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DERIVATION OF A MODEL FOR THE CALCULATION OF IMPACT LOADS OF AIR POLLUTANTS TO PAINTINGS IN MICROCLIMATE FRAMES

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The derivation of a model to evaluate the potential impact of gaseous pollutants on paintings installed in microclimate frames (mc-frames), and some examples of modelling results, is presented. The model can be used to study how basic design properties of microclimate frames, such as their air exchange rate, their volume and/or the inclusion of absorbers can affect the pollution fluxes to paintings inside the frames. The modelling indicated that a magnitude increase in air exchange rate from a low level of ~1 d^{-1} can significantly increase the impact of infiltrating pollutants, but will give only a small reduction in the potential impact of the small molecular weight organic acids (i.e. acetic and formic acid) that are emitted inside the frames. The reason for this is the small amount of pollutant removed by each single air exchange, as compared to the large internal emission and deposition fluxes of these gases.

1   Introduction

Microclimate (mc) frames are increasingly used to protect paintings in museums. The mc-frames protect against climate (RH and T) fluctuations and UV exposure. They also protect against external pollution including dust and soiling, and against physical damage and theft. The negative sides are added weight, difficulty of handling, risk of breakage, trapping of internally generated pollutants and cost[1-4]. This paper describes the development of a steady state mass balance model to be used for calculating impact fluxes of gaseous air pollutants to paintings enclosed in microclimate (mc) frames. The paper discusses the properties of the model in relation to the needed input data and their uncertainty, and the interpretation of the model results in terms of pollutant impact on paintings in mc-frames. Examples of modelling results are presented for two paintings in mc-frames located in two different European museums. The input data for the two frames were obtained from measurements made in the EU project PROPAINT.[5] The modelling can be used to study the effect of the air exchange rate, mc-frame geometry (volume and inside area) and inclusion of absorbing materials on the impact fluxes of gaseous pol-

lutants to paintings in mc-frames. The model is presently a research model valid within the range of conditions defined by the mc-frames used for its testing. As such, one of the frames with an air exchange of 14.9 d^{-1} and approaching the condition of free air exchange, was used as a limiting case. The aim is to further develop the model to make it more robust and to test it for a larger range of microclimates, e.g. for showcases. This paper describes the model derivation illustrated with examples of modelling for two mc-frames. The description of materials and methods and results from the measurement of the pollutant gases is reported in the PROPAINT Final Report.[5]

2   Methodology

2.1   Experimental

The main characteristics of the two mc-frames and the paintings for which pollutant impact modelling and comparison of protection against gaseous pollutants were performed, are given in Table 1. The mc-frame in Kenwood, English Heritage (no. 1, Table 1) had a broken Al-barrier film. The "Leonardo frame" no. 2 was a more open enclosure with a glass front positioned against an opening in a wall in where the painting was positioned.

The modelling for the two mc-frames and paintings was performed based on measurements of the concentrations of the major gaseous pollutants (NO$_2$, O$_3$, acetic and formic acid) known to be potentially degrading to paintings and usually to be present outside and inside of the mc-frames,[5] of the air exchange rates, net volumes and internal areas of the mc-frames, and of the areas of the paintings in the frames. Other pollutant gases are known to have degradation effects on paintings (e.g. SO$_2$) or to be present inside mc-frames in considerable amounts (various higher molecular weight VOCs),[6-10] but due to their very low reported concentrations[5] or the unknown degradation risk for paintings (the VOCs) these were not included in the modelling.

The measurements of the gaseous pollutants inside the mc-frames were made in the accessible small volumes inside the mc-frames. These volumes were on the back side of the painting in mc-frame no.1 and in the front of the painting in mc-frame no. 2, where the whole internal volume of the enclosure was found in front of the painting. Similar modelling could be performed for other pollutants or combinations of pollutants of concern.

A detailed description of the measurement methods used and of results from measurements are reported in the "PROPAINT Final report".[5] In Table 1 the input data used for the modelling and some additional information for two frames are reported.

Frame		1. EH, Kenwood (EH K)	2. Krakow, Leonardo (NMK1)
Microclimate frame characteristics			
Type of mc-frame		New frame	Purpose built
Age of mc-frame (years)		20+	5
Air exchange rate (day^{-1})		1.4	15
Net volume (m^3)		0.041	0.32
Frame area (internal) (m^2)		2.0	4.5
Frame minus glass area (internal) (m^2)		1.1	1.5
Object inside mc-frames		Oil on panel	Tempera on panel
Painting area (m^2)		1.8	0.6
Materials inside mc-frame		Wood, glass, oil tempered Hardboard silicone seal, aluminium foil, PVC coated cable, brass screws	Glass ~60% of this enclosure, fibre board, tapestry, Velcro ®
Location* with materials, N = Naturally ventilated		Public gallery (N), Plaster, wood.	Public gallery (N), Waxed wood, tapestry, lime plaster and emulsion paint.
Pollutant measurements			
NO$_2$ conc. (µg m^{-3})	I	2.0	2.0
	O	20.2	23
	St.dev.	(0.70)	(0)
O$_3$ conc. (µg m^{-3})	I	<1.0	3.3
	O	9.0	7.4
	St.dev.	(0.3)	(0.9)
Formic acid conc. (µg m^{-3})	I	511	<0.5
	St.dev.	(86)	-
	O	11.1	10.3
	St.dev.	(0.2)	(5.5)
Acetic acid conc. (µg m^{-3})	I	1548	317
	St.dev.	(146)	(71)
	O	52.1	23
	St.dev.	(1.2)	(15)

* Glass is not included

Table 1: Main characteristics of two of the mc-frames studied in the PROPAINT project, used to illustrate results obtained from the modelling. 1. English Heritage mc-frame with the painting "London Bridge" by Claude de Jongh (1630) at Kenwood House, London. 2. Mc-frame from the National Museum of Krakow with the painting "Lady with Ermine" by Leonardo da Vinci (1452-1519), Czartoryskich Museum, Krakow, Poland. For the pollutant measurements I = inside frame, O = outside frame and the values in brackets are the standard deviation of two measurements.

2.2   Recommended pollution levels

The recommended levels for the pollutant concentrations used in modelling were the "air quality targets for museums, galleries, libraries and archival collections" as recommended by ASHRAE[6] and also suggested by Tetreault[7]: NO$_2$ + O$_3$ = 2 µg m^{-3} and acetic +formic acid = 100 µg m^{-3}. These levels are based on ten years Lowest Observed Adverse Effect Doses (LOAEDs).[7] Other references suggest different levels: Lower recommended levels

for O_3 (0 ppb) for general museum environments than for NO_2 (2.5 ppb), but higher levels for paper (O_3: 13 ppb, NO_2: 5 ppb) are reported.[8] It is reported that "attempts have been made to set standard levels for acetic acid resulting in a suggested low threshold level of 10 μg m^{-3} for conservation environments".[9] This is in the lower range of typical outdoor background concentrations. It is also simply recommended to use of best available technology to control acetic acid concentrations.[10] Any recommended levels found suitable could have been used in the modelling. The debate about the validity of using the LOAED concept in conservation is not a subject for discussion in this paper. Suffice it to say that to determine the minimum pollutant dose exposure that gives an observable effect on a material, the method of observation should be defined. The effects of small doses that cannot be seen with the eye can often be observed with physical or chemical characterisation methods.

Even if the ASHRAE recommended level for NO_2 and O_3 is the same one should be aware that the observed effects of these gases are often different, for different materials. Somewhat lower observed effects levels for O_3 than for NO_2 are reported in general on colourants and organic materials.[7] Acetic and formic acid are usually grouped when qualitatively describing degradation effects.[7,8] Similar observed effect levels are reported for acetic and formic acid exposure of metals.[7] A lowest observed acetic acid effect on metals for a yearly dose of 600 μg m^{-3} in typical museum conditions at RH = 50% is reported.[11] The observed effects of acetic acid are most commonly reported for lead and copper. It is reported that no effect of acetic acid on lead is observed for concentrations below 317 μg m^{-3}, which is also used as the British Museum Performance Target for lead objects in display cases.[12] There is little information about observed degradation of paintings or organic objects due to acetic acid exposure. A LOAEL for cotton in Whatman papers of 3000 μg m^{-3} and a LOAED of 5000 μg m^{-3} yr are reported based on pH measurements.[13]

2.3 Model derivation

The modelling was based on steady state mass-balance equations.[14] The modelling was performed for a combination of oxidising gases (the sum of the concentrations of $NO_2 + O_3$ = "Gas 1") infiltrating from outside the frame and organic acids (the sum of the concentrations of acetic and formic acid = "Gas 2"), the presence of which in the mc-frames was mainly due to their emission inside the frames. The starting point for the math-

ematical modelling was the mass balance equation describing the steady state average concentration of a pollutant in a frame:

$$\frac{d\overline{C}_i}{dt} = Qf C_o - Q\overline{C}_{is} - v_{df}\overline{C}_{is}\frac{A_f}{V} - v_{do}\overline{C}_{is}\frac{A_o}{V} - v_{da}\overline{C}_{is}\frac{A_a}{V} + e\frac{A_e}{V} + H = 0$$

Equation 1

Where Q is the air exchange rate (s^{-1}), f is the frame filtration factor (dimensionless, $0 < f < 1$), C_0, C_i and C_{is} are the concentrations of the pollutant gas in the room and inside the mc-frame depending on time and for the steady state, respectively (μg m^{-3}), e is the emission rate (μg m^{-2} s^{-1}), H is the production rate from homogeneous, chemical reaction(s) in the air inside the frame (μg m^{-3} s^{-1}), v_{df}, v_{do} and v_{da} are the deposition velocities to the frame internal, object and absorber surfaces (m s^{-1}), A_e, A_f, A_o, and A_a are the areas of emitting material, mc-frame inside, object (painting), and absorber material surfaces (m^2), respectively, and V is the inside mc-frame net volume (m^3). For the internal area of an mc-frame, A_f, the total internal frame area minus the area of the glass front was used, assuming a deposition velocity to clean glass = 0. This value ($v_d = 0$) for the deposition to clean glass was also used for acetic and formic acid. A time resolution of days (day^{-1}) was used. To simplify expressions in further derivations, v_d (absorber) was set equal to = 0, having in mind that this part could easily be added as an additional area, adjusted for the relative deposition velocity to the absorber to that to the frame interior, in a similar way as for possible deposition of the organic acids to the glass. In this way the effect of introducing an absorber into the mc-frame, such as e.g. active carbon, could be calculated.

The flux to the object (painting) in the mc-frame was calculated from:

$$F_o = v_{do}\overline{C}_{is}$$

Equation 2

with average C_{is} given from equation 3:

$$\overline{C}_{is} = \frac{QfVC_0}{QV + v_{do}A_o + v_{df}A_f} + \frac{eA_e + HV}{QV + v_{do}A_o + v_{df}A_f}$$

Equation 3

where the flux and internal concentration are calculated to be partly from infiltration, first part of equation 3, and partly from inside of frame emission and homogeneous reaction, second part of equation 3. Depending on the reaction mechanism the expression for H may include C_{is} or not, and thus as a result of the algebra from equation 1 to equation 3, be part of the numerator or denominator in equation 3. Any particular homogeneous reaction paths were not included in the modelling

and possible removal due to homogeneous reaction (in the gas phase) was considered as deposition, and possible production as emission. It is possible that e.g. some of the formic acid measured inside the frame is produced by oxidation of formaldehyde in the gas phase (homogeneous reaction) inside the frame and that this give a loss of O_3. Any such possible loss of infiltrating O_3 (or NO_2) was calculated as deposition to the painting and would give an overestimation of the impact flux to the painting due to infiltration. Any resulting homogeneous production of acetic or formic acid e.g. from formaldehyde was simply calculated as a part of the "total emission plus reaction rate of acetic plus formic acid". The term HV is included to indicate that such reactions could contribute to the measured concentration values.

The total emission rate (mass per unit time) of Gas 2 was calculated from equation 4 using the measured values for the mc-frames as input:

$$eA_e + HV = \overline{C}_{is}\left(QV + v_{df}A_f + v_{do}A_o\right) - C_0 QfV$$
Equation 4

The deposition velocity for Gas 1, to both the frame inside and the painting, was calculated from equation 5, setting the two deposition velocities equal ($v_{do} = v_{df}$) and assuming no internal production of Gas 1 from internal emission or reaction. This value was also used for the deposition velocity of the infiltrating fraction of Gas 2.

$$v_{df,o} = \frac{QV\left(\dfrac{fC_0}{C_{is}} - 1\right)}{A_f + A_o}$$
Equation 5

The value obtained for the relatively open "Leonardo enclosure" (Table 1) was used for the. surface deposition velocity. ($v_{so\,(object)} = v_{sf\,(frame)} = 0.012$ cm s^{-1}) This value is in the middle between the v_s values reported for NO_2 and O_3 to paintings.[15] This value was used for both Gas 1 and Gas 2. The filtration factor (f in equation 4) was set equal to 1 (no pollution loss in the sealing) and the filtration effect then rather calculated as a transport resistance; i.e. a transport limited deposition velocity dependent on the air exchange rate, $v_t(Q)$:

$$v_t\left(Q\right) = \frac{Q}{Q_m}\left(\frac{1}{v_{dm}} - \frac{1}{v_s}\right)^{-1}$$
Equation 6

where Q_m is the measured value for the air exchange rate and v_{dm} the total deposition velocity calculated for each frame from the measured data (equation 5), and assuming as the best

approximation a linear dependence of v_t on the air exchange rate. The values for the air exchange dependent total deposition velocities, $v_d(Q)$, were then calculated from:[16]

$$\frac{1}{v_d(Q)} = \frac{1}{v_s} + \frac{1}{v_t(Q)}$$
Equation 7

The total pollution deposition to the painting inside the frame was then calculated as the "Gas 1 equivalent impact flux" for the n gases of interest.

$$F_o(tot) = \sum_1^n F_o \cdot (C_{R1} / C_{Rn})$$
Equation 8

The "impact sum" of the fluxes of the infiltrating oxidising gases (Gas 1 = NO_2 and O_3), and of the organic acids (Gas 2 = formic and acetic) that mainly comes from emission, inside the mc-frames, was calculated as follows:

$$F_o(ox + ac) = F_o(NO_2 + O_3) + F_o(Form.ac + Ac.ac) \cdot C_{R1}/C_{R2}$$
Equation 9

Where C_{R1} and C_{R2} are the recommended concentration levels for Gas 1 and Gas 2, respectively.

The total potential impact flux to the painting at the location, but without the mc-frame protection, F_u, and at the recommended level, F_r, for the pollutants were calculated from:

$$F_u(ox + ac) = F_{u,Gas1} + F_{u,Gas2} \cdot C_{R1}/C_{R2}$$
Equation 10
$$F_r(ox + ac) = F_{r,Gas1} + F_{r,Gas2} \cdot C_{R1}/C_{R2}$$
Equation 11

The fluxes in Eq. 10 and 11 were calculated as for Fo in Eq. 2, using the room concentration, C_0, and considering the room air to be well mixed, giving vd = vs = 0.012 cm s^{-1}.

The model was written in Excel for easy parameter input and results output.

The model enables studies of the effect of varying air exchange rate, and of the effect of changing the volume geometry (V) assuming constant total emission of Gas 2 inside the microclimate frames. The possible inclusion of an absorber material can be modelled by adding an internal area equal to the absorber area (A_a) times the fraction of the deposition velocity to the absorber, to that to the frame interior (v_{da} / v_{df}).

The calculation of an "impact concentration" is a simplified procedure for the assessment of the impact of air pollutants on the paintings, compared to doing the modelling of the impact flux. The
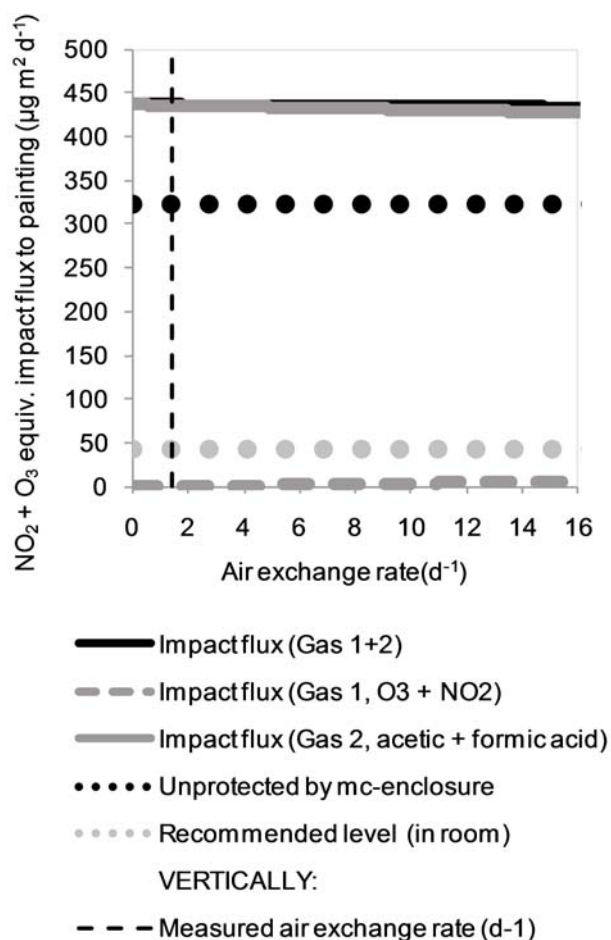
Figure 1: Evaluation of performance for the microclimate frame no. 1 (EH, Kenwood frame, Table 1). The impact flux of Gas 1 plus Gas 2 and the total impact flux from infiltration of Gas 1 and from inside of mc-frame emission of Gas 2, are shown. The impact flux from infiltration of Gas 2 was ~0.
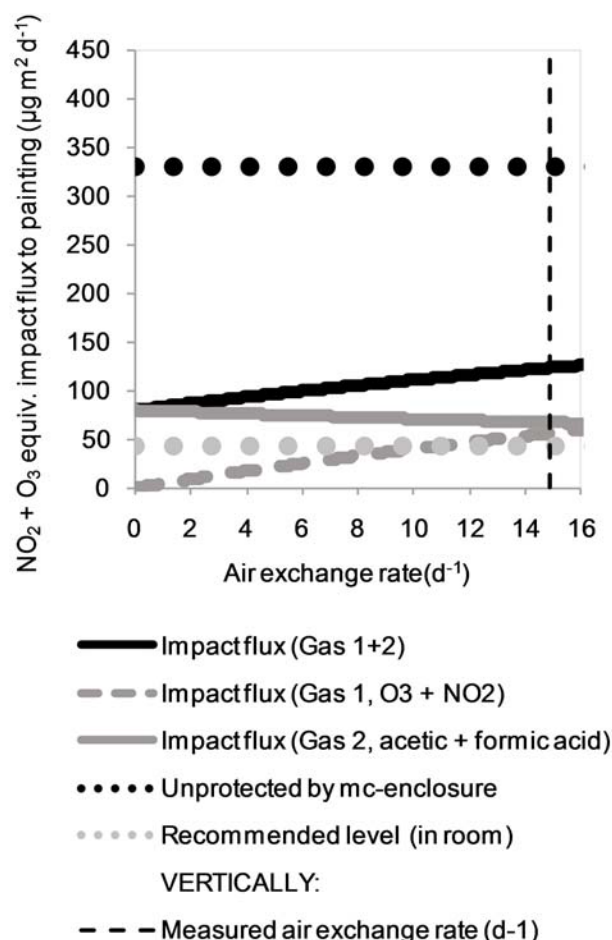

Figure 2: Evaluation of performance for the microclimate enclosure no. 2 (Krakow, Leonardo frame, Table 1). The impact flux of Gas 1 plus Gas 2 and the total impact flux from infiltration of Gas 1 and from inside of mc-frame emission of Gas 2, are shown. The impact flux from infiltration of Gas 2 was ~0.

impact concentration can be calculated from equation 9 using the measured values for the concentrations as input (instead of the calculated fluxes). This is a good approximation of the impact as the difference between the flux and the concentration is only the factor of the deposition velocity (equation 2). For the infiltrating gases in the well sealed mc-frame no. 1 (Table 1) the deposition velocity was calculated to be low and the impact flux was found to be so low, ~0, that it could for the practical evaluation be ignored, as would be the case for other well sealed mc-frames. In the EC PROPAINT project, the protection effect of 11 mc-frames was calculated as the "impact concentration" in the rooms minus the "impact concentration" still remaining inside the mc-frames. The impact of the infiltrating gases given by the first expression on the right side of equation 9, was then included only for frames with an air exchange >6.7 d^{-1}, and for completeness the low measured values of SO_2 were also included.[5]

3   Modelling results - examples

Illustrations of modelling results for the two frames in Table 1 are given in Figures 1 and 2. For the microclimate frame in Kenwood (Figure 1) with a broken Al-barrier film the total calculated impact flux to the painting was higher than calculated for the unprotected situation in the room. Considerable protection was calculated for the "Leonardo enclosure" (Figure 2) as compared to the room situation. No one of the two microclimate frames satisfied the recommended level, although the Leonardo enclosure was considerably closer. Ventilation of the microclimate frame in Kenwood would decrease the impact flux (move it towards the room situation), but only very slightly for a moderate or even quite large increase in the air exchange. Similarly, for the Leonardo enclosure, the impact flux of Gas 2 only decreases slowly as the air exchange rate increases. In contrast to the Kenwood frame, the Leonardo enclosure would benefit from better sealing as that would signifi-

cantly reduce the calculated impact from infiltrating oxidants (i.e. NO_2 + O_3).

4 Discussion

4.1 Results

The modelling clearly shows how increasing ventilation of microclimate frames can give significant increase in the impact flux of infiltrating gaseous pollutants to the paintings in the frames. This effect would be larger for higher room concentrations of the pollutants and higher net volumes of frames.

The modelling indicated that the emission and deposition fluxes of light molecular weight organic acids (i.e. acetic plus formic acid) inside the microclimate frames were much larger than the ventilation fluxes, so that a moderate or even quite large increase in air exchange would not significantly reduce the deposition fluxes and thus be an effective mitigation measure. A hypothetical increase in the air exchange from low values (~1 d^{-1}) to more than magnitude higher values (~15 d^{-1}), would, assuming that ventilation did not affect the emission rates, not significantly decrease the concentrations of the internally emitted organic acids (formic and acetic acid) and their impact fluxes to the paintings (Figure 1 and 2). The reason for this is the low volumes of the frames and thus small amount of pollutant removed by each single air exchange, as compared to the internal emission and deposition fluxes.

Some of the deposition of the organic acids inside the mc-frames may happen to parts of the painting, backing, frame etc. that are themselves emitters. This would reduce the net deposition which could also be negative (net emission), e.g. for a wooden frame. This should be considered in studies of the possible related chemical degradation processes of the materials.

The reported results illustrate the application of the model for a set of pollutants with potential impact calculated on the basis of recommended levels. It is important that the general physical model which is presented here in principle does not depend on input for any particular pollutants or recommended levels, but can be applied for a set of pollutants with some related assessment of their degradation potential reported as concentration in air. As such, it is a physical flux or dose - response model, where the detail and unit for the calculated degradation response will depend on the detail in the description and quantification of the dose - response mechanism. In e.g. corrosion science there exists detailed chemical models that transfer

quantified fluxes to quantified corrosion effects.[17] The model could be used to predict such effects for known mechanisms on paintings. In conservation practice the assessed degradation risk due to the environment is often expressed as recommended levels for pollutants, which should then reflect the rate with which the related degradation process will affect the value of the painting(s), however that is defined. This translation is not only a "simple" procedure based on the science and it will not be a topic for discussion in this paper. However as these recommended levels are the guidelines for the conservators in their daily work they are used as the "target values" for the modelling in this paper, keeping in mind that more detailed chemical and, or physical effects can be assessed and quantified when description of more detailed dose - response relationships are available.

4.2 Measurements, modelling and mc-frame design

Both for the reason of available space and due to visual interference it was not possible to do the passive sampling between the glass and the painting in mc-frame no. 2, and in most mc-frames this would be difficult. Thus, the modelled and calculated impacts are directly relevant for objects in contact with this major internal volume of the mc-frame. To understand the effect of air pollutants on the paintings it would be important to understand how the pollutants are distributed inside the frames between the back side and the front side of the painting, and how they deposit on its different parts and may affect materials in panel and canvas paintings in synergy with other factors such as light and temperature. More detailed studies of such subjects are essential to understand how average loads of pollutants, and other environmental factors, cause the actual observed degradation effects of paintings.

4.3 Interference of passive sampling inside the mc-frames

An evaluation was performed if the passive diffusive samplers by their gas absorption were themselves affecting the measured concentrations inside the mc-frames. This would be the case if the deposition fluxes to the samplers were a significant part of the total deposition, to the samplers and to the inside of the mc-frames. It would also be the case if there was a starvation effect so that the diffusion of the pollutants to the samplers extended beyond andreduced their concentration

at the diffusion barrier (the top net) of the samplers and thus the measured concentration.

The surface deposition velocity to the samplers is known to be ~0.1 cm s^{-1}. For the surface deposition inside the frames a deposition velocity of 0.012 cm s^{-1} was used for both Gas 1 and Gas 2. Deposition velocities of 0.012 cm s^{-1} and 2.5·10^{-4} cm s^{-1} were calculated for the infiltrating Gas 1 in the quite open enclosure (no. 2) and the tighter mc-frame, no. 1 (Table 1), respectively. These values were also used for the infiltrating fraction of Gas 2. The area available for passive sampling is for each sampler 3.14 cm^2 giving ratios of the internal mc-frames (minus glass) plus painting area / passive sampler areas of approximately 6700 (frame 2) and 9200 (frame 1). This gave (inside frame / sampler flux ratios) of 0.012 / 0.1 · (3350 and 4600) = 400 to 550 for the parallel sampling of acetic and formic acid performed inside the mc-frames. For the single NO$_2$ and O$_3$ samplers the values would be the double. If "starvation" is happening and the deposition velocity to the sampler is reduced to a lower value than ~0.1 cm s^{-1} the interference would be less significant.

For pollutants infiltrating in the tight frame no. 1, the calculated deposition velocity is more than magnitude lower than the surface deposition velocities measured to a range of materials.[15] This value indicate transport resistance, v_t, as calculated in equation 6, due to the mc-frame sealing. The deposition of the infiltrating gases to the passive samplers was then determined by the limited transport from the outside and the ratio of the fluxes to the frame and sampler will simply equal the ratio of the internal area to sampler area, as given in the text above.

Thus, for the use of parallel sampling the highest calculated interference is 0.25% (frame / sampler flux ratio = 400). With six passive samplers (sensitive to different gases with parallels only for acetic plus formic acid) inside the mc-frames the chance for interference was higher, possibly ~ 1%.

Due the expected near static conditions inside the frames it is likely that some "starvation" was occurring for the passive sampling of the organic pollutants emitted inside the frames. It is difficult to assess the magnitude of this possible error without additional research or comparison with active measurements.

4.4 Deposition velocities

The value for the surface deposition velocity (0.012 cm s^{-1}) calculated by equation 5 for the infiltrating Gas 1 is between the higher values

reported for v_s for O$_3$ (0.086 cm s^{-1}) and SO$_2$ (0.063 cm s^{-1}) to paintings at RH = 50%, and the lower value reported for NO$_2$ (0.004 cm s^{-1}).[15] Deposition velocities for acetic acid have been measured to silver (0.005 cm s^{-1}) [18] and for acetic and formic acid to copper (0.007 and 0.014 cm s^{-1}, respectively).[19] A relatively higher value for v_s is expected for coarser surface materials inside the mc-frames, but a relatively lower value ~ 0 for the (clean) glass area, as has been found for the inorganic gases.[15] The calculated laminar air flow velocity through the more open enclosure, no. 2, is = 4 times higher than the calculated deposition velocity. This enclosure probably has much less deposition of pollutant gas in the sealing and thus less transport resistance than frame no. 1. The calculated value for the deposition velocity is probably close to the average v_s for the materials inside this frame. It is expected that the inside v_s values for the different mc-frames are different due to different materials with different areas, but the value of 0.012 cm s^{-1} is a probable average.

If it is found that the deposition velocity of the organic acids to clean glass are significantly larger than zero, the glass area or a fraction of the area corresponding to the fraction of the deposition velocity to the glass to that to the rest of the frame interior, could be added in the modelling.

4.5 Experimental disturbance of the equilibrium

For some time after the start of the measurements, after the passive gas diffusion samplers were installed and the mc-frames were closed, the concentration of acetic plus formic acid inside the mc-frames would be below the steady state equilibrium concentration, and the concentration of NO$_2$ plus O$_3$ inside the frames would be above the steady state equilibrium concentration. The analytical solution to the steady state mass balance equation no. 1, for the time to reach a specific concentration, C_i, inside the mc-frames, is given by:

$$t = -\frac{1}{B} \ln \frac{\overline{C_i} - \overline{C_{is}}}{\overline{C_0} - \overline{C_{is}}}$$

Equation 12
where

$$B = Q + v_{df}\frac{A_f}{V} - v_{do}\frac{A_o}{V} - v_{da}\frac{A_a}{V}$$

Equation 13

The solution to equation 12 shows that the time to reach 99% of the steady state equilibrium concentration after closing the frames was 4 min and 76 min for mc-frames no 1 and 2 respectively. For four other frames this time varied between 8 and

25 min. For frame no. 2 this is only 0.17% of the total measurement time giving even less error in the measurement value for the increasing concentration of acetic plus formic acid, but somewhat higher error for NO_2 plus O_3 due to its decreasing concentration to low values, during this time. For the other frames the error would be less. A possible too low measurement of the internal concentration, due to other experimental errors, does not affect this result as the concentration of acetic acid plus formic acid outside the mc-frames, C_0 in equation 12, was in all cases very low.

4.6   Modelling specificity

Technically, the modelling could be performed including all the different specific separate pollutant gases, in our case NO_2, O_3, acetic and formic acid. However this would make the use of the model and the evaluation and presentation of results more complicated. It was evaluated that the modelling for two groups of gases (Gas 1 and Gas 2) expected to take part in the main oxidising and acidic surface degradation mechanisms, represented the gaseous pollutant impact on the paintings in the mc-frames in the best way. It is then assumed that the concentration of $NO_2 \approx O_3$ inside the frames. Their average deposition velocity can then be used. It is also assumed that the deposition velocity and recommended levels for formic acid are the same as for acetic acid. NO_2 and O_3 concentrations were low and generally similar inside the frames although with some variation.[5] This would give some uncertainty in the calculated value for their (Gas 1) impact flux. This is generally of little importance for most mc frames, that are well sealed, such as mc-frame no. 1, and for which the impact flux of Gas 1 would be only a small fraction of the impact flux from Gas 2. For the more open mc-enclosures, no. 2 (Figure 2) the impact of the infiltrating Gas 1 was however high. The ratio of NO_2 to O_3 was in this case for the room and inside the enclosure equal to 3.1 and 0.6, respectively. Thus the use of different deposition velocities and recommended levels for these two gases would have influenced the result.

5   Conclusions

It was demonstrated that the average potential pollution impact, based on available recommended levels for the pollutants inside microclimate frames for paintings, can be evaluated by the use of a mass balance model. The modelling can be based on recommended levels for the pollutants or some observation of degradation effect that can be related to concentration values for the pollutant gases.

The performed modelling indicated that ventilation can introduce significant amounts of external pollutants, but is usually not a very effective way to reduce impacts of internally emitted gases to the paintings in the mc-frames. The reason for this is the relatively small volumes and thus small amounts of pollutants removed for each air exchange as compared to the internal emission and deposition fluxes.

The modelling can be used for any gaseous pollutants for which concentration values are available and for which some degradation effect measure related to the concentration values, e.g. recommended levels, are available. The model can be used to study how change in design features of mc-frames such as internal volume and installation and area of installed of absorber materials will affect the load of gaseous pollutant pollutants on paintings inside mc-frames and thus the protection effect of mc-frames against the pollutants.

To understand the specific effects of pollution loads on paintings inside mc-frames it is however necessary to do more detailed studies of the interaction between the environments and paintings inside the frames.

6   Acknowledgements

7   Literature

1. S. Hackney, *The Evolution of a conservation framing policy at Tate*. In: T. Padfield, K. Borchersen (eds.), Museum Microclimates. Proc. Copenhagen Conference, 19-23 Nov. 2007. Copenhagen, The National Museum of Denmark, 2007, 229-235.

2. M. Richards, *The benefits and disadvantages of adding silica gel to microclimate packages for panel paintings*. In: T. Padfield, K. Borchersen, K. (eds.), Museum Microclimates. Proc. Copenhagen Conference, 19-23 Nov. 2007. Copenhagen, The National Museum of Denmark, 2007, pp. 237-244.

3. D. Camuffo, G. Sturaro, A. Valentino, *Showcases: a really effective mean for protecting artworks?* Thermochim. Acta 2000, **365**, 65-77.

4. J. Wadum, *Microclimate Boxes for Panel Paintings*. In: K. Dardes, A. Rothe (eds). The Structural Conservation of Panel Paintings. Proc. of a Symposium at the J. Paul Getty Museum, April 1995, Los Angeles, 1998, pp. 497-524.

5. E. Dahlin (ed.), *EU project POPAINT*, *Final report, Improved Protection of Paintings during Exhibition, Storage and Transit*, NILU OR 42/2010, http://propaint.nilu.no/, 2010.

6. American Society of Heating, Refrigerating and Air-Conditioning Engineers. Museums, libraries, and archives (chapter 21). ASHRAE Applications Handbook (SI Edition), ASHRAE, Atlanta, 2007.

7. J. Tétreault, *Airborne Pollutants in Museums, Galleries, and Archives: Risk Assessment, Control Strategies and Preservation Management*, Ottawa: Canadian Conservation Institute, 2003.

8. N. Blades, T. Oreszczyn, B. Bordass, M. Cassar, *Guidelines on pollution control in museum buildings*. Published by the Museums Association and distributed with Museum Practice, London, Nov. 2000, p. 15.

9. E. Sacchi, C. Muller, *Air Quality Monitoring At Historic Sites. Redefining an Environmental Classification System for Gaseous Pollution*. ASHRAEE Journal, August 2005.

10. P.B. Hatchfield, *Pollutants in the Museum Environment*, Archetype, London, 2002.

11. J. Tetreault, J. Siroi, E. Stamatopoulou, *Study of Lead corrosion in Acetic Acid Environment*, Stud. Conserv. 43. 1998, 17-32.

12. D. Thickett, S. Bradley, L. Lee, Assessment *of the Risks to Metal Artefacts posed by Volatile Carbonyl Pollutants*. In: W. Mourey and L. Robbiola (eds.) Proc. of the International Conference on Metals Conservation, Draguignan, 1998, James & James, London, 1998, pp. 260-264.

13. A-L. Dupont, J. Tetreault, *Study of Cellulose Degradation in Acetic Acid Environments*, Stud. Conserv. 2000, **45**, 201-210.

14. W.W. Nazaroff, G. Cass, *Mathematical Modelling of Chemically Reactive Pollutants in Indoor Air*, Environ. Sci. Technol. 1986, **20**, 924-934.

15. T. Grøntoft, M.R. Raychaudhuri, *Compilation of tables of surface deposition velocities for O_3, NO_2 and SO_2 to a range of indoor surfaces*. Atmos. Environ. 2004, **38**, 533- 544.

16. J.A. Cano-Ruiz, D. Kong, R.B. Balas, W.W. Nazaroff, *Removal of reactive gases at indoor surfaces. Combining mass transport and surface kinetics*. Atmos. Environ. 1993, **27A**, 2039-2050.

17. T.E. Graedel, C. Leygraf, *Atmospheric Corrosion*, Electrochemical Society Series, John Wiley, New York, 2000.

18. T.E. Graedel, *Corrosion mechanisms for silver exposed to the atmosphere*, J. Electrochem. Soc. 1992, **139**, 1963-1970.

19. H. Gil, *Quantitative in situ analysis of initial atmospheric corrosion of copper induced by carboxylic acids*. Licentiate Thesis. Department of Chemistry. Royal Institute of Technology (KTH) Stockholm, 2007.

$F_o(ox + ac)$ = Impact flux of oxidizing (NO2 + O3) and acidic (formic + acetic acid) gases to the object in the mc-frame (μg m^{-2} s^{-1})

$F_o(tot)$ = the total Gas 1 equivalent pollution (Gas 1 + Gas 2) impact flux (μg m^{-2} s^{-1})

F_r = Hypothetical impact flux of pollutant gas (Gas 1 or Gas 2) to the object at the recommended level in the room without mc-frame protection (μg m^{-2} s^{-1})

$F_r(ox + ac)$ = Hypothetical impact flux of oxidizing ($NO_2 + O_3$) and acidic (formic + acetic acid) gases to the object at the recommended level in the room without mc-frame protection (μg m^{-2} s^{-1})

F_u = Potential impact flux of pollutant gas (Gas 1 or Gas 2) to the object in the room without mc-frame protection (μg m^{-2} s^{-1})

$F_u (ox + ac)$ = Potential impact flux of oxidizing (NO2 + O3) and acidic (formic + acetic acid) gases to the object in the room without mc-frame protection (μg m^{-2} s^{-1})

H = production rate from homogeneous chemical reaction(s) inside the frame (μg m^{-3}s^{-1})

n = number of pollutant gas component included in the modelling (dimensionless)

Q = air exchange rate (s^{-1})

Q_m = measured value for the air exchange rate (s^{-1})

t = time (s)

V = net volume of mc-frame (m^3)

v_{da}= deposition velocities to absorber surfaces (m s^{-1})

v_{df} = deposition velocities to the frame internal (m s^{-1})

v_{dm} = the total deposition velocity calculated for each frame from the measured data (m s^{-1})

v_{do} = deposition velocities to the object (m s^{-1})

v_s = surface deposition velocity (m s^{-1})

v_{sf} = surface deposition velocity to frame (m s^{-1})

v_{so} = surface deposition velocity to object (m s^{-1})

v_t = transport limited deposition velocity (m s^{-1})

$v_d(Q)$ = air exchange dependent total deposition velocity (m s^{-1})

$v_t(Q)$ = air exchange dependent transport limited deposition velocity (m s^{-1})

8 List of symbols:

A_a = area of absorber material surfaces (m^2)

A_e = area of emitting material (m^2)

A_f = area of mc-frame inside (m^2)

A_o = area of object (painting) (m^2)

C_i = concentrations of the pollutant gas inside the mc-frame depending on time (μg m^{-3}),

C_{is} = concentrations of the pollutant gas inside the mc-frame for the steady state (μg m^{-3})

C_0 = concentrations of the pollutant gas in the room (μg m^{-3})

C_{Rn} = Recommended threshold level for Gas no. n (μg m^{-3})

e = the emission rate (μg m^{-2} s^{-1})

f = frame filtration factor (dimensionless, 0 < f <1)

F_o = the pollutant flux to the object (painting) (μg m^{-2} s^{-1})

$F_o(Form.ac + Ac.ac)$ = Flux of formic + acetic acids object (painting) (μg m^{-2} s^{-1})

$F_o(NO_2 + O_3)$ = Flux of NO2 + O3 to object (painting) (μg m^{-2} s^{-1})