

## Frontiers of Preventive Conservation

David Thickett

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## Frontiers of Preventive Conservation

David Thickett

English Heritage Trust, London, UK

### ABSTRACT

This work considers areas where our present lack of knowledge curtails the effectiveness or efficiency of preventive conservation practice. Mixed media, especially archaeological metals and organics have incompatible requirements for relative humidity (RH). An approach based on understanding the risk versus RH for both materials and considering the showcase performance is elucidated as a solution. Pollution, both the mixed atmospheres around most cultural heritage and the complex, variable nature of deposited particles, are further areas in need of more research. Damage functions and measurement of object deterioration rates are investigated as a path forward, and examples are given.

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### Introduction

The main principles of preventive conservation have long been elucidated, but successful management of change requires a great level of detail, for both knowledge of the susceptibility of objects and successful systems of control, both technical and organisational. Technological solutions are now available for very tight control of environments, but limited budgets mean prioritisation is even more essential. Across the large mixed collections of many institutions, only detailed knowledge of the likely response of objects in their present environments allows critical prioritisation. This work considers areas where our present lack of knowledge curtails the effectiveness or efficiency of preventive conservation practice. This lack of knowledge is in many instances, the critical determinant in whether we achieve sustainable environments to promote preservation.

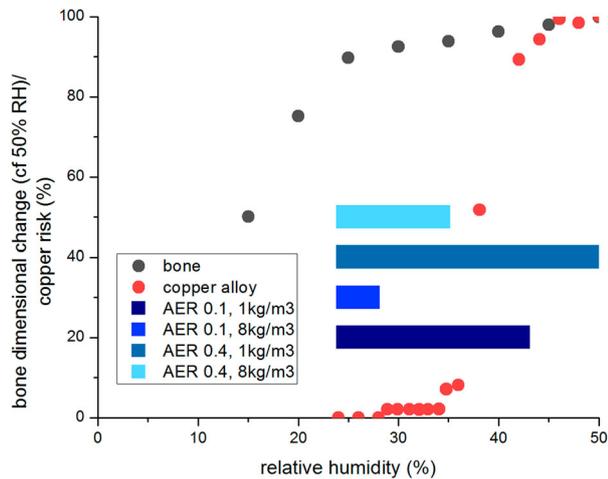
Even if full environmental information is available, (temperature ( $T$ ), relative humidity (RH), light and ultraviolet data near the object, gaseous pollution concentration and particulate deposition rates) we still cannot definitely assess the changes likely to many object types (Thickett and Lankester 2012). Many display situations have objects with differing environmental requirements displayed together. Decision-making in these instances is extremely challenging. Risk assessment often transposes value or significance assessments on top of the change function (Strlič et al. 2013). However, if the change function is over or under-assessed, the risk assessment will be wrong. As a field, we still are in the early stages of assessing which properties of a particular object contribute to its value or significance and how deterioration of those properties degrade that value. There is a limited amount of

information about the risk when objects are exposed to environments outside narrow RH bands or with certain pollution concentrations.

### Mixed materials

One critical instance is with showcases containing mixed materials, especially organics and archaeological iron and copper alloys. The contradictory RH requirements given in the literature (<30% for archaeological iron, <38% for copper alloy, >40% for organics) are difficult to match. Elucidation of the risk against RH for the materials allows the least damaging RH band to be determined. Figure 1 shows the results of research into the corrosion rate of archaeological copper alloys against RH (Thickett 2016) and bone (Candidas and Thickett 2017). The risk from copper alloy corrosion shown in Figure 1 has been assessed by experiments to determine the amount of corrosion, and surveying archaeological curators to assess the impact of that corrosion on object value.

Standards give a lower RH of 35% for archaeological bone (Brown 2007). The measurements of the isotherm show the slope is very shallow from 50% to 25% RH and then steepens dramatically. It is unlikely that the stress induced is sufficient for plastic deformation above the 25% value, although work in this area has not been published. Research started with Collaborative Doctoral Project funding by the UK Arts and Humanities Research Council to address this. Archaeological copper alloy can start corroding from 28%, so 25–28% would be a reasonable, extremely low risk, RH range. However, this tight RH range would be very expensive to maintain and the question of how much risk beyond it becomes essential in many situations.



**Figure 1.** Impact of RH on the contraction of bone and risk to archaeological copper alloy.

The bone has a much steeper slope, dropping below 25%, than the copper increasing beyond 28%. It is difficult to compare the deterioration of two different materials and the relative scales could be set in a number of different ways. The control potential of the showcase needs then to be considered to produce the optimum solution.

Figure 1 includes the RH band modelled with 1 or 8 kg/m<sup>3</sup> of silica gel in showcases with air exchange rates of 0.1 and 0.4 per day in a typical historic castle room (average 75% RH) and changing the silica gel every three months. A 0.1 per day air exchange rate showcase with 8 kg/m<sup>3</sup> of silica gel will present an

extremely low risk of further copper alloy deterioration. However, laboratory experiments have shown that even this RH will cause a very slow deterioration of susceptible artefacts. Procuring a showcase to this air exchange rate will be more expensive than procuring one to 0.4 per day. With 8 kg/m<sup>3</sup> of silica gel the RH will be kept below the increase in reaction rate at 34%. The deterioration rate will be slightly higher, but still very low. Using the smaller but commonly specified 1 kg/m<sup>3</sup>, would result in unacceptable deterioration for the copper alloy. Whilst the final decision will be informed by many factors, this approach at least provides an evidence base on which to assess the preventive conservation part of that decision and prediction of the likely consequences of different scenarios.

### Gaseous pollution

Object reaction to pollution is complex in the multi-pollutant atmospheres present in many buildings, store rooms and especially enclosures. The latter often have over 200 separate species present. Table 1 lists the pollutants so far reported to have caused damage to cultural heritage materials. The literature on pollution damage is very dispersed, and much work resides only in the grey literature. This makes interpretation of monitoring results challenging. Analytical monitoring of specific gaseous species in an existing showcase and emission-based materials testing both fundamentally rely on knowing the gases to analyse

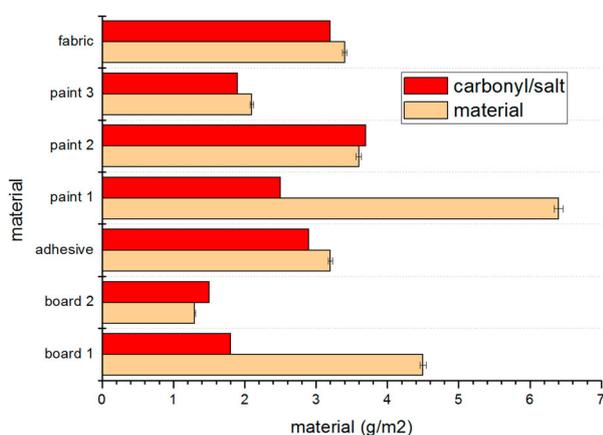
**Table 1.** Pollutants reported to cause damage to materials.

Compounds	Types of compounds
Acetic acid, D (Tétreault 2003)	Chlorides (29% of 200 Oddy Cu tests have Cl in corrosion product), Cu (Tétreault 2003)
Formic acid, D (Tétreault 2003)	Mercaptans, Ag
Nitric acid, D (Tétreault 2003)	Peroxides, R
Hydrogen sulphide, Ag (Tétreault 2003)	
Carbonyl sulphide, Ag (Tétreault 2003)	
Dimethyl sulphide, Ag (Tétreault 2003)	
Formaldehyde, B (Tétreault 2003)	
Acetaldehyde, B (Tétreault 2003)	
Styrene, T (Tétreault 2003)	
Ammonia, DT (Tétreault 2003)	
Ethyl acetate, T (Tétreault 2003)	
Ethyl formate, T (BM)	
Ethyl propanate, T (BM)	
Methyl acetate, T (BM)	
Methyl propanate, T (BM)	
Propanoic acid, T (BM)	
Butanoic acid, T (BM)	
Vanillin, T (Strlič et al. 2010)	
Iso butyl benzol, T (Strlič et al. 2010)	
Hexanal, T (Strlič et al. 2010)	
1,4 diethylbenzene, T (Strlič et al. 2010)	
Furfural, T (Strlič et al. 2010)	
Toluene, T (Strlič et al. 2010)	
2 pentyfuran, T (Strlič et al. 2010)	
Diethylamine ethanol, T (Winston Revie 2011)	
Octadecylamine, T (Winston Revie 2011)	
1,2,2,6,6-pentamethyl-4-piperidinol, Cu (Stanek et al. 2016)	
2,2,6,6-tetramethyl-4-piperidinol, Cu (Stanek et al. 2016)	

Key: D – KOH sorbent diffusion tube following method of Gibson et al. (1997), B – aldehyde badge by BISREA; T – tenax tube and GCMS analysis by Gradko, DT – Tartaric acid sorbent diffusion tube, Ag – silver Oddy test (Robinet and Thickett 2004); Cu – copper Oddy test, R – Russel test (Daniels 1984). BM British Museum (unpublished).

for and their damaging and safe concentrations. The MEMORI project drew together much literature in this area and rationalised it on a dedicated open access website.<sup>1</sup> The synergistic effects are known for only a few pollutants, with others likely to be present and RH often having a very significant role. Corrosion testing of lead above a series of paints and wood products has shown that, in at least some cases, as yet unidentified species are contributing significantly to corrosion. Acetic and formic acid and formaldehyde account for over 95% of the corrosion observed in many instances, but on two cases significant extra corrosion was occurring not attributable to any of the other 34 known corrosive species.

Materials were selected that had failed Oddy tests with lead, but passed with silver, copper and paper and which could easily be reduced to small pieces. Further emission tests were undertaken as detailed in Table 1. Two boards, an adhesive, three paints and fabric were selected and worked to produce pieces less than 1 mm in size, by sawing, cutting with scissors or applying to a glass-plate, drying and then scoring with a knife. A 2 g sample of each material was acclimatised to 75% RH above saturated sodium chloride solution, until no more mass gain was measured. The equilibrium concentrations in a 500 ml vessel were measured with diffusion tubes, Tenax tubes, and diffusion badges, see Table 1 for details. The absence of a variety of known corrosive gases was inferred from the negative tests. Accurately weighed lead pieces were then exposed above fresh samples of the materials equilibrated at 75% RH and above carbonyl/sodium chloride/water solutions calculated to generate the same atmospheric concentrations of acetic and formic acid and formaldehyde and acetaldehyde, as above the materials. All tests were undertaken in triplicate. After 30 days, the lead pieces were stripped with 50 g/L ammonium acetate at 60°C, carefully dried and weighed (ASTM 2003). The loss of lead



**Figure 2.** Corrosion of lead above materials and the same carbonyl atmosphere they generate.

due to corrosion was calculated in g/m<sup>2</sup>. Results are shown in Figure 2.

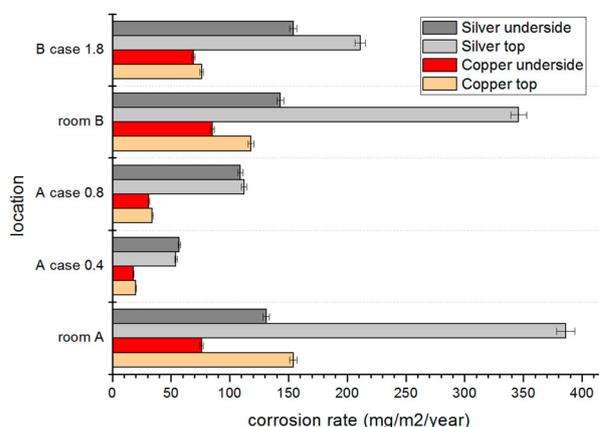
Most of the materials produced similar amounts of corrosion to the carbonyl atmospheres. Paint 1 and Board 1 produced much more corrosion, well beyond any experimental errors. Board 1 gave a positive Russell test (Daniels 1984) indicating the presence of oxidising material, paint 1 gave a negative Russell test. Paint 1 appears to be causing some of the corrosion by emitting an unidentified species.

This potential for unknown corrosive species, synergistic effects and lack of properly defined thresholds, limits the utility of chamber emission tests for new enclosures and gas analyses to determine risk for existing enclosures. Unfortunately, there is a tendency to set instrumental detection limits as thresholds for pollutants, which is problematic, as these often bear no relationship to how aggressive the pollutant is.

Significant further research is required to generate accurate threshold levels for pollutant RH combinations to accurately assess deterioration risk.

## Dust

Unlike gaseous pollutants, where the chemical species such as sulphur dioxide are identical everywhere, particulate composition varies greatly with location, for example as investigated by Worobiec et al. (2006) for Wawel Castle, Krakow, Poland. Whilst the visual impact of coarse dust has been elucidated, along with methods of control, much less is known about the interaction of dust with objects (Thickett and Costa 2014). Silver and copper strips were cleaned, exposed and analysed to ISO 11844 (ISO 2008) at Rangers House, south London. The method was modified to expose the strips at 45°C in a frame, so that the temperature, RH and gaseous pollution was identical on the top and underside of the strip, but the underside would experience much less dust



**Figure 3.** Effect of dust on corrosion rate of copper and silver, indicated by differences in corrosion rate on top and underside metal coupons at 45°C.

deposition. A custom-built cell was used to analyse a 2 cm diameter circle on either side of the metal strip electrochemically (Thickett and Costa 2014) (Figure 3).

In rooms A and B in Rangers House, the corrosion rates are up to three times higher on the top surface compared to the underside. The RH and gaseous pollution concentration have been tested with similar frames and proved to be very similar above the top surface and below the underside. Whilst some dust particles will deposit on the underside surface, the amount will be very significantly reduced from the top surface. Corrosion rates are significantly reduced in showcases, and the reduction follows decreasing air exchange rate. The difference between the two surfaces also reduces in more tightly sealed showcases. Whilst the interaction of dust and metal is most researched, recent work has shown reaction with mastic and paper (Thickett and Costa 2014; Thickett and Pretzel 2010; Grau-Bové et al. 2016). Studying the effects of different dust compositions is experimentally difficult, although initial attempts have been made (Thickett 2008). Studying the effects *in situ*, on collections/in heritage locations, is perhaps a more promising route, although it does require full characterisation of the dust particles. Differences in deposition onto object surfaces, and the surfaces of substrates suitable for such characterisation, may be an issue.

## Damage functions

Comparing environments or determining how high the risk is to a particular object, in a particular environment, is critical to preventive conservation. Many deterioration phenomena involve the interaction of several environmental parameters. Metal corrosion is often a strong function of RH, several pollutant concentrations and particulate deposition. These parameters can have strong seasonal variations and concentrating on just one, often RH, can mislead as to the magnitude of

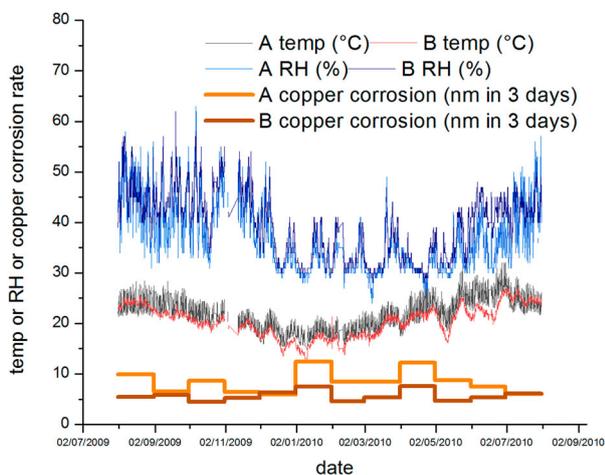
risk presented by the environment. Damage functions combine the environmental parameters, ideally to estimate the risk. At Apsley House, London, a copper statue was suggested for loan into one of two rooms. As the historical context has been lost for many of the rooms, the loan could equally be placed in either without historical precedent, which is often present in historic houses. Figure 4 shows the temperature and RH data for the rooms for a year prior to the installation. Pollution data were available; measured at monthly intervals with diffusion tubes for nitrogen dioxide, sulphur dioxide, ozone, hydrogen chloride and hydrogen sulphide (Gibson et al. 1997; Ankersmit, Doménech Carbó, and Tennent 2004). These data were fed into the damage function developed for copper (Thickett, Chisholm, and Lankester 2013). Monthly results are shown in Figure 4.

As can be seen, room B is generally cooler and has a generally higher RH. However, room A has higher predicted copper corrosion rates. The annual predicted corrosion rates would be 101 nm for room A and 68.4 nm for room B. This places room A in corrosion category IC3 medium indoor and room B in IC2, low indoor according to ISO 11844 (ISO 2008). Measurement with an Ongaard 3000 system corroborated the general magnitude of the room B corrosion for the loan period of six months. The predicted and measured data are probably at odds with what would have been expected from considering only the RH data. Additionally the highest corrosion rates are during periods of lower RH. This is due to the strong influences of the pollutant gases on the corrosion rate.

At present only a few damage functions are available (Ashley-Smith 2013; Thickett, Chisholm, and Lankester 2013), but research is developing new ones, tailored towards heritage environments. Damage functions are only valid across the environmental measurement range from which they were developed. However, they do promise a better method to assess environmental data. They provide an integrated approach, much better describing the likelihood of deterioration than relying on single parameters.

## Measurements on objects

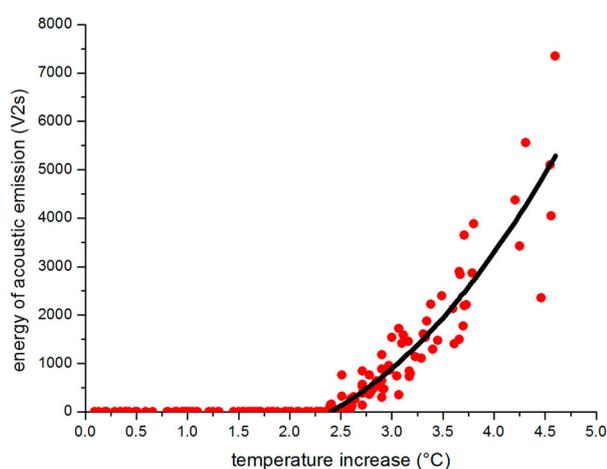
There are significant issues using surrogate materials results to determine environmental susceptibility of objects. The composition of objects is often very variable and frequently not fully known. Aged materials can react very differently from fresh materials. Surrogate studies have many advantages; the ability to use destructive techniques, to apply statistical experimental design, that uniform material can be exposed to several sets of conditions simultaneously, amongst others. The best studies often contain a second stage, 'checking' that the results are borne out in real collections. Traditionally this was by observation, perhaps



**Figure 4.** Predicted copper corrosion rate from published damage functions applied to environmental and pollution data in two rooms.

supplemented with some analysis. Advances in instrumentation have now reached the point that, in at least some instances, non-invasive, repeatable measurements can be made on actual objects. A series of measurements can determine the decay rate *in situ*. Examples of such an approach are Thickett et al. (2017), Accardo, Caneva, and Massa (1983) and Strojceki et al. (2014). There are numerous issues to overcome, such as accurately repositioning measurements on often heterogeneous surfaces, long-term instrument stability and environmental noise. The representativeness of a particular object or group of objects measured is an important issue. Some guidance can be gleaned from the epidemiology field (Dean, Sullivan, and Soe 2013). Work with acoustic emission sensors, validated the method for Limoge enamel plaques and measured the effect of heating from tungsten lighting (Thickett, Chisholm, and Lankester 2013). This work indicated that keeping the air temperature gain below 2.1°C would stop delamination between the enamel and metal layers. This is difficult to achieve in many heritage buildings, and the question arises as to how damaging greater temperature gains may be. The initial works application to actual objects was limited by the necessity to have a sensor on the front, decorated face of the enamel, interfering with visitor appreciation. The opening hours of the property were modified with several closed days per week. This allowed measurements of several other enamel plaques (12 in total measured), improving the amount of data and usefulness of the data set. Figure 5 shows the amount of acoustic emission energy detected against the measured air temperature gain.

The threshold is better defined as 2.31–2.35°C, c.f. 2.12–2.54°C. Below this value, cracking of the glass or the glass/metal interface cannot be detected. Studies generally have one value that shows a detectable change above another that does not. Large intervals limit the usefulness of the result. Several types of fit were tried for the data including, linear, log, quadratic,



**Figure 5.** Energy of acoustic emission versus temperature gain monitored from 12 enamel plaques.

exponential, power and second, third, fourth order polynomials. The second order polynomial below gave the lowest standard error by some margin and had a coefficient of determination,  $R^2$  of 0.85.

Energy of acoustic emissions  $\{V^2s\} = 574.1(T\{^{\circ}C\} - 2.35)^2 + 1073.4(T\{^{\circ}C\} - 2.35)$ .

Application of the equation to air temperature gain gives an indication of the risk at temperatures above 2.35°C. The equation correlates well with 30-minute temperature difference intervals and it could be expected that the effect is quite rapid due to the lack of relaxation mechanisms, unlike the response of organic materials to RH fluctuations.

## Conclusions

Interpreting measured environmental data in terms of a prognosis of change to objects is still at the limit, and often beyond, our present scientific understanding. Developments in sensor and data transmission technologies continue to make environmental data more widely available. Developments in control technologies mean it is possible to provide almost any space, and certainly any showcase or store, with any particular environment. The critical knowledge gaps in response and then damage function (and hence risk) very much limits interpreting the data and specifying control measures. Whilst much progress has been made over the past three decades, much work remains. Mixed media objects, on displays or in storage, often cause particular problems. The move away from very tight, very safe limits has been significantly hampered by our lack of understanding material or object response and also the risk beyond these limits. Pollution, both the mixed atmospheres around most cultural heritage and the complex, variable nature of deposited particles are further areas in need of more research. Damage functions appear to offer a way forward. Our improved ability to measure objects' response or state *in situ*, can provide very significant evidence if the limitations can be overcome, and enough objects can be so measured and their response compared to their environment over the long term. This approach, including research into how the measured properties affect value may close some of our critical knowledge gaps and push the frontiers back, permitting better evidence-based decisions.

## Note

1. MEMORI was concluded in 2015. See <http://memori.nilu.no/Mitigation> (accessed 12 October 2017).

## Disclosure statement

No potential conflict of interest was reported by the author.

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