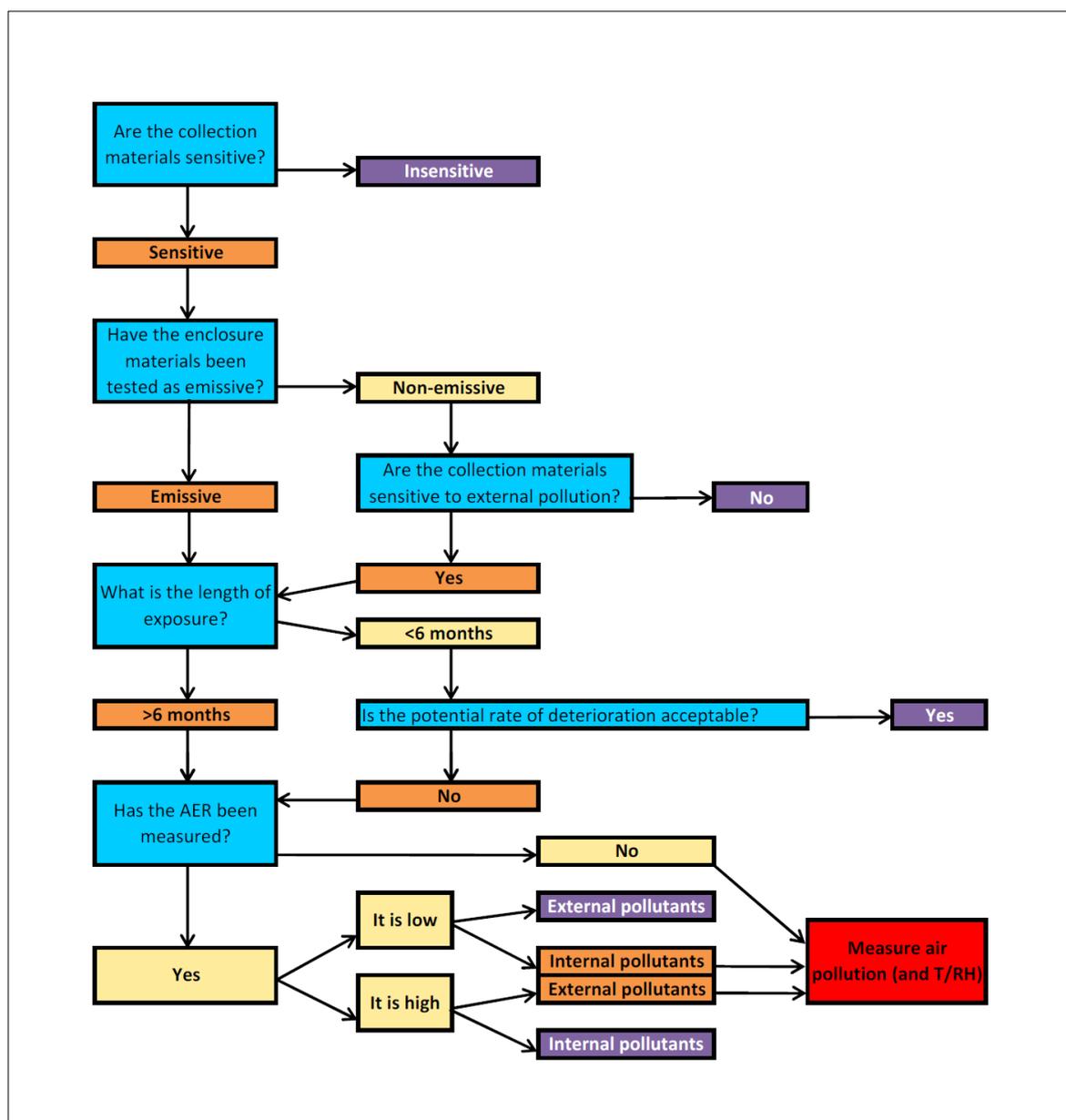


Figure 18: Identification of pollutant damage risk decision support model.

A flow chart helps identify potentially high risk enclosures, where measurements should be carried out. The dosimeter response tables, and supporting information, developed from the literature review and the research performed in MEMORI, allows end-users to evaluate their measurements. A set of questions, with interactive results, helps end-users identify the most effective mitigation strategies, including the cost and energy usage. This is supported by additional documentation to provide in depth information. A number of supplementary tools have been developed to aid end-users in answering the mitigation questions (Figure 19). These include a silica gel lifetime tool, a dehumidifier capacity tool (Figure 20) and a pollutant modelling tool. This decision support model is integrated with general preventive conservation advice.

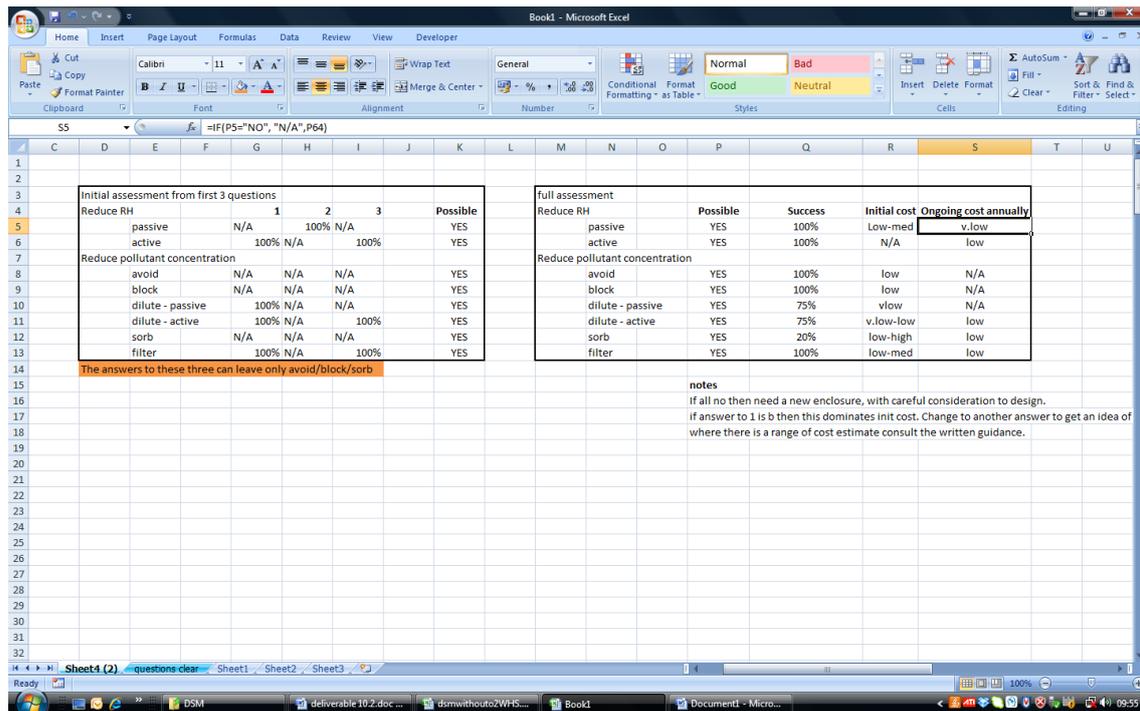


Figure 19: The results section from the mitigation part of the decision support model. The user defined answers feed through to here to inform end-users of the possibility, success rate, initial cost and ongoing cost annually of each mitigation technique, in relation to their own scenario.

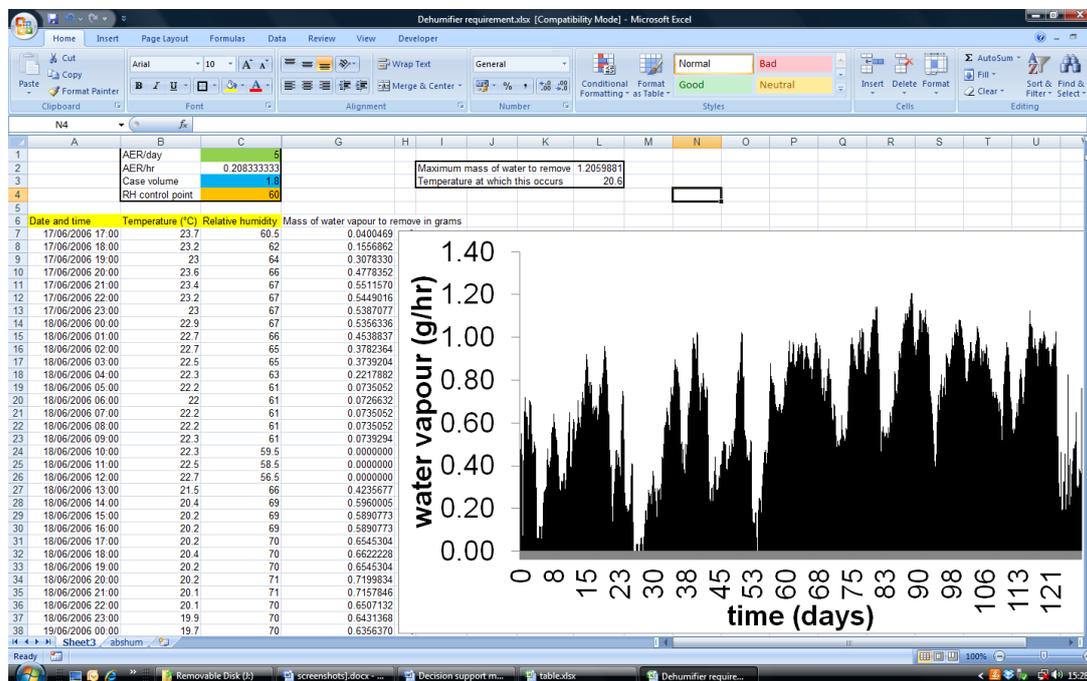


Figure 20: The dehumidifier requirement model from the decision support model. This determines the mass of water to be removed to reach a given relative humidity. This can indicate whether the dehumidifier capacity is large enough for an enclosure. Additionally it can determine whether there is sufficient capacity to split the dehumidifier between enclosures, should other parameters be correct.

This work enables end-users with limited knowledge of pollutant damage and mitigation strategies to reduce the risk of damage to their collections. They can identify enclosures of high risk, assess measurement results, decide where mitigation is required, and implement the most effective strategy within their budget, all tailored to each individual's demands.

## **4 The potential impact, the main dissemination activities and exploitation of results**

### **4.1 Benefits from the MEMORI technology – opportunities for heritage institutions and other business fields**

Following the market analysis described in the MEMORI business plan, developed by Association Culture & Work together with NILU Innovation, the MEMORI technology may offer opportunities beyond the cultural heritage field. The Cultural Heritage market size is not too broad and the market itself is segmented in the following user groups:

- Cultural heritage exhibitors
  - Museums (large and small)
  - Galleries
  - Archives
  - Libraries
  - Theaters
  - Private persons collections
  - Cultural heritage sites (e.g. historical buildings)
- Cultural heritage service companies
  - Conservation companies
  - Manufacturers of showcases
  - Art transportation companies
  - Insurances
  - Consultancies

Their benefits from MEMORI were described in the marketing brochure and validated with members of the end-user panel. Benefits were also identified clearly in the final conference and accepted by the community of conservators and art historians.

More interesting in terms of additional opportunities are the transfer fields for the MEMORI technology such as

- Health and hygiene
- Mining
- Safety
- Pollutant-free rooms for big data processor facilities

In the latter, sensor technologies play an important role in the monitoring and maintenance of indoor climate in rooms which have to be kept pollutant free. Additional transfer fields are likely to show up at a time when more experiences with the technology are available. Partner NILU Innovation is interested to explore these transfer business fields at a later time.

## 4.2 Consultation with end-users via a web based survey

A web based survey with the title „The current situation and management of indoor air quality (IAQ) in European museums, archives and libraries“ was performed between January 30, 2012 and March 4, 2012. The aim of the survey was an empirical study on indoor air quality (IAQ) in European collections. The objectives of the study were the identification and evaluation of the current situation and the management of IAQ in collections. This will help to get a better understanding of the IAQ in European collections and to provide the conservation market with innovative non-destructive diagnosis technologies for easy assessment of environmental impact on indoor cultural heritage. A summary can be found on the MEMORI project web pages (<http://www.memori-project.eu/531.html>).

The survey was conducted in 103 European museums and cultural heritage institutions Europe wide on coping with damage by airborne pollutants. According to the results of the survey there are three main reasons for not measuring airborne pollutants: (1) there is not enough awareness about airborne pollutants, (2) there is a lack of financial resources and (3) there is not enough (qualified) staff in museums. Accordingly the dissemination activities of MEMORI focused on these facts to raise awareness about the overall topic in order to convince executing bodies to invest in damage prevention. This was implemented in 3 different arrangements (training days) for heritage institutions.

## 4.3 Training days for heritage institutions

The **first training day for stakeholders** related to the use of the MEMORI technology was cooperatively organized with NILU as part of the 2<sup>nd</sup> EWCHP workshop September 26<sup>th</sup>, 2012 in Oslo. The aim was to present the MEMORI dosimeter and to sensitize the participants for the overall topic. The training day had 19 participants, mostly representatives of museums and restoration companies, but also from research institutes, mostly from northern European countries. The outcome is documented in detail on the project website at <http://www.memori-project.eu/645.html> .

The **second training day took place in Pisa, June 20<sup>th</sup>, 2013** as part of the conference „Environmental Monitoring for Cultural Heritage: from Research to Application“. It was organized cooperatively by Association Culture & Work with University of Pisa, Department of Chemistry and Industrial Chemistry and Opera Primaziale Pisana, the institution responsible for the monumental complex of the cathedral of Pisa. Participants were 60 high class professionals and decision makers mainly from all over Italy and other Mediterranean countries, representatives from conservation departments of museums, architects, geologists, archeologists, scientists (mainly chemistry), conservation/restoration companies, freelancers, service providers and museum operators. The training day was an integrated part of the conference and provided a detailed presentation of the MEMORI dosimeter technology end-user and an interactive session along a questionnaire. The outcome is documented in detail on the project website at <http://www.memori-project.eu/645.html> .

A **third training day** was offered as pre-event of the MEMORI final conference in Madrid October 3<sup>rd</sup>, 2013. All together 40 participants from 13 European countries and Japan attended the training school “Innovation for conservation. The MEMORI technology - how to manage your indoor air quality”. During the training day, the MEMORI technology was presented including first results of measurements in 16 European museums and collections. Representatives of Tate (UK), English Heritage (UK) and National Museum in Krakow (Poland) showcased the relevance of damage prevention and reported about their experiences with the measurements. Participants were actively invited for discussion and practical exercises. The outcome is documented in detail on the project website at <http://www.memori-project.eu/645.html>.

#### **4.4 Business- and Marketing Plan**

From the beginning of the MEMORI project, it did not only focus on the necessary research for bringing two dosimeter types together but also on how to commercialize this product/service combination. The MEMORI technology was also seen as a business opportunity for transportation companies, restoration companies and start-ups in the respective fields. Therefore MEMORI technology was communicated in all training schools as a business opportunity as well.

A detailed business and marketing plan was developed by the partners ACW and NILU Innovation and in cooperation with representatives of the end-user advisory group of the project. It is now the basic instrument for market transfer of the MEMORI technology for NILU Innovation which is responsible for the commercialization of the final product and services in cooperation with distributors.

#### **4.5 Transfer of MEMORI technology to other business fields**

Additional business fields for the MEMORI technology were identified e.g. in health, mining and facility management of pollutant-free rooms. The German SME Health Media ([www.health-media.de](http://www.health-media.de)) developed a device which measures pollen and mildew concentration and considers the MEMORI technology as an additional option, e.g. by a combined device. Results of the MEMORI measurements will be presented at a later stage to this company and others in order to identify possible business cooperation together with NILU Innovation and NILU.

#### **4.6 Main dissemination activities and exploitation of results**

The integrated involvement of end-users, representing conservators, curators and managers responsible for movable cultural heritage, and professional companies marketing conservation equipment and consulting services, assured the best possible relevance of the project development and results. The aim was to satisfy the needs of the end-users and assure the most realistic and effective ways to disseminate information and to market the products and services available from the project.

The results from the project were disseminated and were made available as widely and quickly as possible to the conservation market and end-users including the need for additional information about degradation effects and best preventive conservation practice and with responsibility for implementing protection measures for movable

cultural heritage assets. The partner Fraunhofer ISC was responsible for the coordination of the dissemination activities during the project period.

#### 4.7 Project web-page and Facebook site

The official MEMORI project website (Figure 21a) has been available since March 24, 2011 under the following address: [www.memori-project.eu](http://www.memori-project.eu). The content was enhanced during the project and all relevant information linked to the MEMORI project and the partners is available on the web-pages. A Facebook site (Figure 21b), was created in August 2013 in order to build a community of interested persons for the MEMORI technology before the MEMORI final conference: <https://www.facebook.com/MemoriTechnology>. The set-up and content was provided by partner Association Culture & work.

a)



b)



Figure 21: The front page of the MEMORI website (a) and the front page of the Facebook website (b).

#### 4.8 MEMORI brochure

A brochure presenting the main aims and objectives of the MEMORI project was produced in 4500 copies at the beginning of the project period (Figure 22). The brochures have been spread by all partners via conferences and fairs to the scientific community, to end-users and to SMEs all over Europe and beyond. The brochure is also available on the MEMORI webpage (<http://www.memori-project.eu/316.html>).



Figure 22: The cover page of the MEMORI brochure.

#### 4.9 MEMORI marketing brochure

An information and marketing brochure for the MEMORI technology was drafted and designed by Association Culture & Work, NILU, SIT and NILU Innovation in cooperation (Figure 23). It was used for dissemination purposes and end-user seminars. As not all relevant information for marketing purposes could already be integrated in the first run (published February 2013, a second run was published September 2013). The added value of the second run is in the description of first results of the MEMORI technology measured in 16 high-class museums and collections Europe-wide and in Japan.



Figure 23: First page of the MEMORI information and marketing brochure.

#### 4.10 MEMORI film “New air for museums”

The film “New air for museums” presenting the concept of the MEMORI project was produced by Euronews (in 12 languages) and broadcasted all around Europe on 13<sup>th</sup> May 2013. The film is available on the MEMORI webpage for download (in English); (<http://www.memori-project.eu/memori.html>).

#### 4.11 End-user symposia

For getting advice and the discussion of the results and guidelines with the end-users three major symposia were organized: one at the start of the project (February 8<sup>th</sup> to 9<sup>th</sup>, 2011 in Bronnbach, Germany), one midterm (May 3<sup>rd</sup> to 4<sup>th</sup>, 2012 in Kjeller, Norway), and one at the end (October 3<sup>rd</sup> to 4<sup>th</sup>, 2013 in Madrid, Spain). The members of the international end- user advisory board are listed in Table 1.

*Table 1: Members of the MEMORI end-user advisory panel.*

<b>Name</b>	<b>Position</b>	<b>Institution</b>
Bergeaud, Claire	Director of collection care management	Musée National Picasso Paris, France
Gothorp, Cliff	Founder of company	Preservation Equipment Ltd, United Kingdom
Ishizaki, Takeshi	Deputy Director General	National Research Institute for Cultural Properties, Tokyo, Japan
Jackunaite, Regina	Curator of Cinema Department	Lithuanian Theatre, Music and Cinema Museum, Lithuania
Obarzanowski, Michal	Conservator	National Museum in Krakow, Poland
Pitzen, Christoph	Diplom-Restaurator	Württembergisches Landesmuseum, Germany
Sommer-Larsen, Anne / Hjulstad, Guro	Head of conservation department/ Conservator	The Museum of Cultural History, University of Oslo, Norway
Kuzucuoglu, Alpaslan Hamdi	Conservator	Istanbul University, Department of Conservation and Restoration of Artefacts, Turkey

The first symposium (Figure 24, left) pointed out the aims of MEMORI and it was discussed how the work could be performed to obtain results that will benefit the end-users as far as possible. During the midterm symposium the progress and direction of the project was evaluated. Moreover, it gave the end-users ample opportunity to discuss results and give advice about how to optimize the benefit as set out by the project objectives. In the final end-user symposium (Figure 24, right) the consortium was engaged in interactive presentation of the project results with the end-user panel. The end-users evaluated the final results and gave advice on adjustment to obtain the full benefit after project finalization. Suggestions and advice of the end-users will be taken into account for the final marketing strategy / market transfer from a prototype to a commercially available product.



*Figure 24: Participants of the MEMORI end-user advisory panel during the first symposium in Bronnbach, Germany (left). End-user panel discussion during the afternoon session of the MEMORI conference (right).*

#### 4.12 Dissemination activities for public and scientific community

The outcome of the different work packages of the MEMORI project was published and presented on different occasions and in different ways. A summary of the activities is shown in Figure 25. The recorded activities were classified as follows:

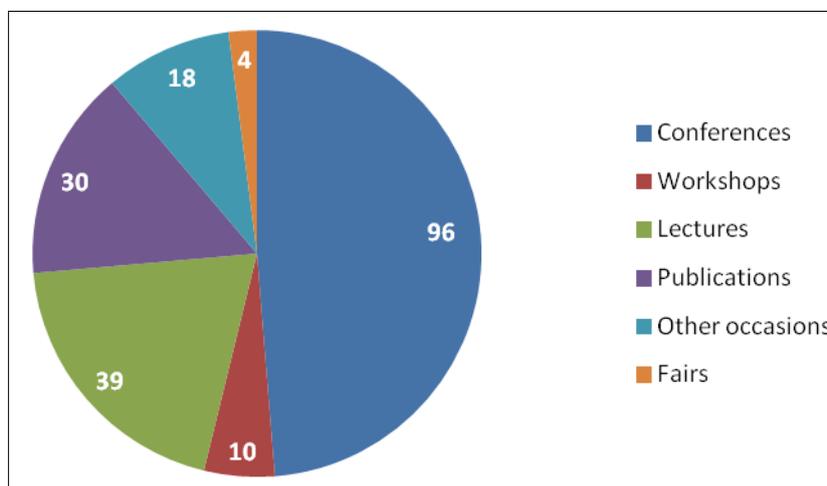


Figure 25: Diagram showing the different public relation activities are given. “Publications” only include scientific publications.

##### *Conferences*

Scientific conferences worldwide, related to cultural heritage preservation, have been attended during the lifetime of the project by the MEMORI partners. The dissemination activities included the presentation of the outcome of the work packages via posters or oral presentations. Mostly, also the MEMORI brochures were distributed during these events; also during conferences with no active contribution (no oral presentation or poster). On some of the 96 attended conferences, several speakers of the MEMORI consortium were present and / or posters were shown.

The final results of the three years research project were presented during the MEMORI conference on 4<sup>th</sup> October 2013, in Madrid, Spain. More than 100 participants attended the MEMORI conference at the Museo Nacional Centro de Arte Reina Sofía. Information about the conference as well as the presentations are available for download from the MEMORI web-site (<http://www.memori-project.eu/682.html>).

##### *Workshops*

Workshops were performed in the framework of the project to disseminate the results of the different work packages on a more practical level and also to introduce the handling of the MEMORI technology. Three so called “training days” for young professionals were performed (see chapter 4.3). In addition, further 7 workshops had been performed.

##### *Press releases including newsletters and scientific/non-scientific publications*

Several press releases were produced for different types of media like professional journals for end-users, business journals and for the interested public. All together, 30 scientific publications and 2 non-scientific publications had been made (Annex Template A2 – other occasions).

Press releases in daily *newspapers* were performed mainly at the beginning and the end of the project by all participating countries in the respective languages by their own press channels. Some press releases are available on the MEMORI webpages (e.g. <http://www.memori-project.eu/316.html>). It can be estimated that around 50 press releases had been performed during the project.

An *information and marketing brochure* for the MEMORI technology was cooperatively drafted (see chapter 4.9). It was printed in 2000 copies (first edition 500 copies, second edition 1500 copies) and was used for dissemination purposes and end-user seminars. It is also available on the MEMORI webpage (<http://www.memori-project.eu/316.html>).

Moreover, internet media and web based tools were used for dissemination activities. Most of the MEMORI partners made information about MEMORI available on the web-sites of their institutions and link them to the MEMORI web page. In addition, four electronic *Newsletters* were created by partner ACW in cooperation with most partners and distributed to about 5000 email addresses of institutions respectively persons working in the field of cultural heritage conservation worldwide (Figure 26). All Newsletters are also available at the MEMORI web-page (<http://www.memori-project.eu/316.html>).



Figure 26: Cover of the latest electronic Newsletter.

### **Fairs**

Fairs had been special events to disseminate the MEMORI technology to a very wide range of interested audience working in the field of cultural heritage, museums and conservation. The MEMORI project was presented at four fairs with a MEMORI information desk. For example, the “Fair of Art and Restauration of Florence” was attended by about 1.500 persons, during the “Denkmal 2012” more than 13.000 visitors were counted, and around 29.000 persons visited the “AR&PA Innovation fair” in Valladolid.

### **Lectures**

Several lectures had been given to young scientists and conservation students at universities as well as to specialised staff in Museums.

***Other occasions***

The MEMORI project was also presented during other occasions like radio broadcasts, web-interviews, informal meetings and presentations for the general public.

**4.13 Summary**

The main dissemination activities and exploitation of results were various and have been performed in order to enter public awareness. Not only specialists were informed, but also the public and, in particular, the community of end-users.

The size of audience for the public relation activities is difficult to estimate, but some numbers should be mentioned here: around 2.000 persons attended conferences only; more than 2.000 people were informed via lectures; the electronic newsletters were distributed to around 5.000 email addresses; and the fairs were attended by more than 43.000 persons according to the information given by the local organizers. Press releases in newspapers, and radio broadcasts reached a more general, interested public.

## 5 MEMORI website and contact details.

The MEMORI project public website has the following address:

[www.memori-project.eu](http://www.memori-project.eu)

Contact person for the MEMORI website :

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The MEMORI project beneficiaries are:

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