Activated carbon adsorbing materials were installed in a number of showcases with heritage objects belonging to English Heritage. The reduction of acetic plus formic acid concentration in air, which could be achieved by the installation of the different adsorbing materials, was investigated. The concentrations of the gases were measured before and after installation of the adsorbers. The reduction in the acetic plus formic acid concentration depended both on the activated carbon adsorbing material which was installed, and on the ventilation rate of the showcases.

The installation of carbon cloth, rather than foam, and of foam rather than granulate, and lower ventilation rates gave larger % reduction. The adsorption rate to activated carbon cloth was found to be 1.4 times higher than to activated carbon foam, and 4.4 times higher than to activated carbon granulate. Where activated carbon cloth or foam was installed in showcases with a ventilation rate of two to five air exchanges per day, the reduction in the concentration was from 78 to 96%, to give levels below the recommended target level. Where activated carbon cloth was installed in a showcase with a very high air exchange of 29 per day the reduction was 44 %. Where activated carbon granulate was installed in showcases with air exchanges from four to six per day the reduction was from three to 28%. The expected ventilation dependent concentration of the acids inside the showcases, without and with the adsorbing materials installed, was found with a mass balance box model. From a practical point of view the activated carbon cloth was better to install than the foam, which was better to install than the granulate. Charcoal is easily lost from the adsorbing materials during working and mounting, leaving black particles and dust.

1 Introduction

The aim of this study was to obtain more information about how properties of active carbon adsorbing materials and of showcases affect the efficiency of installation of the adsorbing materials in the showcases, to reduce the concentration of the gases and to mitigate their damage impacts on the objects.

It is well known that organic acidic air pollutants, such as especially acetic and formic acid, can cause damage to a range of cultural heritage materials and objects indoors. Some effects are corrosion, dissolution and, or leaching of metals, glass, ceramics, limestone, corals, shells and calcium based fossils, acid hydrolysis and, or oxidation of organic materials such as paper, varnish and synthetic polymers. The sensitivity of different materials and object surfaces to acidic attack will depend on the material properties, including factors such as its inherent pH, e.g. for paper and the ageing properties and corrosion layers, "patina", present on the surface. Heritage objects can be exposed to the acids by direct contact with acidic, e.g. wood, surfaces, or by deposition of the acids from the air. The sources for the pollutants can be both construction materials and the heritage
objects themselves\textsuperscript{15,16,17}. The rate of damage will usually increase with increasing concentration of the acids in the air, resulting in increased deposition on surfaces, and thus reduced pH and increasing amount of the acid ions available for reaction\textsuperscript{13}. The damage will also depend on climatic conditions, such as the relative humidity and temperature\textsuperscript{4,13}. By controlling the factors that affect the damage rate, the damage effect of the acids can be reduced\textsuperscript{1,18}.

The concentration of organic acids in rooms in museums and archives is usually so low that it poses little damage risk to objects. The volumes and ventilation rates of the rooms are usually sufficient to dilute the concentration of the acids to low levels ($< \sim 100 \, \mu g \, m^{-3}$). The situation is however different inside showcases, which are often used to protect objects. The volume to emissive surface ratio, and usually the ventilation rate, of showcases is much smaller than for rooms, which leads to the build-up of the organic acids to much higher concentrations inside the showcases\textsuperscript{19,20,21}. Concentrations of several thousand $\mu g \, m^{-3}$ of acetic plus formic acid has been measured inside showcases, and concentration values in the hundreds are not uncommon. Such amounts of organic acids have been observed to quickly tarnish and corrode materials like lead\textsuperscript{22} and medieval glass\textsuperscript{10,23}, and is expected to damage a range of other materials\textsuperscript{1}.

To reduce the concentration of organic acids inside showcases adsorbing media can be installed\textsuperscript{24}. Activated carbon has been shown to be among the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/figure1.png}
\caption{The six numbered test showcases (see Table 1). In showcases no. 1 to 5 the activated carbon adsorbing material is installed. Showcases no. 1 and 2 are the left and right chamber of Showcase C. The front of showcases no. 4, 5 and 6 were off only at the moment of installation of adsorbers and taking the photo. In showcase no. 5 an air exchange rate logger is also shown. Showcase no. 6 is shown before the activated carbon was installed.}
\end{figure}
Table 1: Measurement locations, periods and adsorbent media installed in the test showcases.

<table>
<thead>
<tr>
<th>Site</th>
<th>Showcases evaluated</th>
<th>Measurement periods (~1 month)</th>
<th>Adsorbent media installed (Activated carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Both sites (as for Period 2)</td>
<td>All cases (as for Period 2)</td>
<td>23/7-22/08 (Osborne House, Swiss Cottage, control case and room: 24/7-20/08)</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Period 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chesters Roman Fort and Museum</td>
<td>1A - Showcase C, left chamber</td>
<td>27/8-27/09</td>
<td>Granulate K48: 2 bags covered with a neutral colour fabric</td>
</tr>
<tr>
<td></td>
<td>2A - Showcase C, right chamber</td>
<td></td>
<td>Granulate MEMORI 6: 2 bags covered with a neutral colour fabric</td>
</tr>
<tr>
<td></td>
<td>3 - Showcase F</td>
<td></td>
<td>Cloth: Single sheet, back of cloth displayed</td>
</tr>
<tr>
<td></td>
<td>CC - Control case</td>
<td></td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>CR - Room</td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>Osborne House, Swiss Cottage</td>
<td>4 - Showcase 32</td>
<td>29/8-28/09</td>
<td>Granulate K48: 4 bags covered with a neutral colour fabric to disguise its appearance</td>
</tr>
<tr>
<td></td>
<td>5 - Showcase 40</td>
<td></td>
<td>Cloth: Double sheet, back of cloth displayed</td>
</tr>
<tr>
<td></td>
<td>6 - Showcase 41</td>
<td></td>
<td>Granulate MEMORI 6: 4 bags with granulate, covered with a neutral colour fabric</td>
</tr>
<tr>
<td></td>
<td>OC - Control case</td>
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<td>None</td>
</tr>
<tr>
<td></td>
<td>OR - Room</td>
<td></td>
<td>None</td>
</tr>
<tr>
<td>Period 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chesters Roman Fort and Museum</td>
<td>1B - Showcase C, left chamber</td>
<td>11/12-11/01</td>
<td>Foam MEMORI 8: 1 cm thick foam, covered with a neutral colour fabric</td>
</tr>
<tr>
<td></td>
<td>2B - Showcase C, right chamber</td>
<td></td>
<td>Foam MEMORI 8: 3 cm thick foam, covered with a neutral colour fabric</td>
</tr>
<tr>
<td></td>
<td>CC - Control case</td>
<td></td>
<td>None</td>
</tr>
</tbody>
</table>

Description of adsorbents

<table>
<thead>
<tr>
<th>Adsorbent category</th>
<th>Adsorbent media</th>
<th>Manufacturer / supplier</th>
<th>Description/properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure carbons, granulate</td>
<td>Activated charcoal K48 (labelled LLFA)</td>
<td>Purafil</td>
<td>Pure carbon activated charcoal; coconut shell, extra fine pores, powder granulate chips (2.4-2.8 mm)</td>
</tr>
<tr>
<td>Impregnated carbons, granulate</td>
<td>MEMORI 6 (labelled Enceladus)</td>
<td>EMCEL</td>
<td>Powder granular Impregnated Activated Carbon; coconut shell, especially impregnated for chemisorption of formaldehyde</td>
</tr>
<tr>
<td>Charcoal foams</td>
<td>MEMORI 8</td>
<td>EMCEL</td>
<td>Activated Carbon Coated Foam; reticulated polyurethane foam which is coated with activated granular carbon</td>
</tr>
<tr>
<td>Charcoal cloth</td>
<td>CCI-activated carbon cloth type FM10/T150</td>
<td>Long life for art</td>
<td>Woven, bonded on one side to a white non-woven cloth; alkaline impregnated</td>
</tr>
</tbody>
</table>
most effective adsorbing materials\textsuperscript{25,26}. Activated carbon is produced from carbonaceous materials, such as wood, nutshells, peat, hard coal or lignite. They have a fine-porous structure and a high total surface (300-2000 m\textsuperscript{2}/g). The density varies between 200 kg/m\textsuperscript{3} and 600 kg/m\textsuperscript{3}. Activated charcoal is available as powder or granulate. To improve the adsorption capacity, the charcoal can be impregnated, mostly with alkaline substances\textsuperscript{27}. Activated charcoals are differentiated by their adsorption capacity as determined by their pore size diameter: micro-pores <1 nm, meso-pores 1-25 nm and macro-pores > 25 nm.

This paper reports results from the installation of different types of activated carbon adsorbers in a range of protective showcases, used by English Heritage to protect objects in their collections. A previously developed and extensively tested air quality model for showcases\textsuperscript{28,29,30} was used to calculate the efficiency of the different installed adsorbers in reducing the concentration of acetic plus formic acid inside the showcases.

2 Experimental

2.1 Measurement locations

Activated carbon adsorbers were installed in six showcases at the English Heritage sites of Chesters Roman Fort and Museum in northern England and Osborne House, Swiss Cottage, on the Isle of Wight, UK, shown in Figure 1. Views of the rooms are shown in Figure 2. The showcases in Chesters Roman Fort and Museum were desktop style cases, manufactured from lacquered wood, where previous pollution measurements indicated very high levels. The showcases in Osborne House, Swiss Cottage were upright cases, with shelves, constructed from painted wood, where elevated levels of pollutants had previously been measured.

The measurement locations, periods of one month (27-31 days) and adsorbent media installed are described in detail in Table 1. The showcases were selected to offer situations, which were similar or with known variation in the geometry and ventilation rate, suited for the comparison of the effect of installing different active carbon adsorbing materials. Showcases no. 1 and 2 were the left and right chamber of one large showcase and thus very similar. The two sub-chambers were physically divided by a wood board, but there could be some, undetermined, direct ventilation and thus inherent relationship between them.

Showcase no. 3 was the same type, but was tighter and had a higher volume. Showcases no. 4 to 6 were selected to be similar, but with varying ventilation rates.

The objects in the showcases were the same throughout the experiments.

2.2 Measurement of organic acid concentrations inside showcases and installation of activated carbon adsorbers

Measurements were made of the average concentration of acetic and formic acid over the test period, inside the showcases and simultaneously in the museum rooms, before and together with subsequent installation of different types of activated carbon adsorbers (Table 1). No other changes then the installation of the adsorbers were made in the showcases. In showcases no. 1 and 2 new different adsorbing materials were installed in a third period (1B and 2B, Table 1). The measurements were made in duplicate with NILU passive pollution samplers of the IVL (Swedish Environmental Research Institute) badge type (Figure 3)\textsuperscript{31,32}. The experimental uncertainty of the duplicate passive sampling was found to be, on average, a standard deviation of 16 % and 18 % of the measured acetic and formic acid concentrations, respectively, but varying between 0 and 69 % for acetic acid and between 0 and 64 % for formic acid. The detection limit reported from the laboratory was 0.5 \mu g m\textsuperscript{-3} . At both the Chester and Osborne sites the concentrations of the two acids were also measured in one similar type control showcase, where no adsorbing material was installed (Figure 4 and Table 1). The control showcases were subjected to the same opening routines as the test cases during the measurements and installation of adsorbers.

Activated carbon granulate, foam and cloth were installed in the showcases. Two types of granulate (“K48” in 1A and 4, and “MEMORI 6” in 2A and 6), two thicknesses of foam (MEMORI8, 1cm in 1B and MEMORI8, 3cm in 2B) and cloth in single sheet (showcase 3) and double sheet (showcase 5) were used (Table 1).

For each of the two types of activated charcoal granulate that were used, 3 kg of adsorbent was placed within each showcase. This was deployed in polythene bags, which were cut open to create a flap, that was secured open during the test to maximize the available surface area, and that could be sealed back once the trials were complete. The bags were deployed in the top halves of each of the Chester showcases (Figure 1.1 and 1.2), and covering the whole shelf area in the Osborne cases (Figure 1.4 and 1.6). The bags were covered with neutral colour fabric that had passed Oddy test\textsuperscript{33}. In permanent deployment the granulate would have been placed in a container, such as a metallic perforated cassette similar to ProSorb cassettes in size, rather than in the polythene bags. English Heritage have also used Tyvek bags to contain loose granulates. Tests may be required to ensure permeability of such different container materials.
The charcoal cloth in showcase no. 3 (Table 1) covered the base of the showcase (59*166 cm). The cloth was deployed with the back of the cloth visible from the case, for aesthetic reasons, as shown in Figure 1.3. The cloth in showcase no. 5 was doubled over to fit in the bottom of the case (Figure 1.5). The cloth lost some fibres during installation, but only a small number, and in permanent use this wouldn’t be significant.

3 Modelling of the adsorbant efficiency and concentrations of organic acids in the showcases

To determine the relative adsorbing efficiency of the tested activated carbon materials mathematical modelling was performed to predict the change in the concentration of acetic plus formic acids inside the showcase due to the introduction of the adsorbing materials, and for possible changes of the ventilation rate of the showcases. The modelling considered only...
concentrations of acetic plus formic acid and no other pollution gases that could be present. The model calculations were based on the measured values for the concentration of the organic acids (acetic and formic acid) inside the showcases with and without adsorbing media included, in the rooms where the showcases were located, and on measured values for the ventilation rate and geometry of the showcases.

Before calculating the adsorbing efficiency the concentration value for acetic plus formic acid, measured before installing the adsorbers in the showcases, was adjusted according to the measured change in the control showcases. The adsorbing efficiency was then calculated by the equation:

$$E = \frac{(M1 \times C2/C1) - M2}{M1 \times C2/C1} \times 100 \quad (1)$$

where $E$ is the adsorbing efficiency (% reduction in acetic plus formic acid concentration in the showcase due to the installation of the adsorbing material), $M1$ and $M2$ are the concentrations of acetic plus formic acid measured in the showcases with and without adsorbing material installed, and $C1$ and $C2$ are the concentrations of acetic plus formic acid measured simultaneously, with $M1$ and $M2$, in the control showcase with no adsorbing material installed (all $\mu g \, m^{-3}$).

The measured sum of the concentration of acetic and formic acid is reported, with the purpose to investigate the efficiency of the adsorbing media by easily readable modelling. The separate original measured concentration values for acetic and formic acid are reported in Table 2. For the first period, “without adsorber installed” in the showcases, the sums of these separate concentrations were significantly higher than the control adjusted sums of the concentration of the two gases, used in the modelling. This was due to the lower concentration measured in the control showcases in the second period when the adsorbing media were installed ($C2/C1$, see discussion) and the application of Equation 1. Due to the applied model formulation the modelled concentrations are reported as concentration divided by 20028.

The adsorbing efficiency of the activated carbon adsorbers was determined as the value for the deposition velocity30 of acetic plus formic acid to the activated carbon adsorber, that gave close to the same result for the measured and calculated (modelled) concentrations.

---

Figure 6. Modelling results (see also Table 2) for the showcases (Table 1). The value for the “recommended level” is always 400 $\mu g \, m^{-3}$.
tion of the acids in the showcases (see Figure 7). The adsorption rate at any concentration level is obtained by multiplying the deposition velocity with that concentration level.

The same value for the deposition velocity to the showcase internals was used for the modelling of all the showcases28. The air exchange rates of the showcases were measured with the CO₂ method34. The value for the internal showcase area used in the modelling includes the glass.

4 Results

Table 2 reports input data for the modelling and the results from measurement and modelling for the three measurement periods. Figure 6 shows the modelling results for the six showcases (eight tests). The concentrations that were measured in period 1 without adsorbers installed, and adjusted according to the control showcases by Equation 1, are included as input data to the modelling in Table 2. These concentration values are given in Figure 6 by the intersection of the vertical dotted line, denoting the measured air exchange of the

<table>
<thead>
<tr>
<th>Showcase / location no.</th>
<th>1A</th>
<th>1B</th>
<th>2A</th>
<th>2B</th>
<th>3</th>
<th>CC*</th>
<th>CR*</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>OC*</th>
<th>OR*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of activated carbon adsorber</td>
<td>Granulate</td>
<td>Foam</td>
<td>Granulate</td>
<td>Foam</td>
<td>Cloth</td>
<td>control room</td>
<td>Granulate</td>
<td>Cloth</td>
<td>Granulate</td>
<td>control room</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Volume (m³)</td>
<td>0.087</td>
<td>0.087</td>
<td>0.084</td>
<td>0.084</td>
<td>0.179</td>
<td></td>
<td>0.57</td>
<td>0.61</td>
<td>0.56</td>
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<tr>
<td>Internal showcase area (m²)</td>
<td>1.507</td>
<td>1.507</td>
<td>1.521</td>
<td>1.521</td>
<td>4.4655</td>
<td></td>
<td>4.071</td>
<td>4.943</td>
<td>4.636</td>
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<td>Object area (m²)</td>
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<td>0.136</td>
<td>0.11</td>
<td>0.11</td>
<td>0.283</td>
<td></td>
<td>0.437</td>
<td>0.428</td>
<td>0.36</td>
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<tr>
<td>Air exchange rate (d⁻¹)</td>
<td>4.93</td>
<td>4.93</td>
<td>3.83</td>
<td>3.83</td>
<td>1.87</td>
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<td>5.7</td>
<td>29.2</td>
<td>18.4</td>
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<td>Showcase joint length (m)</td>
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<td>2.62</td>
<td>4.52</td>
<td>4.52</td>
<td>4.52</td>
<td></td>
<td>5.46</td>
<td>5.46</td>
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<td>Showcase joint depth (m)</td>
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<td>2.3×10⁻¹</td>
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<td>2.3×10⁻³</td>
<td>2.3×10⁻³</td>
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<td>5.3×10⁻³</td>
<td>5.3×10⁻³</td>
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<td>Showcase joint width (m)</td>
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<td>3×10⁻⁴</td>
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<td>Adsorber area (m²)</td>
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<td>0.29</td>
<td>0.05</td>
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<td>0.3255</td>
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<tr>
<td>Dep. velocity to showcase internal (m s⁻¹)</td>
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<td>1.6×10⁻⁵</td>
<td>1.6×10⁻⁵</td>
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<tr>
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<td>20</td>
<td>20</td>
<td>20</td>
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<td>19.7</td>
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<tr>
<td>Relative humidity (%)</td>
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<td>66</td>
<td>68</td>
<td>68</td>
<td>68</td>
<td>66</td>
<td>66</td>
<td></td>
<td></td>
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<tr>
<td>Measured conc. without adsorber (µg m⁻³)</td>
<td>1660</td>
<td>1660</td>
<td>1260</td>
<td>1260</td>
<td>1010</td>
<td>2690</td>
<td>30</td>
<td>166</td>
<td>52</td>
<td>20.5</td>
<td>722</td>
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<tr>
<td>Acetic acid (µg m⁻³)</td>
<td>1040</td>
<td>1040</td>
<td>840</td>
<td>840</td>
<td>475</td>
<td>1690</td>
<td>17</td>
<td>140</td>
<td>31</td>
<td>16</td>
<td>567</td>
<td>13</td>
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<td>Formic acid (µg m⁻³)</td>
<td>620</td>
<td>620</td>
<td>420</td>
<td>420</td>
<td>535</td>
<td>1000</td>
<td>13</td>
<td>26</td>
<td>21</td>
<td>4.5</td>
<td>155</td>
<td>7</td>
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<tr>
<td>Adjusted conc. without adsorber (µg m⁻³)</td>
<td>856</td>
<td>1077</td>
<td>633</td>
<td>814</td>
<td>510</td>
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<td>37</td>
<td>12</td>
<td>4.5</td>
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<td>Results Period 2:</td>
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<td>Temperature (°C)</td>
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<td>Relative humidity (%)</td>
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<tr>
<td>Deposition velocity to adsorber (m s⁻¹)</td>
<td>1.6×10⁻⁴</td>
<td>1.6×10⁻⁴</td>
<td>7.1×10⁻⁴</td>
<td>1.6×10⁻⁴</td>
<td>7.1×10⁻⁴</td>
<td>1.6×10⁻⁴</td>
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<tr>
<td>Measured conc. with adsorber (µg m⁻³)</td>
<td>667</td>
<td>454</td>
<td>21</td>
<td>1360</td>
<td>10.2</td>
<td>36</td>
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<td>4</td>
<td>161</td>
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<tr>
<td>Acetic acid (µg m⁻³)</td>
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<td>306</td>
<td>6</td>
<td>888</td>
<td>7</td>
<td>30</td>
<td>4</td>
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<td>131</td>
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<td>Formic acid (µg m⁻³)</td>
<td>217</td>
<td>148</td>
<td>15</td>
<td>472</td>
<td>3.2</td>
<td>6</td>
<td>3</td>
<td>1.5</td>
<td>30</td>
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<td>Modelled conc. with adsorber (µg m⁻³)</td>
<td>660</td>
<td>490</td>
<td>53</td>
<td>33</td>
<td>7</td>
<td>4</td>
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<tr>
<td>Modelled reduction in conc. (%)</td>
<td>22</td>
<td>23</td>
<td>90</td>
<td>12</td>
<td>44</td>
<td>6</td>
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<tr>
<td>Measured reduction in conc. (%)</td>
<td>20</td>
<td>28</td>
<td>96</td>
<td>3</td>
<td>44</td>
<td>7</td>
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<td>Results Period 3:</td>
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<tr>
<td>Temperature (°C)</td>
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<td>8.4</td>
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<td>Relative humidity (%)</td>
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<td>51</td>
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<td>Deposition velocity to adsorber (m s⁻¹)</td>
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<td>5×10⁻⁴</td>
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<tr>
<td>Measured conc. with adsorber (µg m⁻³)</td>
<td>237</td>
<td>135</td>
<td>1750</td>
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<td>Acetic acid (µg m⁻³)</td>
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<td>Formic acid (µg m⁻³)</td>
<td>40</td>
<td>24</td>
<td>277</td>
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<tr>
<td>Modelled conc. with adsorber (µg m⁻³)</td>
<td>193</td>
<td>162</td>
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<tr>
<td>Modelled reduction in conc. (%)</td>
<td>82</td>
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<tr>
<td>Measured reduction in conc. (%)</td>
<td>78</td>
<td>83</td>
<td></td>
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Table 2: Input data to the modelling, and results values from measurements and modelling, of the English Heritage showcases. conc. = concentration of acetic plus formic acid

*aAdsorbers were never installed in the control cases (CC and OC) and rooms (CR and OR).

*bThe model input values for the showcases are adjusted according to the measured results values in Period 1, for the test cases and control cases, by Equation 1.

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showcases, and the pink solid curve, denoting the modelled ventilation dependent concentration of acetic plus formic acid in the showcase without adsorber installed. The intersection of the vertical dotted line and the blue dotted curve, denoting the modelled ventilation dependent concentration of acetic plus formic acid in the showcase with adsorber installed, represents the model fit to the measured value for the concentration of acetic plus formic acid in the showcase with the adsorbers installed. The horizontal black dotted line gives the suggested recommended level for acetic plus formic acid in the showcases, of 400 µg m⁻³, which is the lower level where a corrosion effect of organic acids has typically been observed on materials such as sensitive glass and lead. The horizontal red dotted line, termed "unprotected by m(micro-climate)-enclosure", gives the measured room concentration of acetic plus formic acid. In Figure 6 the "optimal air exchange rate" given by the bold black vertical dotted line is shown only for showcase no. 6, as the concentration inside the other showcases was higher than the room concentration, and would be reduced by opening the showcases. Figure 7 shows the measured % reduction in concentration of the acetic plus formic acid due to installation of activated carbon adsorbers in the showcases, and the close to similar % reduction calculated by the model by adjusting the deposition velocity. The concentration values measured in the showcases in period 1, without adsorbers installed, adjusted according to the control showcases by Equation 1, and measured with adsorbers installed in the subsequent periods (Table 1), were used in the model calculations.

5 Discussion

The installation of the activated carbon adsorbing materials reduced the concentrations of acetic plus formic acid inside all the showcases, but with very different relative amounts. The reduction varied from 20 to 96 % inside showcases with high initial concentrations of the acids (from 510 to 1077 µg m⁻³, as adjusted by Equation 1). The % reduction was 3, 7 and 44% for three showcases with low initial concentrations (37, 5 and 12 µg m⁻³, as adjusted by Equation 1). For three showcases (1B, 2B and 3) the reduction was to below the recommended level for the pollutants, thus meeting a defined target for the mitigation action (Figure 6-1B, 6-2B and 6-3).

Ideally, to obtain accurate results for the adsorbing efficiency, the test conditions should be strictly controlled to assure similar conditions, except for the installation of the adsorbers. Such test could be performed in a laboratory. In "real life" tests with showcases in use at heritage locations, such strict control of experimental conditions is difficult. To obtain valid results similar co-located English Heritage showcases were therefore selected for the tests. The organic acid concentrations were measured inside the same showcases in subsequent periods with and without adsorbers installed. The uncertainty in the result would then mainly be due to possible changing concentrations in the showcases between the subsequent periods, unrelated to the installation of the adsorbing media. To check, and make the best possible control, for this possible interference it was decided to measure the concentrations of the organic acids in similar co-located "control showcases" where the adsorbers were not installed. These results, C2/C1 in Equation 1, were used to "control", i.e. to adjust, the concentration values measured in the test showcases in the first period, before calculating the efficiency of the adsorbing media, as percentage reduction in concentration due to the installation of the adsorbers.

The C2/C1 ratio in Equation 1 was 0.5 and 0.64 for the second and third periods, respectively, in the room at Chesters, and 0.22 for the second period in room at Osborne House (Table 2). This large change in the measured concentrations of acetic plus formic acid inside the control showcases from the first to the subsequent measurement periods, show the importance of the control adjustment performed by using Equation 1. The reason for the reduction of the concentration in the control showcases to the second, and third periods may have been the repeated ventilation when installing the samplers, and most likely the reduction in temperatures in the cases to the second and especially the third winter period (Table 1). In the Chesters showcases, for which temperature and relative humidity data are available, the average reduction in temperature to the second and third periods was 15 % and 60 %, the average reduction in relative humidity was 3 % and 8 %. The relative humidity in the control case did however not change significantly (Table 3). The concentrations measured in the control showcases were much higher than measured in the test cases, especially in Osborne House. This was unexpected as showcases of similar design were selected as test and control cases. The reason was most likely some difference in the construction materials, especially the wood, and, or in the tightness of the showcases, which was not apparent. With resources available for pre-testing of the showcases, a better selection of the control cases, especially in Osborne House, may have been made. However, the relative changes in the concentrations in the showcases between subsequent measurement periods, due to other reasons than the adsorbers, will probably be quite similar at different concentration levels. The changes in the measured concentrations in the control showcases, to the subsequent measurement periods, were also larger than expected. These changes made the implemented control adjustment necessary and critical. However, this also raises some questions about the reasons for the temporal changes in concentra-
lations, and if these changes were actually similar in the control cases and the test cases, as was assumed. These questions are unfortunately not possible to answer with certainty. When reading the results this undetermined uncertainty in the control adjustment should be kept in mind.

A similar value for the deposition velocities (adsorption rates at similar concentration) were found to the similar kinds of adsorbing materials (Table 2 and Figure 7). The deposition velocity to the activated carbon cloths in showcases no. 3 and 5 and to the foams in no. 1B and 2B, were found to be 4.4 and 3.1 times larger, respectively, than to the bags with activated carbon granulate in no. 1A, 2A, 4 and 6. The likely reason for this is that the cloth and foam has smaller pore size diameter and thus larger surface areas for adsorption than the granulate. The deposition velocity found to the activated carbon cloths in showcases no. 3 and 5, was found to be about 2.3 times smaller than values measured for the surface deposition velocity of inorganic pollutant gases to activated carbon cloth in laboratory experiments (0.0015 – 0.0017 m s\(^{-1}\))\(^{36}\). The likely reason for this was the much lower air velocity inside the showcases than in the experimental chamber (<0.03 cm/s in showcase no. 5 vs. 0.1 cm/s in the experimental chamber).

Due to the higher adsorption rate of the activated carbon cloths the largest % reduction in the acetic plus formic acid concentration was found in showcase no. 3. Even if the deposition velocity to the activated carbon foam used in showcases no. 1B and 2B was found to be lower than to the activated carbon cloth used in showcase no. 5, the % reduction of the organic acids in these two showcases was larger than in no. 5 (Table 2, Figure 7). The reason for this was the much lower air exchange rate in showcases no. 1B and 2B than in no. 5 (Table 2). The very high air exchange rate in showcase no. 5 reduced the concentration of the organic acids to a low level. Still, the activated carbon cloth removed nearly 50 % of the remaining amount of acetic plus formic acid in the air in this showcase (Figure 7). For showcase no. 6 increased ventilation would, contrary to the other five showcases, give a higher internal concentration of acetic plus formic acid, as the concentration of the acids in the unprotected situation, i.e. in the room, was higher than inside the showcase. The contribution to the concentration of acetic plus formic acid from the air ventilated into this showcase, was larger than the contribution from the internal emission.

The deposition velocity to the different types of activated carbon adsorbing materials seemed not to depend on the thickness or amount of the material, but only on the surface characteristics. Still, it is important to note that the adsorption capacity, and thus lifetime and cost of installation, is expected to depend on the amount of material installed.

The foams were easier and nicer to install than the loose granulates, but not as good as charcoal cloth. The foam that was 1 cm in depth was easier to work with compared with that 3 cm in depth. Space is often limited in showcases and thinner materials have a great advantage in these instances. Charcoal material is easily lost during working, e.g. cutting, and mounting can leave black fibres, particles and dust. Fibres from the activated carbon cloth was a less problem than dust from the foams. Shedding of charcoal fibres and particles is significant in presentation terms and their effects on some object types is unclear. Several activated charcoal cloths contain chloride and this aggressively attacks silver and copper alloys (even through separation layers) in accelerated tests\(^{35}\).

6 Conclusion
The installation of activated carbon adsorbing materials in a number showcases used by English Heritage to protect cultural heritage objects, reduced the measured concentration of acetic plus formic acid in the showcases significantly. Activated carbon cloth was found to be more effective than foam and much more effective than granulate. Where activated carbon cloth or foam were installed in showcases with a ventilation rate of two to five air exchanges per day, the reduction was from 78 to 96%, to give levels below the recommended target level. In a showcase with activated carbon cloth and a very high ventilation rate of 29 air exchanges per day, the reduction was 44%. Where activated carbon granulate was installed in showcases with ventilation rates of four to six air exchanges per day, the reduction was from three to 28%.

The deposition velocity, and thus the reduction in pollutant concentration at similar conditions, was found to be very different for the different kinds of activated carbon adsorbing materials that were tested. The deposition velocity to the activated carbon cloth was found to be 1.4 times higher than to foam, and 4.4 times higher than to granulate.

The charcoal cloth was better to install than the foam which was better to install than the granulate. Charcoal material is easily lost during working which can be negative in presentation terms. As charcoal cloths can contain chloride this can be a corrosion risk.

7 Acknowledgement
This work was supported by the EU project MEMORI (Grant Agreement No. 265152). We want to thank our MEMORI partner Alexandra Schieweck at the Fraunhofer Institute for Wood Research (WIKI) for her work with supplying activated carbon adsorbing materials. We also want to thank our institutions NILU-Norwegian Institute for Air Research and English Heritage for their support.

8 References


