PERFORMANCE EVALUATION FOR MUSEUM ENCLOSURES. MEASUREMENT, MODELLING AND MITIGATION OF POLLUTANT IMPACT ON OBJECTS IN MUSEUM ENCLOSURES

FULL PAPER

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Results of measurement and modelling of pollutant gases inside and outside 11 enclosures used to protect exhibited objects in 10 European museums are presented. Monthly average values for ozone, nitrogen dioxide, formic and acetic acid, temperature and relative humidity inside the enclosures, and yearly average values for the pollutants inside and outside the enclosures are presented for each enclosure. An available pollution impact model was adapted to the use with enclosures. Model calculations are presented for the expected change in concentrations of the oxidizing: ozone and nitrogen dioxide, and acidic: acetic and formic acid, pollutants depending on possible change in the ventilation rate of the enclosures and on inclusion of active carbon absorber to reduce the concentrations. The modelling results are presented as the 'impact concentration' of the pollutants by weighing the measured concentrations with their respective recommended levels. In several of the enclosures a clear correlation was observed between temperature and/or relative humidity and the concentration of acetic and formic acid. The modelling showed that all of the enclosures protected against air pollutants, but that only one of the 11 enclosures satisfied the recommended level. The recommended level could be reached for all the enclosures by reducing the ventilation or including active carbon absorber to cover the floor area.

1   Introduction

For a long time, various types of protective enclosures have been used to protect cultural heritage objects and their use is becoming even more common today. Special transport cases are used, e.g. for loan between museums. In museums and other heritage institutions objects are stored in purpose-designed boxes and are exhibited in showcases or microclimate frames. The enclosures are made from different materials and have different designs, and their protection effect will vary. Properties such as the ventilation rate, volume, building materials and possible measures to control climate and pollution levels will determine the quality of enclosure environments.[1,2] A decision-making model with design criteria for building high-quality microclimate frames for paintings have been published.[2] Enclosures can significantly stabilize relative humidity[3] and protect against external pollutants.[3-7] The concentration of internally emitted volatile organic pollutants can however be high.[7-10] The low molecular weight formic and acetic acids can affect e.g. metals, mineralogical spec-

imens and paper.[11,12] Considerable reduction of the concentration of gaseous pollutants and simultaneous reduction of the corrosion of sensitive materials have been observed in laboratory experiments[13] and in museum showcases[14] when absorbing materials such as active carbon were installed.

The general impact level of gaseous pollutants that infiltrate into and are emitted inside enclosures can be calculated from the recommended levels for the pollutants.[15,16] Alternatively, the expected impact on particular materials or objects with known sensitivity to the pollutants can be assessed.

It was demonstrated that tight microclimate frames for paintings protect against gaseous pollution in the environment if the internal emission of formic and acetic acid is not unusually high; and that the acids could not easily be ventilated out of the frames by moderately increasing the ventilation. The effect of changes in volume and installation of absorbing materials was investigated.[15,16]

In this work the model that was used to do these calculations was slightly modified and applied to calculate the impact concentrations to objects inside larger enclosures. The pollutants in the enclosures were measured in the EU project MASTER[2]. The effect of mitigation measures to reduce the concentration of gaseous pollutants in the enclosures was investigated.

2 Materials and Methods

The concentration of air pollutants and climate was measured in and outside 11 enclosures, used for display or storage of heritage objects, in 10 European museums and historic buildings (Tab. 1). The expected concentration of the air pollutants depending on the ventilation rate of the enclosures was calculated with the available model,[15,16] which was previously used for micro-climate frames for paintings.[2]

Museum / historic building	Location	Enclosure No.
The Museum of Decorative Arts & Design	Oslo, Norway	1
Trøndelag Folk Museum	Trondheim, Norway	2
Blickling Hall	Norfolk, UK	3
Tower of London, Bloody Tower	London, UK	4
Haus der Geschichte Baden-Württemberg	Stuttgart, Germany	5
Schwarzwälder Trachtenmuseum	Haslach, Germany	6
National Museum in Krakow, The Jan Matejko House (7) and the Czartoryskich Museum (11)	Krakow, Poland	7, 11
The Karol Szymanowski Museum "Atma"	Zakopane, Poland	8
Wignacourt Collegiate Museum	Rabat, Malta	9
The Historical Museum of Crete	Heraklion, Crete	10

Table 1: Museum locations where air pollution was measured in the EU project MASTER (Nos. 1-10) and PROPAINT (No. 11).
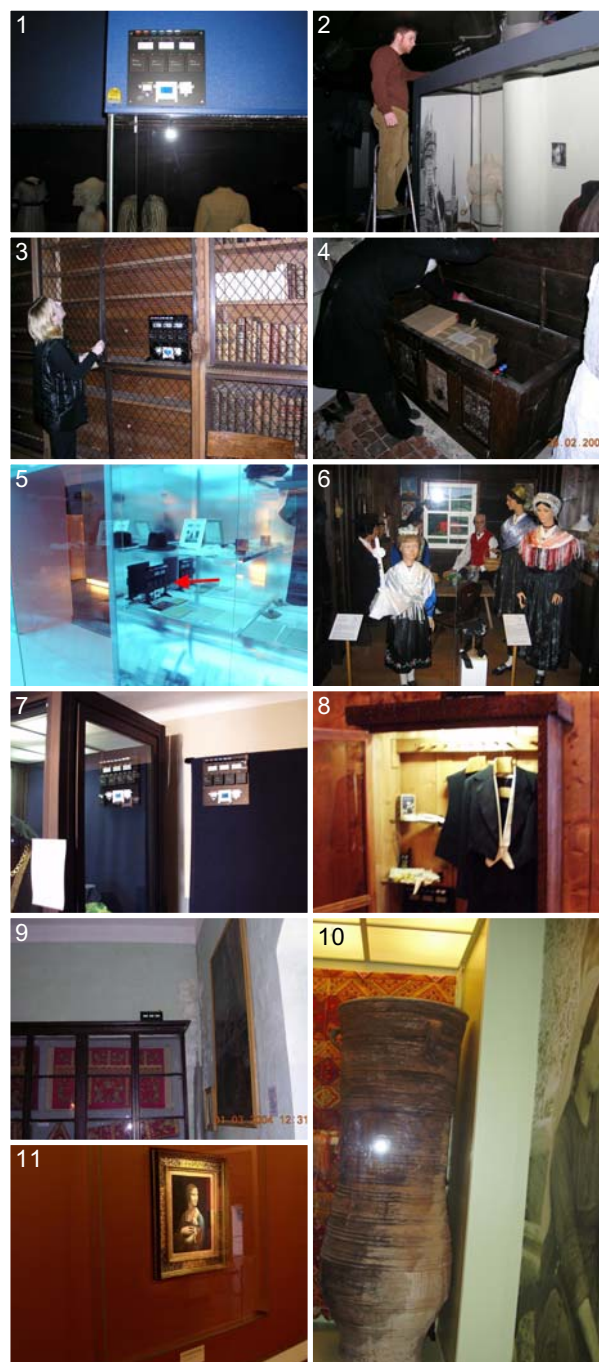

Figure 1: Locations where measurements of gaseous air pollutants were performed. Legend: cf. Table 1.

The measurements at ten of the locations were performed in the EU MASTER project.[1] The measurements at location No. 11 were performed in the EU PROPAINT project,[2] while Fig. 1 shows the locations.

2.1 Experimental

Passive pollution samplers were exposed for periods of one month at locations inside and just outside of the enclosures. At the 10 MASTER locations the samplers were exposed for every month during one year from March 2005 until February 2006.[1] At the location No. 11, the sampling was performed during April 2008.

The measurements were performed with IVL type batch samplers,[17] produced and analysed at the Swedish environmental institute, IVL (ozone) or at the Norwegian Institute for Air Research, NILU (all the other gases). The analysis was performed by ion chromatography (ozone, formic and acetic acid) and photometry (nitrogen dioxide). The detection limits after one month of exposure were: for nitrogen dioxide approximately 0.03 $\mu g\ m^{-3}$, for acetic acid and formic acid 0.5 $\mu g\ m^{-3}$, and for ozone 1 $\mu g\ m^{-3}$.

2.2   Model

The 'potential impact concentration' of the pollutant gases NO_2+O_3 (Gas 1) and acetic+formic acid (Gas 2) inside the enclosures was calculated by weighing the concentrations and fluxes of the pollutants with their recommended tolerable levels as reported in the conservation literature.[11,15,18]

Some modifications were made to the earlier applied model. In tight enclosures much of the deposition of infiltrating pollutants is expected to happen in the very narrow free path of the sealing or other available narrow cracks. In the earlier applied model, to account for this effect, the deposition velocity for the total frame internal was allowed to increase linearly with ventilation rate up to the limit value measured for a microclimate frame with a high air exchange and little removal of the pollutants during infiltration. In the modelling performed for enclosures in this work, instead a penetration factor was used.[19]

The penetration factor, P ($0 < P < 1$) is given by:

$$P = exp(-2vz\ /\ Ud)\qquad(1)$$

where v is the total deposition velocity, z is the crack depth, which is the shortest distance of the flow through a crack, U is the mean air speed in the crack, and d is the crack height. This can be reformulated to:

$$P = exp(-2vzl\ /\ VQ)\qquad(2)$$

where l is the length of the cracks through which the infiltration happens, V is the volume and Q is the ventilation rate of the enclosure. Eq. (2) relates the volume that flows to the crack surfaces during deposition (the numerator) to the volume of air that flows through the crack (the denominator). Thus, for an enclosure with known geometry (V, z, l) and ventilation rate, the penetration factor can be calculated from the deposition velocity in the crack. The crack length for infiltration into the modelled enclosures was calculated as 25% of the total joint (edges) length, plus the observed additional cracks for one of the cases (No. 11). The crack depth, z, was set to 0.01 m as a probable representative value for the enclosures. For one enclosure with an additional deep crack (No. 11) the average crack depth was calculated to be 0.028 m. The ventilation rate of two of the enclosures (Nos. 10[20] and 11) was measured.

The deposition velocity to the frame internal is given by:[15]

$$v_{df,\ 0} = QV(PC_0/C_i-1)/(A_f+A_0)\qquad(3)$$

where C_0 is the concentration outside the enclosure, C_i the concentration inside the enclosure, A_f the total internal surface area of the enclosure and A_0 the total surface area of the objects inside the enclosure. The penetration factor and the deposition velocity to the internal surfaces in the two enclosures (No. 10 and 11) were calculated from Eq. (2) and Eq. (3) using the measured outside-to-inside concentration (C_0/C_i) of the sum of oxidising pollutants, NO_2+O_3 (i.e. Gas 1). The calculated deposition velocity for the enclosure No.10 was used to calculate the penetration factors for enclosures Nos. 1 to 10, from (2). The ventilation rate was then calculated for the enclosures from (3). The value for the deposition velocity calculated for NO_2+O_3 was also used for acetic+formic acid.

The use of a penetration factor has the advantage that the model formulation is physically more correct and that the relationship between the calculated ventilation dependent concentration and flux is simpler, as the deposition velocity used in the modelling for one gas and enclosure has a constant value:

$$F = C_1v_1 + C_2v_2 \cdot C_{R1}/C_{R2}\qquad(4)$$

where F is the total calculated impact flux for the pollutant gases (NO_2, O_3, acetic and formic acid), C_1 is the sum of the concentration, or impact concentration, of NO_2 and O_3, C_2 is the sum of the concentration of acetic and formic acid, v_1 is the average deposition velocity of NO_2 and O_3, v_2 is the average deposition velocity of acetic+formic acid, C_{R1} is the recommended concentration level for NO_2+O_3, 2 $\mu g\ m^{-3}$, and C_{R2} is the recommended concentration level for acetic+formic acid, which was set equal to that reported for acetic acid in the literature,100 $\mu g\ m^{-3}$, see Tab. 5 in ref. no. 11 and in further literature.[15,18] $C_2(C_{R1}/C_{R2})$ is the impact concentration of acetic+formic acid.

When v_1 equals v_2, (4) reduces to:

$$F = v (C_1 + C_2 \cdot C_{R1}/C_{R2})\qquad(5)$$

and the impact flux and impact concentrations are directly correlated by a single factor which is the deposition velocity. The calculated impact concentrations for the enclosures are reported instead of fluxes, to allow a more direct comparison with the recommended concentration values for pollutants as reported in the literature,[11,18] and to more readily allow assessment of the effect of variation in deposition velocities and thus fluxes of pollutants that can cause damage to the objects. The concentration values for NO_2+O_3 (Gas 1) and acetic+formic acid (Gas 2) at the point for the measured ventilation rate is equal to the measured value for NO_2+O_3 and equal to the measured value for acetic+formic acid divided by 50, which is the proportion of the recommended value for NO_2+O_3 to that for acetic+formic acid.[4]

A tight enclosure will have a small penetration factor which implies that most of an infiltrating pollutant is trapped in the seal. For a less tight enclosure the penetration factor will be larger and more of the infiltrating pollutant will deposit in the frame internal space. As the infiltration of O_3 and NO_2 can significantly contribute to the pollution load inside relatively open enclosures, the effect of the sealing in hindering pollution ingress is important. The penetration factor is less important for exposure of enclosed objects to acetic and formic acid inside enclosures as the presence of these, and many other volatile organic gases,

is mainly due to emission from the enclosure materials and/or the enclosed objects.

The optimal ventilation rate was calculated as the ventilation rate where the impact flux, F, was the lowest.[4] As the same deposition velocity was used for all the pollutant gases, NO_2+O_3 and acetic+formic acid, for each enclosure, the impact flux is directly related to the impact concentration and the point for the lowest impact flux, F, is also the point for the lowest impact concentration.

3 Results

3.1 Measurements

Fig. 2 shows the average monthly values for the pollutants measured over a year at the ten locations.

Tabs. 2 and 3 show the average annual values for the pollutants and values for the frame design parameters that were used as input to the modelling, and the calculated values for the penetration factor, deposition velocity, emission rate and optimal ventilation

Enclosure No. (Tab. 1)	I / O	1	2	3	4	5	6	7	8	9	10	11
Nitrogen dioxide ($\mu g\ m^{-3}$)	I	2.0 ±0.3	6.6 ±0.2	2.6 ±0.0	8.7 ±2.0	26.5±1.6	6.1 ±0.1	2.9 ±0.0	2.0 ±0.0	4.1 ±0.0	1.1 ±0.3	2
	O	15.9 ±0.3	11.0±0.0	2.8 ±0.0	32.1±0.3	33.9±0.1	9.8 ±0.3	14.1±0.3	7.2 ±0.1	5.7 ±0.3	13.3±0.0	23 ±0
Ozone ($\mu g\ m^{-3}$)	I	1.2 ±0.3	2.9 ±1.2	1.4 ±0.0	1.3 ±0.3	1.7 ±0.0	2.6 ±0.2	1.9 ±0.2	1.0 ±0.0	5.2 ±0.7	1.4 ±0.3	3.3
	O	1.3 ±0.2	11.3±0.1	1.6 ±0.0	7.2 ±0.2	5.0 ±0.2	8.5 ±0.4	1.2 ±0.1	3.4 ±0.1	6.4 ±0.0	19.0±0.3	7.4 ±0.9
Formic acid ($\mu g\ m^{-3}$)	I	219 ±117	12 ±1	3.9 ±0.1	6.9 ±0.6	3.7 ±0.0	7.0 ±0.2	17 ±2	52 ±6	3.0 ±0.6	47 ±25	b.d.
	O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	10.3±5.5
Acetic acid ($\mu g\ m^{-3}$)	I	252 ±178	48 ±3	36 ±3	101±7	16 ±3	38 ±3	251±1	277±24	19 ±1	779±71	317±71
	O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	23 ±15
Acetic+formic acid ($\mu g\ m^{-3}$)*	O	*50*	*20*	*30*	*50*	*19*	*20*	*50*	*50*	*20*	*50*	33

Table 2: Pollutant concentrations (annual averages). The values are reported with the standard deviation for two measurements. I: inside enclosure. O: outside enclosure. b.d. = below detection limit. n.a. = not available.

* The values in italics (enclosures No. 1-10) do not represent measurements but expected/approximate values.

Enclosure No. Design parameters	1	2	3	4	5	6	7	8	9	10	11
Enclosure net volume (minus objects) (m^3)	55.4	1.8	0.2	0.3	0.3	10.8	1.4	0.4	1.4	1.4	0.3
Internal enclosure area (minus glass) (m^2)	28.8	8.0	1.7	4.3	0.0	26.6	3.6	2.0	6.5	6.7	1.5
Object area (m^2)	34.8	3.4	0.0	2.2	0.4	15.8	2.6	1.2	1.9	4.5	0.6
Absorber area included (m^2)	29.3	1.2	0.4	0.9	0.5	4.8	0.8	0.5	0.8	0.8	2.1
Room ventilation system / rate (qualitative)[1]	N	M	N / No	N / H	M / VL	N / No	N	N	N / VL	N / No	N
Material surfaces in enclosure[2]	Painted wood, glass, textiles	Painted wood, glass, textiles	Wood	Wood, paper	Glass, paper,	Painted wood, wood, textile, plastic	Painted wood, glass, textile, leather	Wood, glass, textile, paper	Wood, glass, textile	Wood, ceramics, textile	Glass, Fiber board, Tapestry, Velcro ®, Painting
Dimension (m) (hight x width x depth)	2.1x9.9x5	2x1.7x0.6	0.5x0.9x0.4	0.6x1.5x0.6	0.5x1.0x0.5	2.4x2.5x2.0	2.0x1.0x0.8	2.0x1.0x0.5	2.0x1.5x0.5	2.0x0.9x0.9	1.5x1.4x0.15
Total joint length (m)	51.8	17.2	7.3	10.8	8.0	27.6	15.2	14.0	16.0	15.0	15.3
Ventilation rate (day^{-1})	0.4	6.7	108.3	10.0	6.9	5.1	3.0	4.8	29.2	1.1	14.9
Penetration factor	0.98	0.99	1.00	0.98	0.97	1.00	0.97	0.98	1.00	0.93	0.72
Deposition velocity (m^{-1})	16×10^{-6}	16×10^{-6}	16×10^{-6}	16×10^{-6}	16×10^{-6}	16×10^{-6}	16×10^{-6}	16×10^{-6}	16×10^{-6}	16×10^{-6}	81×10^{-6}
Emission rate ($\mu g\ day^{-1}$)[3]	51400	1450	297	1180	12	4110	3310	4060	367	14300	6050
Optimal ventilation rate (day^{-1})[2]	0.01	0.02	0	0.05	0.03	0	0.04	0.13	0.02	0.05	1.83

Table 3: Enclosure geometries, ventilation, emission and deposition rates.
1. Legend: N = Natural, M = Mechanical, VL= Very low, No = Noticeable, H = High.
2. The surface material of the object(s) is included.
3. Calculated emission rate in the enclosure for acetic+formic acid, plus possible production, or loss, from homogeneous reactions.[15]
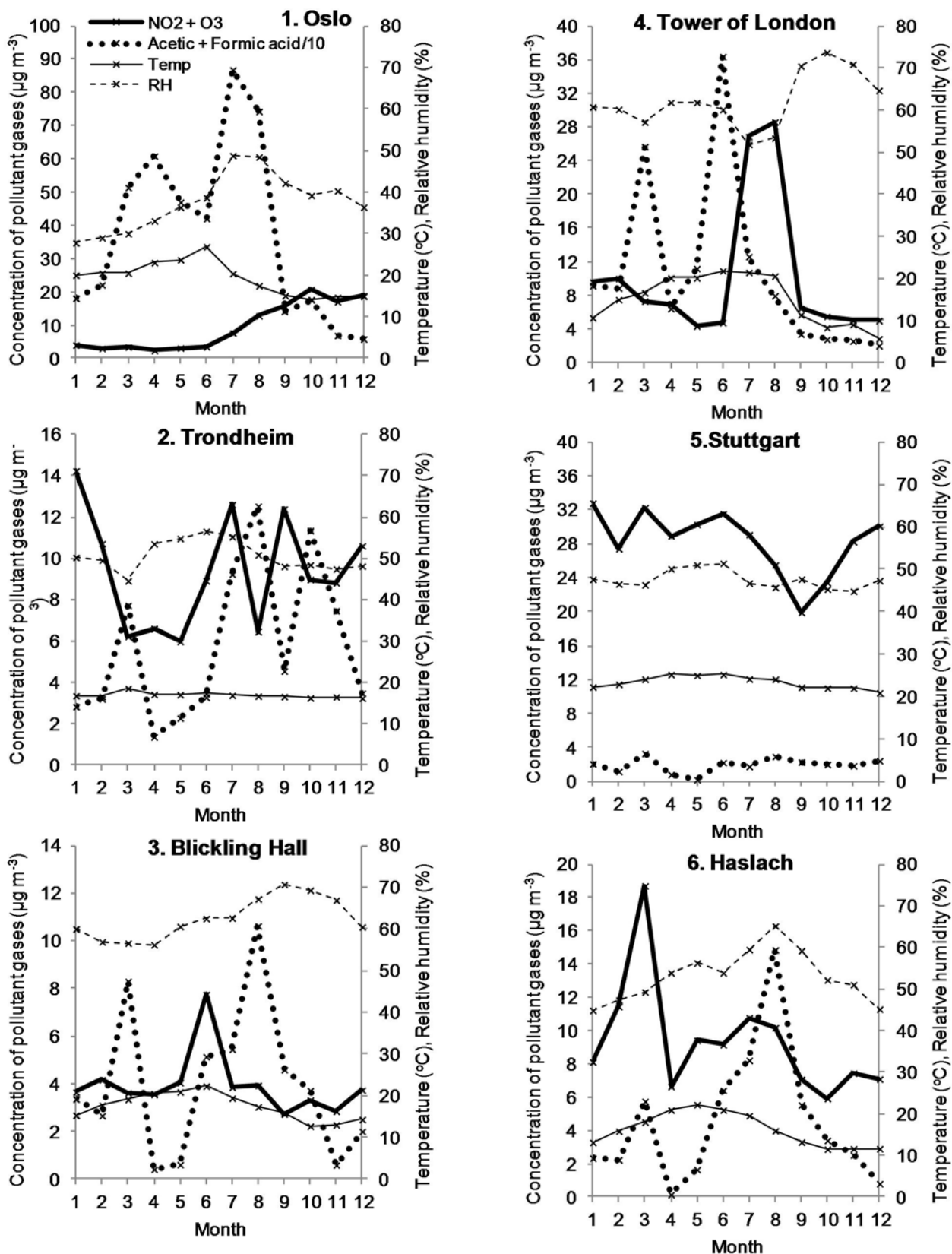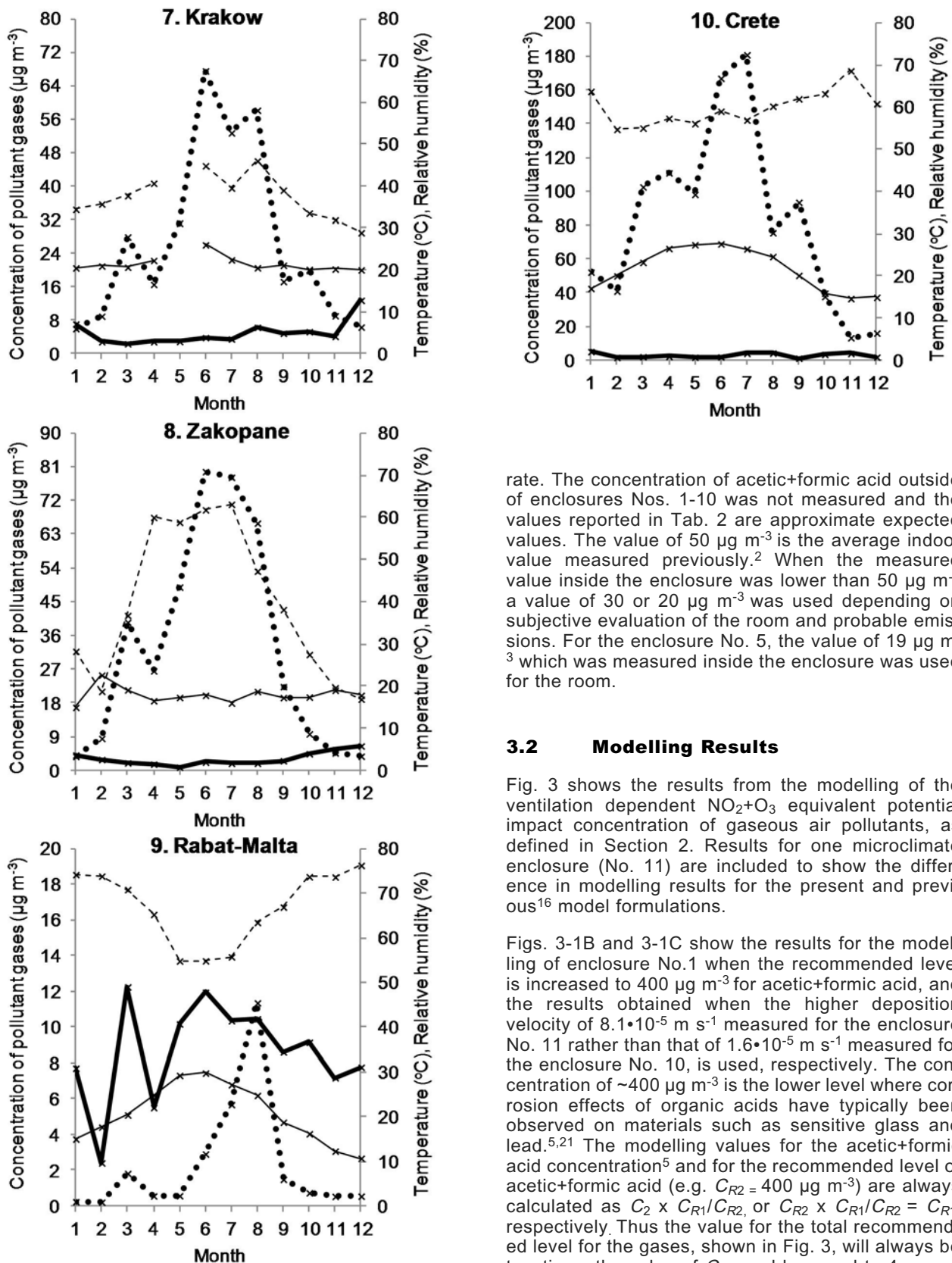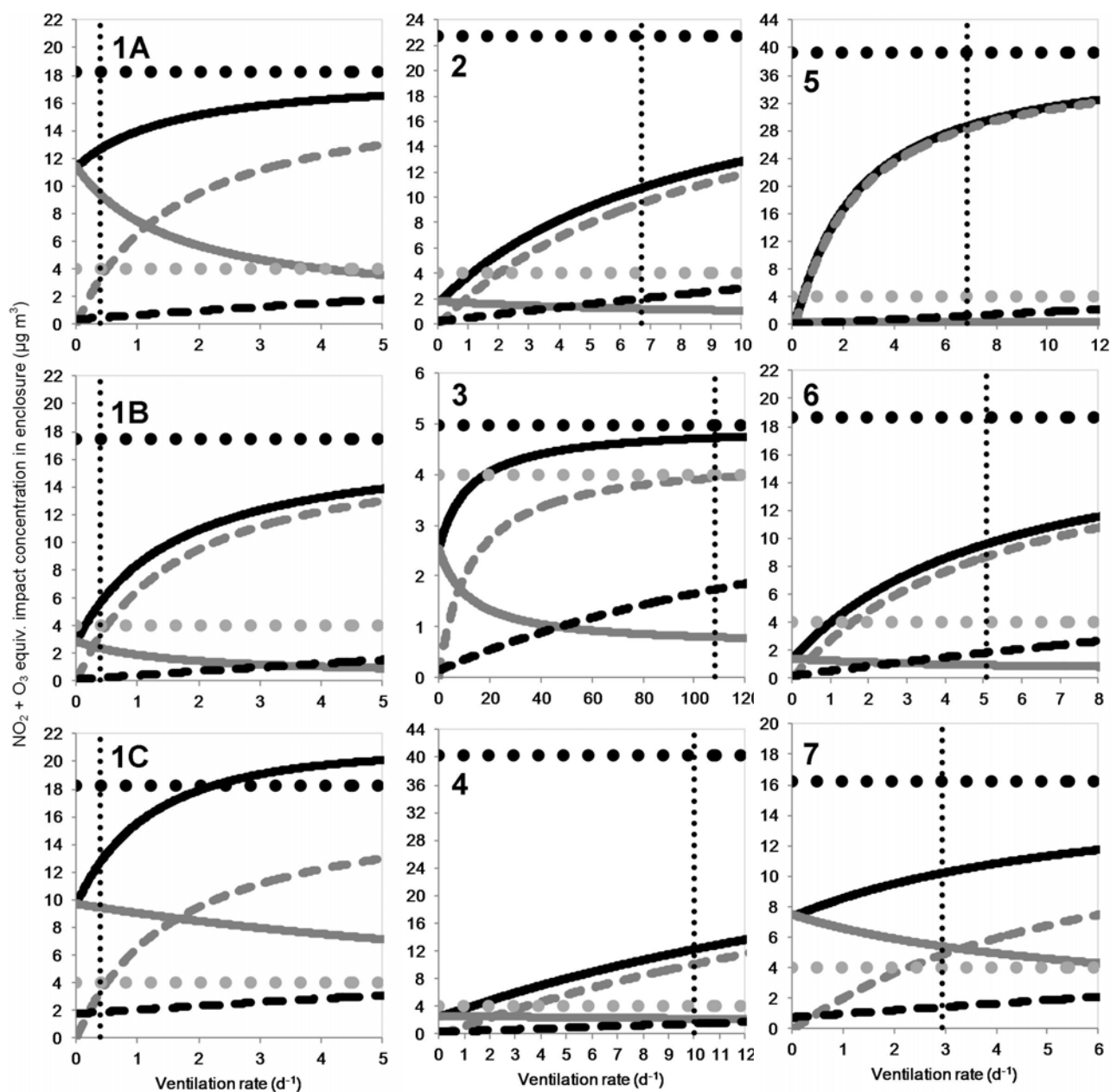
Figure 2:

7. Krakow

8. Zakopane

9. Rabat-Malta

10. Crete

rate. The concentration of acetic+formic acid outside of enclosures Nos. 1-10 was not measured and the values reported in Tab. 2 are approximate expected values. The value of 50 µg m^{-3} is the average indoor value measured previously.[2] When the measured value inside the enclosure was lower than 50 µg m^{-3} a value of 30 or 20 µg m^{-3} was used depending on subjective evaluation of the room and probable emissions. For the enclosure No. 5, the value of 19 µg m^{-3} which was measured inside the enclosure was used for the room.

3.2   Modelling Results

Fig. 3 shows the results from the modelling of the ventilation dependent NO$_2$+O$_3$ equivalent potential impact concentration of gaseous air pollutants, as defined in Section 2. Results for one microclimate enclosure (No. 11) are included to show the difference in modelling results for the present and previous[16] model formulations.

Figs. 3-1B and 3-1C show the results for the modelling of enclosure No.1 when the recommended level is increased to 400 µg m^{-3} for acetic+formic acid, and the results obtained when the higher deposition velocity of 8.1•10^{-5} m s^{-1} measured for the enclosure No. 11 rather than that of 1.6•10^{-5} m s^{-1} measured for the enclosure No. 10, is used, respectively. The concentration of ~400 µg m^{-3} is the lower level where corrosion effects of organic acids have typically been observed on materials such as sensitive glass and lead.[5,21] The modelling values for the acetic+formic acid concentration[5] and for the recommended level of acetic+formic acid (e.g. $C_{R2} = 400$ µg m^{-3}) are always calculated as C_2 x C_{R1}/C_{R2}, or C_{R2} x $C_{R1}/C_{R2} = C_{R1}$, respectively. Thus the value for the total recommended level for the gases, shown in Fig. 3, will always be two times the value of C_{R1}, and be equal to 4 µg m^{-3} when the recommended level for NO$_2$+O$_3$ is set to 2 µg m^{-3}.

Figure 2: Monthly average values from March 2005 until February 2006 for the concentration of NO$_2$+O$_3$, and acetic+formic acid, and for temperature and relative humidity in 10 enclosures in 10 European locations.

4   Discussion

The measured values for acetic+formic acid (Fig. 1) were in most cases higher during the late summer when they reached values from ~80-180 µg m⁻³ in four or the enclosures (1, 7, 8 and 10) and values from ~10-36 µg m⁻³ in five other enclosures (2, 3, 4, 6 and 9). This annual variation clearly correlated with increased temperature for only one enclosure (10), but with indication of correlation also for enclosures No. 1, 4, 7 and 9. The annual variation in acetic+formic acid correlated positively with increased relative humidity for several of the enclosures (Nos. 1, 6, 7 and 8). In enclosure No. 9 (Malta) the relative humidity correlated negatively with the measured concentration of acetic+formic acid and with temperature probably due to dryness of the air in the hot summer. There was no correlation between climate and organic acids in the locations with mechanical ventilation (Nos. 2 and 5).

Several of the locations where relatively low concentrations of acetic+formic acid were measured showed considerable variation between the months which did to some extent correlate inversely with the measured concentration of ozone+nitrogen dioxide (No. 2 and the open enclosure No 3). This could be due to varying ventilation of the enclosures from month to month. In one enclosure (No. 5) very low values of acetic+formic acid were measured through the year. This enclosure was built entirely from glass with only a few emitting organic objects installed. In this enclosure the highest concentrations of NO₂+O₃ were measured with little variation through the year. This can be explained by the relatively high indoor concentration of NO₂ and O₃ (Tab. 2) in the large room where the enclosure was located and low deposition of the gases inside the enclosure. A similar situation can be observed in September and October for location No. 4, Tower of London, which had a high ventilation rate. However, the measured concentrations of acetic+formic acid are higher, probably because of emissions from the wooden chest. For the other loca-
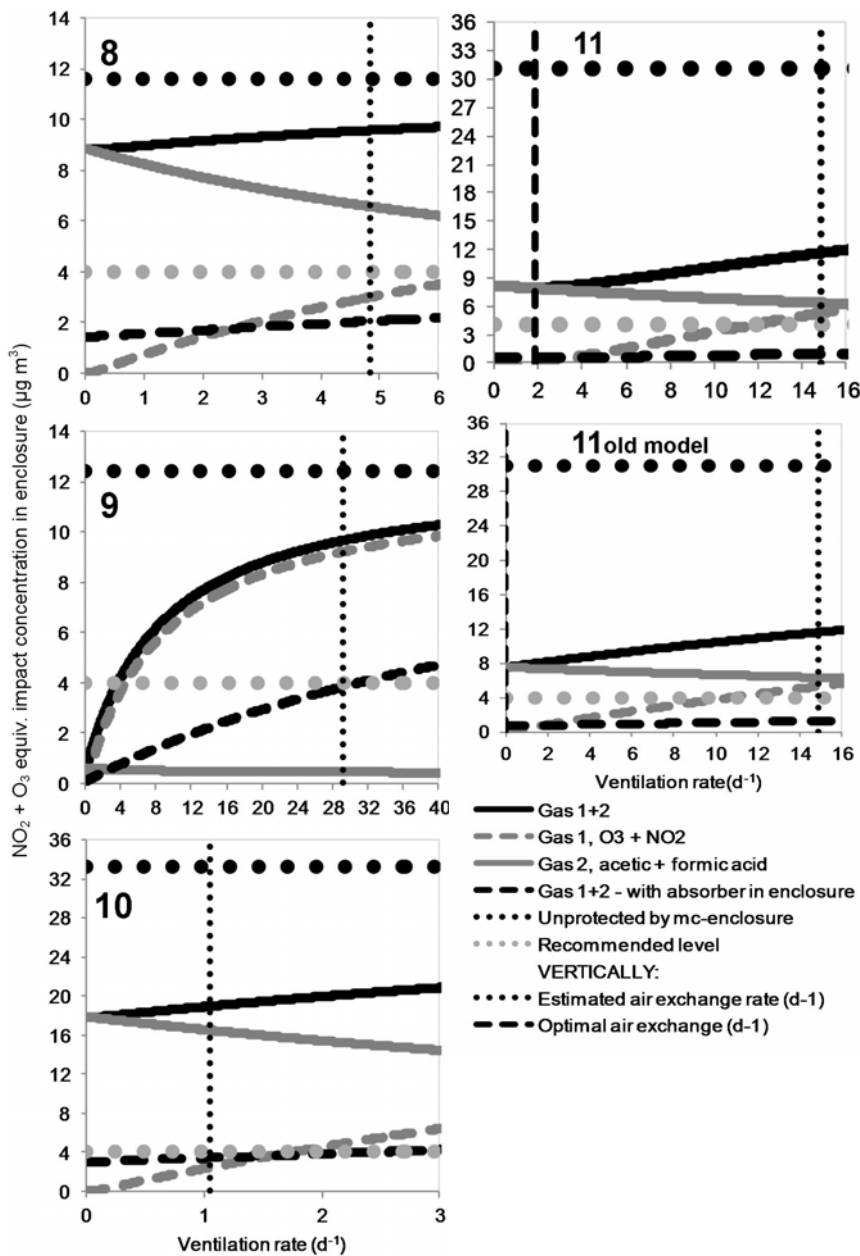
Figure 3: Results for the ventilation dependent NO$_2$+O$_3$ equivalent potential impact concentration of gaseous air pollutants to the objects in enclosures No. 1 to 11 (Tabs. 1 and 3). Figs. 3-1B and 3-1C show the modelling results for the enclosure No. 1 with an increased recommended level of 400 µg m^{-3} (B) and deposition velocity (C) for acetic+formic acid as compared to the 'standard modelling situation' (Tab. 3). Figs. 3-11 and 3-11 'old model' show results for two different model formulations with a penetration factors of P = 0.72 and P = 1, respectively. For enclosures No. 1-10 the optimal ventilation rate is ~0 (not shown).

tions the concentrations of nitrogen dioxide and ozone are in the range from ~5-20 µg m^{-3}. Many factors such as the outdoor concentration, the ventilation of the building and the enclosure, homogeneous reactions with other gases in the air, and the deposition to the indoor and enclosure materials, determine the indoor concentration of nitrogen dioxide and ozone. There is a general correlation between the concentrations of nitrogen dioxide and ozone measured in the rooms and inside the enclosures, and between the inside of enclosure to room concentrations (I/O ratios) and the ventilation rates of the enclosures (Tab. 2). In addition, variation in the NO$_2$ and O$_3$ concentrations between the different locations and enclosures is expected due to different deposition rates to the indoor and inside of enclosure surfaces.

There is considerable variation in the relative humidity between the locations and months. In most cases it varies from ~45-70%. For three locations (Nos. 3, 4 and 9) it was slightly higher than 70% for one or more

months during the year. These locations were relatively open to the outdoors and had high ventilation of the enclosures. Higher humidity and reduced temperature in the late autumn and winter in England (Nos. 3 and 4) and in the winter and spring (No. 9, Malta) could explain the high relative humidity. Reduced relative humidity was measured in the spring and winter in locations No. 1, 6, 7 and especially in location No. 8 (Zakopane). This is probably explained by infiltration of colder and dryer air in the winter and additional indoor heating (except location No. 6) to a temperature of sometimes over 20 °C which further reduces the relative humidity. In the locations which have indoor heating (Nos. 1, 2, 5, 7 and 8) the temperature is ~20 °C or slightly below and relatively stable through the year. In the other locations, the temperature was considerably lower in the winter sinking significantly below 10 °C for one location, No. 4, Tower of London.

The fluxes of air pollutants to surfaces, also termed surface removal rates, are more correlated with

observed object damage than are air concentration values. However, pollutant fluxes are difficult to measure and the relationship between a pollutant flux and the object damage is also not straightforward. In practice, the pollutant effect given, e.g., as no or lowest observable adverse effects levels (NOAEL or LOAEL)[11] is usually reported as recommended concentration values. Recommended concentration levels of pollutants for different materials are different because the deposition velocities are different,[4] but also because the damage caused by similar surface removal rates on different materials is different. In practice, when applying recommended levels, factors other than concentration, that from a mechanistic point of view influence the damage, are often assumed to be constant. The observed damage is then related to the measurable environmental factors such as pollution concentration, temperature, humidity, light conditions and air flow conditions. Therefore, in this work the impact concentration rather than the flux was calculated.

The modelling results suggested very low optimal ventilation rates for all the enclosures (<0.13 d^{-1}) except for the Leonardo enclosure (No. 11), for which some ventilation (1.8 d^{-1}) may reduce the impact of the gaseous pollutants. The reason for this was the lower calculated penetration factor for nitrogen dioxide and ozone into this enclosure and thus the larger effect of some ventilation on the acetic and formic acid. Generally, it seems that very low ventilation (<0.13 d^{-1}) is usually an advantage, but that the absolute sealing of enclosures may not be critical. This would be the case for objects that are sensitive to degradation from both sets of considered pollutants, NO_2+O_3 and acetic+formic acid, proportionally to the recommended levels used in modelling. If objects are less sensitive to the internally emitted pollutants (acetic+formic acid) enclosures should be made tighter. If objects are less sensitive to the infiltrating pollutants (NO_2+O_3) it may be better to ventilate the enclosures, but depending on the concentration levels and relative sensitivity of the objects to the pollutants. When the sensitivity of an object to the pollutant gases is known, modelling can be performed with these sensitivity levels substituted for the recommended levels that are used in this paper. The performed modelling does not consider other pollutants than NO_2, O_3, acetic and formic acid, or other factors that can influence the degradation of objects inside and outside enclosures.

Despite the relatively low concentrations of NO_2+O_3 (Tab. 3) in the enclosures the potential impact concentration from the NO_2+O_3 was calculated to be higher than for acetic+formic acid for 6 of the 11 enclosures (Nos. 2, 3, 4, 5, 6 and 9). For all the enclosures the total impact concentration would be reduced by reducing the ventilation rate of the enclosures. The reason for this is the larger reduction in potential negative impact from the NO_2+O_3 than increase in negative impact from acetic+formic acid (due to the slopes of the model curves) when the ventilation rate is decreased. As can be seen in Fig. 3-1B, the relative negative importance (impact) of NO_2+O_3 as compared to acetic+formic acid and thus the positive effect of reducing the ventilation rate would be larger if the recommended level for the acids was higher (e.g. 400 µg m^{-3} rather than 100 µg m^{-3}). All of the enclosures protect against gaseous

pollutants in the rooms (Tab. 2), but this protection is less for the more open enclosures and those that have high internal concentrations of the organic pollutant gases (Nos. 3, 8 and 9). None of the enclosures satisfy the recommended levels for gaseous pollutants, but this could be reached for all but five of the enclosures, Nos. 1, 7, 8, 10 and 11 which have too high internal concentrations of acetic+formic acid, by reducing the ventilation rate. However, Fig. 3-1B shows that for enclosure No. 1, if the recommended level for acetic+formic acid is determined to be the higher value of 400 µg m^{-3}, the total recommended level could be reached by reducing the ventilation rate.

The calculated emission rates for acetic+formic acid in the enclosures (Tab. 3) correlated positively with the measured values for the concentration in the enclosures, but with some effect of the room concentration. For example, the calculated emission rate for the case No. 6 is relatively high due to the high ventilation rate and lower assumed room concentration.

The reason for the difference in the result for enclosure No. 11 when using the new and old model formulation (Figs. 3-11 and 3-11, 'old model'), is the difference in the penetration factor, P. In this work (Fig. 3-11), P was calculated to be 0.72. In the previous work[16], P was assessed to be equal to 1. Enclosure No. 11 was measured to have a relatively high ventilation rate of 14.9 air exchanges per day. When the present model formulation was used to model other tight micro climate frames, similar results were obtained as by the use of the previous 'old model' formulation.[16]

For all the enclosures it was calculated that the recommended level would be reached if the floor area was covered with active carbon adsorber. The smallest effect of including the adsorber was calculated for enclosures Nos. 3, 9 and 10 due to high ventilation and infiltration rates of NO_2 and O_3 (Nos. 3 and 9) and low ventilation and high internal circulation of organic acids (No. 10).

The modelling was performed to assess the air quality in the enclosures based on general recommended levels for sensitive materials as reported in the conservation literature. The modelling is however a flexible tool which can evaluate the air quality for any selected pollution levels, e.g. for particular registered concentration levels that have been observed to cause damage on particular materials or objects. The model can easily be extended to other, or more, gaseous air pollutants.

4.1 Model uncertainty

The modelling assumes homogeneous mixing of the pollutant gases inside the enclosures. However, a ventilation rate below 1 h^{-1}, estimated for most of the enclosures (Tab. 3), makes this unlikely[22] and the real values for the impact concentration at different locations inside the enclosures may vary considerably from the average values given from the modelling (Fig. 3). The deposition velocities of NO_2+O_3, for cases No. 10 and 11 were calculated from the measured values. For enclosures No. 1-9 (Tab. 3) the same deposition velocity of NO_2+O_3, as was calculat-

ed for the enclosure No. 10, was used in modelling. Considering the similarity of the cases this is a reasonable assumption. However, there will be some variation in the real deposition velocities to the different surfaces inside the enclosures. This means that the real ventilation rates and slopes for the average NO_2+O_3 impact concentration may vary somewhat from the estimated values reported in the modelling diagrams (Figs. 3-1 to 3-9).

The value for the deposition velocity of acetic+formic acid used as input to the modelling determines the calculated emission rate and amount of circulation of the acids inside the enclosures, in a process of desorption-emission and deposition-adsorption and possible surface reaction. For a higher deposition velocity a higher emission rate will be calculated to reach the measured concentration and the effect of ventilation will be lower. This can be seen in Fig. 3-1C where a higher deposition velocity for acetic+formic acid gives a reduced slope for the acidic impact concentration and a reduced effect of ventilation. On the other hand, a lower deposition velocity will increase the slope and the effect of ventilation. The optimal ventilation rate will depend on the circulation rate of the organic acid vapours inside enclosures in combination with infiltration of pollution from outside and the consequent effect of ventilation (see Fig. 3-11). Research should be performed to obtain better measurement data for the circulation rate, i.e. desorption and adsorption rates, of organic vapours inside enclosures.

The concentration of acetic+formic acid in spaces surrounding the enclosures was only measured for the enclosure No. 11. In other cases, a value based on expected similarity with other indoor museum locations was used (see section 3.1). For seven of the enclosures the calculated contribution from infiltrating acetic+formic acid to the concentration of these pollutant gases inside of the enclosures varied from 0.5 to 17%, for one case (No. 2) it was 27% and for three cases, Nos. 3, 5 and 6, it was 211, 213 and 266%. Different, e.g. higher, than assumed concentrations of acetic+formic acid in the rooms would give nearly no change in the model results as the contribution of the organic acids to the total loads was very low in most of the cases with a high percentage contribution from the room (No. 2, 5 and 6) and as the effect of a higher assumed room concentration would be merely to recalculate to a lower internal emission and redistribute to the higher contribution from the room to reach the measured value.

The modelling results for air pollutants in the 11 enclosures are not exact representations of the "real state" in the enclosures, but they should give a good approximation of the expected variation in the air pollution values in the enclosures resulting from changing their ventilation.

5   Conclusion

Measurements and modelling of air pollutants inside 11 enclosures in 10 European museums and historical buildings showed a clear positive correlation between temperature and relative humidity and the presence of acetic and formic acid, inside several of the naturally ventilated enclosures. The 'impact con-

centration', i.e. the concentration weighed with the recommended levels, of infiltrating and internally emitted pollutant gases, was calculated depending on the ventilation rate of the enclosures.

The measurements showed that all except one of the enclosures gave protection against the air pollutants, but that none of the enclosures satisfied the recommended level. The modelling showed that the recommended level could be reached by reducing the ventilation of the enclosures and/or by including an active carbon adsorber to cover the floor area. The model is a flexible tool that can assess the impact of different pollutants and pollutant levels that can cause damage on objects.

6   Acknowledgements

7   References

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