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Ozone exposure inside museums in the historic central district of Krakow, Poland

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Abstract

Ozone present in the indoor atmosphere of museums can lead to the fading of organic artists' pigments and textile dyes that are present in paintings, tapestries and historically important clothing exhibits. Ozone concentrations were measured in outdoor air and within the interior galleries of five institutions that house cultural properties in Krakow. The purpose of these experiments was to determine the degree of penetration of outdoor ozone into these museums, and in the case of the National Museum to determine the effectiveness of the existing ozone removal system at that site. It was found that those museums that are rapidly ventilated through many open doors and windows experienced indoor ozone concentrations about 42–44% as high as those outdoors. The Senator's Hall at Wawel Castle, which houses important tapestries, experiences indoor ozone concentrations that are 17–19% of those outdoors due to ozone removal at interior surfaces during transit through the building from distant air intake points. Methods for further reduction of ozone concentrations in the specific museums studied are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ozone; Indoor air quality; Art conservation

1. Introduction

A variety of textile dyes and artists' pigments will fade when exposed to low concentrations of ozone over an extended period of time. Pigments and dyes based upon the indigo family, the madder lakes, and saffron, for example, are especially susceptible to ozone damage (Whitmore and Cass, 1988; Whitmore et al., 1987). Considering this potential for fading of important works of art and fabrics, as well as the potential for ozone-induced attack on organic materials such as cellulose, textile fibers and the binders used in paints, limits have been recommended on the indoor ozone concentrations in museums and rare book libraries. Recommended long-term average ozone concentrations are no higher than 1–13 ppb, with the most frequent recommendation being to lower indoor ozone concentrations to an average of 1 ppb (Baer and Banks, 1985; National Research Council (NRC), 1986). Accelerated aging experiments conducted by Whitmore et al. (1987; Whitmore and Cass, 1988) show that severe ozone-induced fading of some pigments and textile dyes is observed during 90 days exposure to 400 ppb ozone. The fading process appears to scale according to the product of the ozone concentration times the duration of exposure (Whitmore, 1987; Cass et al., 1991). An indoor ozone concentration of 1 ppb applied over a 100 yr time scale amounts to an exposure of 8.8×10^5 ppb-h which is nearly the same as the 8.6×10^5 ppb-h exposure that occurred at 400 ppb for 90 days needed to reach the faded conditions measured by Whitmore et al. (1987; Whitmore and Cass, 1988). Long-term average outdoor ozone concentrations in Europe at present lie in the range 25–40 ppb in relatively unpolluted areas of the continent, and are rising at an annual rate of 1–2% yr^{-1} (Janach, 1989). Thus, museum collections are

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at some long-term risk of damage if the collections contain susceptible materials and dyes that are exposed directly to a large fraction of the ozone content of outdoor air.

The old central district of the city has been inscribed on UNESCO's World Heritage List of sites designated as having "outstanding universal value to mankind." Twenty-seven museums, many affiliated with the National Museum of Poland, are situated in or very near the historic central district of Krakow (Podlecki, 1992; Chruscicki and Stolot, 1994). The museum collections range from the historical and artistic holdings of Polish royalty at Wawel Castle, to paintings galleries devoted to Renaissance through modern art, religious objects, historical museums, and a recently constructed museum of Japanese art featuring dyed silks, paintings and woodblock prints among its collection.

Many of the museum collections are particularly vulnerable to damage because only one of the older museums in Krakow plus the new Japanese art museum possess air filtration systems, and because certain objects (e.g., tapestries; historically important clothing collections, oriental works of art) contain organic colorants that are expected to fade if exposed to atmospheric ozone over long periods of time (Whitmore and Cass, 1988; Whitmore et al., 1987; Shaver et al., 1983). The purpose of the present paper is to determine the ozone levels in indoor air to which the museum collections in Krakow are exposed. Alternative means for further protecting the collections of specific museums from damage due to ozone exposure will be discussed briefly. Other air contaminants such as SO_2, NO_x, and H_2S also may have detrimental effects on some dyes and the approach presented in this paper could be applied to these other pollutants as well.

2. Monitoring site description

Five of the museums and cultural institutions in the city were examined during the course of this investigation. Their locations and other relevant features of the area are shown in Fig. 1. The most intensive studies were done at the Wawel Castle and at the Matejko Museum. The Wawel Castle (Kuczman, 1990) is located on a hill 20–25 m above the city at the southern end of the central district. King Sigismund II Augustus bequeathed his collection of tapestries from Brussels to Wawel. They form an important part of a collection that also includes decorated tents, banners and carpets captured from the Turks at the Battle of Vienna in 1683. The Matejko Museum is the former home and studio of the eminent historical painter Jan Matejko. It became a museum shortly after his death in 1893. It houses a collection of oil paintings, historical costumes, and the furniture of the Matejko household.

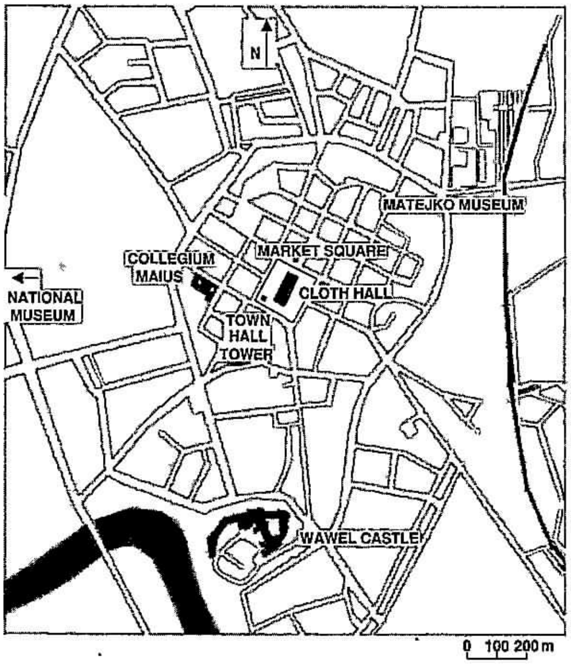

Fig. 1. Map showing central district of Krakow.

Three other sites were included in additional investigations: the Collegium Maius, the Cloth Hall, and the new building of the National Museum. The Gothic Collegium Maius is the oldest building of the Jagiellonian University and dates from the early 15th century. Today it houses the Jagiellonian University Museum including the personal belongings of university professors, university jewels, such as scepters and rings, and unique scientific equipment which was once used for research including instruments used by Copernicus. Measurements also were made inside the upper floor of the Cloth Hall ("Sukiennice") which houses the Gallery of Polish Nineteenth Century Art. The previously mentioned sites all are located within the former walls of the old city in an area where vehicle use is severely restricted (see Fig. 1). By contrast, the new building of the National Museum is located on a heavily trafficked street just outside the central zone of the city and is exposed directly to pollution from vehicle exhaust. It is also the only site studied which possesses an air filtration system.

3. Experimental methods

An ozone-monitoring experiment was conducted during the summer of 1993. The purpose of these experiments was to determine the fraction of the ozone present in outdoor air that was present in the indoor atmosphere of Krakow museums. That indoor/outdoor ozone concentration ratio often can be lowered through changes in building air exchange strategies or through the use of activated carbon air filtration systems. The five sites discussed above were chosen to represent a cross-section of the many museums and cultural institutions present in the city.

Two calibrated ozone monitors (Dasibi Corp., Models 1003-AH and 1003-PC) connected to strip chart recorders were used to obtain dynamic data simultaneously indoors and outdoors for a short period (from 21 to 46 h) at each individual site. The two ozone monitors were used sequentially beginning with the new building of the National Museum on 29–30 June 1993. The museum is one of only two in Krakow to possess an air filtration system. One Dasibi ozone monitor was placed at the air inlet to the National Museum's air filtration system and the indoor monitor was located inside the ventilation system downstream from the activated carbon and particle filter banks.

Active ozone monitoring was moved to the Wawel Castle for 1–3 July 1993. The outdoor monitor was placed on the third floor Loggia, and indoor monitoring was performed in the Senator's Hall also on the third floor of the castle. The Senator's Hall houses the Sigismund Augustus tapestries; the risk that they might fade over time if exposed to excessive ozone concentrations was one of the principle motivations for this study. From 3 to 5 July 1993 the indoor active ozone monitor was placed in the Chemistry Room of the Collegium Maius, and the outdoor monitor was located on a balcony in the central courtyard at that site.

The fourth site chosen was the Cloth Hall ("Sukiennice") located in the Market Square. The indoor active ozone monitor was placed in Gallery "D" on the second floor and outdoor air was sampled through a Teflon inlet line that extended through a window in an alcove of the director's office during 5–7 July 1993. Finally, the ozone monitors were moved to the Matejko Museum for the period from 7 to 8 July 1993.

Diffusion-based DGA passive ozone samplers (Grosjean and Hisham, 1992) also were used to measure long-term average ozone concentrations both indoors and outdoors for time periods ranging from 27 to 33 days in July and August, 1993 at 10 locations distributed among the five institutions. The DGA passive ozone sampler consists of a plastic body, a porous Teflon diffusion barrier open to outdoor air and a paper detection surface coated with an ozone fugitive colorant that is inside the body of the sampler and separated from the diffusion barrier by a well-defined air gap. The diffusion barrier meters ozone to the detection layer in proportion to the outdoor ozone concentration. The change in reflectance of the colorant after exposure of the passive sampler to ambient air is directly related to the ambient ozone concentration.

At the National Museum three passive ozone monitors were used. One was placed at the inlet for outdoor air to the air-conditioning system. The second sampler was located just downstream of the activated carbon filter banks within the air-conditioning system, and a third passive monitor was located in a gallery within the newer air-conditioned section of the building in Hall "H" on the third floor.

Three passive ozone monitors were placed at Wawel Castle. One monitor was located outdoors on the third floor Loggia, one indoor monitor was placed in the Senator's Hall, and a third monitor was located in Room 15 on the same level as the Senator's Hall and nearer the air entry to this portion of the building.

One last outdoor passive monitor was placed outside the Matejko Museum and the final three passive monitors were all placed indoors: one inside the Matejko Museum, one in the chemistry room of the Collegium Maius, and the third in Gallery "D" on the second floor of the Cloth Hall. Outdoor ozone data also were collected over 33-day period of the passive ozone-monitoring experiment from the Krakow municipal continuous ozone monitor in the Town Hall Tower of the Market Square which is located immediately adjacent to the Cloth Hall and one block from the Collegium Maius.

At Wawel Castle and the Matejko Museum perfluorocarbon tracer (PFT) techniques were used to measure the air exchange rates in the galleries of interest. Analysis of the PFT samples was performed by the staff at Brookhaven National Laboratory (Dietz and Cote, 1982). In brief, several PFT sources that emit perfluorocarbons at a small but constant rate were placed at selected locations inside the facilities for 1 yr. Collection tubes through which the tracer permeates were exposed and then analyzed to give the tracer concentration within the rooms from which the total rate of air infiltration ($m^3\ h^{-1}$) into each zone could be calculated. One set of tracer collection tubes was left in place for the duration of the month-long ozone monitoring experiment in July, 1993. Additional one-month samples were taken during subsequent work in October, 1993 and April, 1994 to obtain seasonal comparison data, and an additional set of collection tubes was left in place for 1 yr.

4. Results and discussion

4.1. ozone continuous monitoring experiments

Fig. 2a shows the indoor and outdoor ozone concentrations measured by the continuous air-monitoring instruments at the Cloth Hall Museum located in the Market Square. Data from the municipal ozone-monitoring station at the Town Hall Tower in the Market Square located less than 200 m from our outdoor ozone monitor are also presented for comparison. There is very good agreement between our outdoor instrument and the one in the Town Hall Tower. As seen in Table 1, indoor ozone concentrations within Cloth Hall Museum

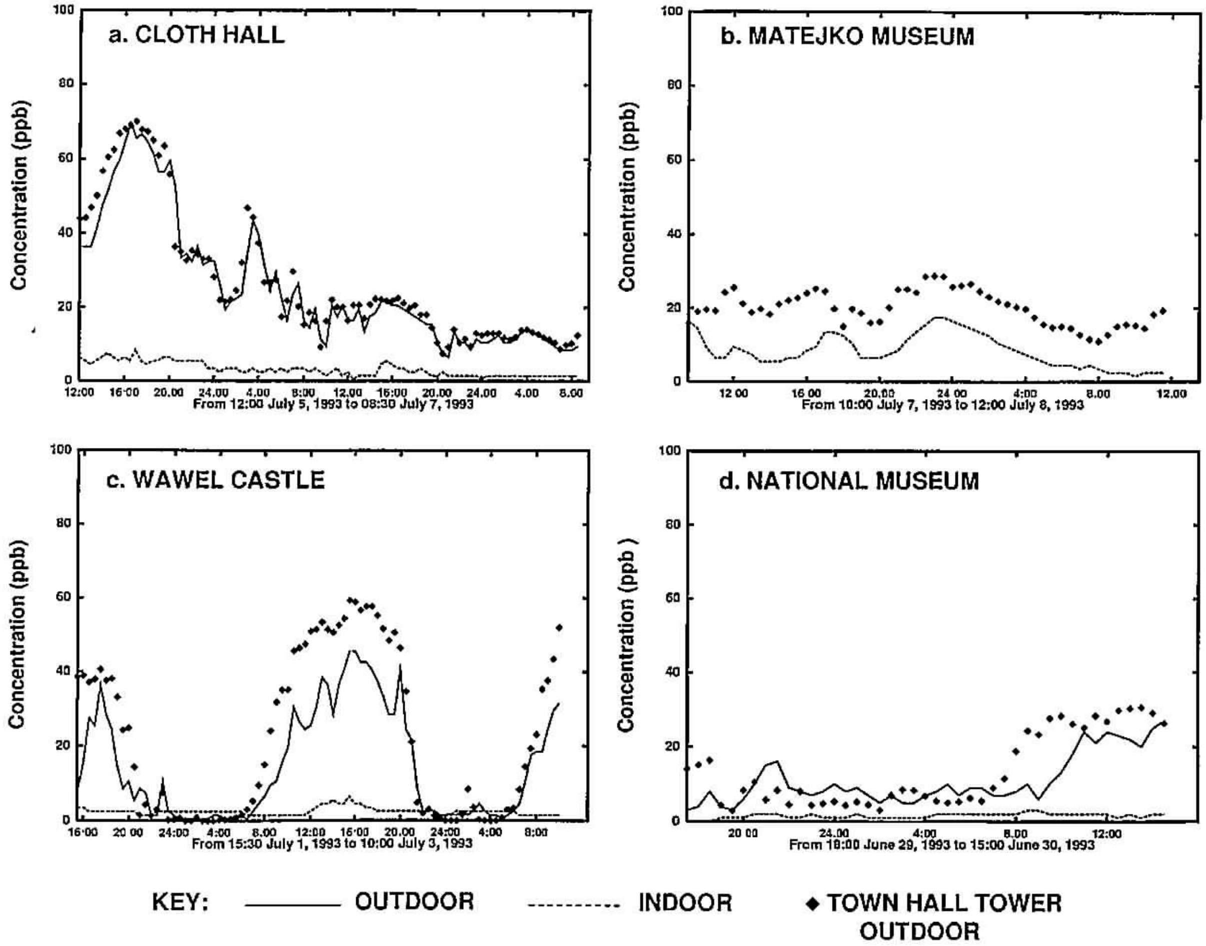

Fig. 2. Ozone concentrations measured at: (a) Cloth Hall; (b) Matejko Museum; (c) Wawel Castle and; (d) National Museum. Comparison with outdoor measurements at the Town Hall Tower is shown in all diagrams.

Gallery D averaged 3.2 ppb compared to 25.7 ppb outdoors over the period 5–7 July 1993. Ozone concentrations indoors at that site averaged 13% of those outdoors, the difference being due to ozone loss by reaction with surfaces within the building including the collection.

The highest indoor ozone levels recorded at any of the Krakow museums were seen inside the Matejko Museum, as shown in Fig. 2b and in Table 1. Indoor ozone concentrations over the period 7–8 July 1993 averaged 8.5 ppb indoors and 20.0 ppb outdoors, yielding an indoor/outdoor ratio of 0.42. The outdoor data at this site are taken from the Town Hall Tower which is located approximately 400 m from the Matejko Museum and thus should be representative of this neighborhood. It was raining with no sun during the period that ozone continuous monitoring occurred at the Matejko Museum and outdoor ozone levels remained low.

Indoor ozone levels at the Senator's Hall of Wawel Castle are shown in Fig. 2c. Indoor ozone levels at that site are low, averaging 2.5 ppb or 17% of the outdoor concentrations at the castle over the 1–3 July 1993 continuous air-monitoring experiment. Results of the PFT tracer-based air exchange rate experiments help to explain why ozone concentrations inside Wawel Castle are a lower fraction of those outdoors than at the Matejko Museum.

The Matejko Museum and Wawel Castle are both naturally ventilated buildings where air exchange occurs through open doors and windows and through other openings in the building shell; no mechanical ventilation system exists in either building. However, as seen in Table 2, the tracer study shows that summertime air exchange rates are at least twice as high at the Matejko Museum (1.26–1.44 air exchanges h^{-1} in the upper-floor

Table 1
Indoor and outdoor concentrations and concentrations ratios determined by ozone continuous air-monitoring instruments

Location	Dates (1993)	Duration (h)	Average O_3 (ppb)	Indoor/outdoor ratio
Cloth Hall	5–7 July	45		
Outdoors (Town Hall Tower)			27.4	
Outdoors (Cloth Hall)			25.7	
Indoor (Gallery D)			3.2	0.13
Matejko Museum	7–8 July	26		
Outdoors (Town Hall Tower)			20.0	
Indoors (3rd floor, west)			8.5	0.42
Wawel Castle	1–3 July	43		
Outdoors (Loggia)			14.7	
Indoors (Senator's Hall)			2.5	0.17
National Museum	29–30 June	21		
Outdoors (air inlet)			11.0	
Indoors (after air filters)			1.5	0.14
Collegium Maius	3–5 July	46		
Outdoors (courtyard)			32.4	
Indoors (chemistry room)			[a]	[a]

[a] Deleted due to suspected mercury vapor interference with ozone monitor.

Table 2
Seasonal air exchange rates (h^{-1}) from PFT tracers

Month	Wawel Castle		Matejko Museum	
	Senator's Hall[a]	Room 7A[b]	West[c]	East[d]
July 93	0.66	0.56	1.26	1.44
Oct 93	0.38	1.15	1.86	2.54
April 94	0.34	1.31	3.72	—
Year[e]	0.33	0.89	2.35	2.26

[a] Measurements made in the Senator's Hall on the third floor.
[b] Measurements made in room 7A immediately adjacent to the Senator's Hall.
[c] Measurements made in the West Gallery of the third floor where sampling equipment was located.
[d] Measurements made in the East Gallery of the third floor opposite a central staircase in the building.
[e] Separate one-year tracer experiment July 1993–July 1994.

galleries) when compared to the rooms studied at Wawel Castle (0.56–0.66 air exchanges h^{-1}). In the absence of a deliberate ozone-removal system, higher air exchange rates (as at the Matejko Museum) lead to higher indoor ozone concentrations. The reason for this is that indoor ozone levels represent a dynamic balance between the rate of ozone introduction into a building from outdoors versus ozone destruction by reaction at interior building surfaces. Higher outdoor air exchange rates increase the rate of introduction of ozone from outdoors and thereby raise indoor ozone levels.

Ozone concentrations downstream of the activated carbon beds of the air-handling system at the National Museum are shown in Fig. 2d compared to the ozone levels in outdoor air entering the building's ventilation system. It is seen that the activated carbon bed has eliminated 86% of the ozone in outdoor air over the 29–30 June 1993 period studied, leaving an ozone concentration of only 1.5 ppb in the building's air supply on the days studied.

Fig. 3 shows the measurements made with ultraviolet photometric ozone monitors in the chemistry exhibition room and outdoors at the Collegium Maius. Again very good agreement is seen between our outdoor instrument and the nearby municipal monitoring station in the Market Square. The indoor "ozone" levels measured in this gallery are suspect. The "ozone" levels measured indoors are nearly constant even though the outdoor levels fluctuate significantly during the course of monitoring. Measurements showing that indoor ozone concentrations exceed outdoor ozone concentrations at night are unlikely to be true when the only source of ozone is from penetration of ozone-laden air from outdoors. Ultraviolet photometric ozone monitors measure ultraviolet light absorption by ozone at a wavelength at which mercury vapor in indoor air would interfere with the measurements. This is seldom a problem because mercury vapor, being toxic, is usually eliminated from indoor air. However, the display of antique scientific instruments in this museum does raise the unusual circumstance that the instruments may be a source of mercury vapor or that there may have been a mercury spill in the museum that was not completely cleaned up. It is possible that contamination from mercury vapor present in the air within the chemistry room caused an erroneously high instrument reading by the continuous ozone monitor at this location. Tobacco smoke could also interfere with the uv photometric ozone measurements, however, smoking is not permitted in the museum.

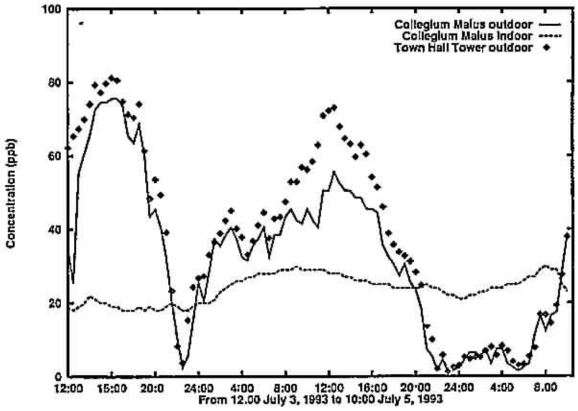

Fig. 3. "Ozone" concentration measured at Collegium Maius and at Town Hall Tower.

4.2. *Ozone passive monitoring experiments*

Results from the month-long ozone passive monitoring experiment are given in Table 3. Outdoor ozone concentrations (21–26 ppb) determined near ground level by the passive monitors at the Matejko Museum and at the National Museum are in excellent agreement with the July average of the continuous ozone-monitoring data taken nearby at the Town Hall Tower in the Market Square (25 ppb). The outdoor ozone concentrations at the Loggia of Wawel Castle high above the street were found to be almost double those in the town center on average over the month of July. Scavenging of ozone by NO emitted by motor vehicles and other fuel combustion sources would be expected to have a greater effect on ozone concentrations measured near ground level, thereby possibly explaining why ozone measurements made at high elevation at Wawel Castle on average exceed those made nearer to ground level within the center of the old city.

The month-long average indoor ozone concentrations and indoor/outdoor ratios shown in Table 3 are in general agreement with the short-term dynamic measurements in most cases. The highest one-month average indoor/outdoor ozone concentration ratios were seen in the Cloth Hall and in the Matejko Museum, averaging 43–44% of those outdoors. Indoor ozone levels and indoor/outdoor ozone ratios were lower elsewhere. Indoor ozone concentrations average 7–8 ppb at Wawel

Table 3

Average ozone concentrations and ozone concentration ratios determined by passive ozone monitors during July, 1993

Location	Duration (days)	Average O_3 (ppb)	Indoor/outdoor O_3 Ratio
Wawel Castle, outdoors	31.8	42[a]	
Wawel Castle, Room 15	31.0	8	0.19
Wawel Castle, Senator's Hall	31.8	7	0.17
Matejko Museum, outdoors	26.9	21[b]	
Matejko Museum, Indoor Gallery	26.9	9	0.43
National Museum, air-inlet from outdoors	33.1	26[b]	
National Museum, after carbon filters	33.1	6	0.23
National Museum, Hall H, 3rd floor	33.1	5	0.19
Town Hall Tower, Market Square, outdoors	31.0	25[c]	
Collegium Maius, chemistry room, indoors	30.0	6	0.24[d]
Cloth Hall Museum, indoors	28.9	11	0.44[d]

[a] On Loggia of Piano Nobile Level, high above the street.

[b] At street level.

[c] Monthly average obtained from continuous uv photometric ozone monitor.

[d] Outdoor concentration taken from continuous ozone monitor at the Town Hall Tower.

Castle, or 17–19% of the concentration outdoors. At Collegium Maius, indoor ozone concentrations average 6 ppb or 24% of those outdoors, a situation that seems to confirm our suspicion that the higher indoor "ozone" levels measured by the ultraviolet photometric continuous monitors at that site are not due to ozone but rather are possibly due to mercury vapor in the indoor air of the chemistry exhibit room. Indoor ozone levels in the National Museum also average 5 ppb, or 19% of those outdoors. Concentrations at the National Museum would be expected to be low given the presence of an activated carbon filter system that on average reduces ozone in the inlet air to the building to 6 ppb or 23% of that outdoors.

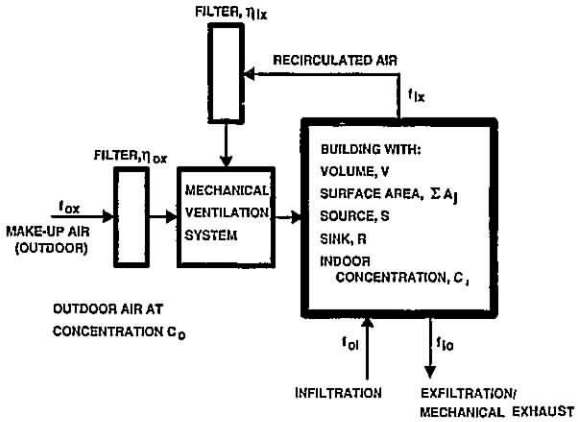

Fig. 4. Schematic diagram of a building's ventilation system.

4.3. Protection of Krakow Museum collections from damage due to atmospheric ozone

The average indoor ozone concentrations within Krakow Museums documented in Table 3 ranged from 11 to 5 ppb according to the July 1993 passive ozone-monitoring experiments. Indoor/outdoor ozone concentration ratios ranged from a high of 0.44 to 0.43 at the Cloth Hall Museum and at the Matejko Museum to a low of 0.24 to 0.17 at the Collegium Maius, the National Museum and the Wawel Castle. The short-term experiments conducted using continuous ozone monitors show similar indoor/outdoor ratios, with the exception that indoor/outdoor ozone concentration ratios in the Cloth Hall were much lower on the two days sampled with continuous ozone monitors (0.13) than over the rest of the month of July (0.44).

The indoor ozone concentration achieved within a museum facility depends on a dynamic competition between the rate of introduction of ozone from outdoors via the ventilation air versus the rate of ozone removal via activated carbon air filtration or by ozone deposition to interior building surfaces (including the collection). It is also possible that indoor ozone surfaces may be present, for example, due to the presence of photocopying machines within a building. For a building that can be represented as a single well-mixed chamber, shown schematically in Fig. 4, the time rate of change of the interior ozone concentration, C_i, depends on the competition between ozone sources and sinks as follows:

$$V\frac{\mathrm{d}C_i}{\mathrm{d}t} = (1-\eta_{\mathrm{ox}})f_{\mathrm{ox}}C_{\mathrm{o}} + (1-\eta_{\mathrm{ix}})f_{\mathrm{ix}}C_{\mathrm{i}} + f_{\mathrm{oi}}C_{\mathrm{o}} - (f_{\mathrm{oi}} + f_{\mathrm{ox}} + f_{\mathrm{ix}})C_{\mathrm{i}} + S - R, \quad (1)$$

where C_o and C_i are the outdoor and indoor ozone concentrations; f_{ox} represents the outdoor air supplied to the buildings air-conditioning system ($m^3\ h^{-1}$); f_{ix} is the indoor air recirculated to the building's air-conditioning system (if any); and f_{oi} is the untreated air that enters the building (through open doors, windows, or cracks in the building).

The efficiency of activated carbon filters that may be inserted into the outdoor air supply (e.g., at the National Museum) is given by η_{ox}; if activated carbon filters are placed in the stream of indoor air that is recirculated to the air-conditioning system, their efficiency would be parameterized by η_{ix}. R is the rate of removal of ozone at indoor surfaces, while S is the rate of indoor ozone emission. In the museums studied here there are no known indoor ozone sources. The ozone removal rate, R, at indoor surfaces is calculated as

$$R = \sum_j v_{\mathrm{d}_j} A_j C_{\mathrm{i}}, \quad (2)$$

where v_{d_j} is the deposition velocity for ozone removal at the jth surface which has surface area A_j. The deposition velocity is the pollutant mass flux to a unit surface area per unit atmospheric concentration, which upon cancellation of units yields values of v_{d_j} having units length/time, hence the name deposition velocity.

If changes in air exchange rates, indoor emissions, and outdoor pollutant concentrations are not highly correlated, then a good approximation to the long-term average indoor ozone concentration is given by the steady-state solution to Eqs. (1) and (2)

$$C_{\mathrm{i}} = C_{\mathrm{o}}\frac{[f_{\mathrm{oi}} + (1-\eta_{\mathrm{ox}})f_{\mathrm{ox}}] + S/C_{\mathrm{o}}}{[\eta_{\mathrm{ix}}f_{\mathrm{ix}} + f_{\mathrm{oi}} + f_{\mathrm{ox}} + \sum_j A_j v_{\mathrm{d}_j}]}. \quad (3)$$

In the situation found in most Krakow museums where there are no indoor sources and no air-conditioning systems, Eq. (3) can be simplified further to yield

$$\frac{C_{\mathrm{i}}}{C_{\mathrm{o}}} = \frac{f_{\mathrm{oi}}}{f_{\mathrm{oi}} + \sum_j A_j v_{\mathrm{d}_j}}. \quad (4)$$

Within those museums that lack an air-conditioning system, the indoor/outdoor ozone concentration ratio depends only on a competition between ozone introduction into the building with the infiltration air versus ozone loss to indoor surfaces. If an effective average deposition velocity to all surfaces is adopted, Eq. (4) becomes

$$\frac{C_i}{C_o} = \frac{1}{1 + (A/f_{oi})v_d} \tag{5}$$

where A is the total surface area for the building and v_d is the effective average deposition velocity. The air flux from outdoors, f_{oi}, is equal to the product of the volume of the building and the number of air exchanges per hour. Thus, the indoor/outdoor ozone concentration ratio depends only on the surface-to-volume ratio for the building, the number of air exchanges per hour, n, and the ozone deposition velocity:

$$\frac{C_i}{C_o} = \frac{1}{1 + (A/V)(v_d/n)}. \tag{6}$$

Eq. (6) can be applied to explain the ozone concentration data taken at the Matejko Museum. Referring to Table 2, 1.26–1.44 air exchanges per hour occurred between outdoors and the interior of the 3rd floor galleries at that site on average during July 1993. The west 3rd floor gallery in which the ozone monitors were located has a volume of 186 m^3 and a surface area of 223 m^2. The Matejko Museum is a compact building ventilated through many small open windows located all over the building. It is reasonable to assume that the rest of the building has a surface-to-volume ratio similar to the west gallery and that the outdoor air-exchange rate for the rest of the building is in the same range as that in the two galleries where measurements were made. A typical value for the ozone deposition velocity to indoor surfaces of 0.051 cm s^{-1} is adopted based on studies by Hales et al. (1974) and by Druzik et al. (1990). At the surface-to-volume ratio indicated for the Matejko Museum, Eq. (6) would predict an indoor/outdoor ozone concentration ratio of 0.36 at a rate of 1.26 air exchanges h^{-1} and an indoor/outdoor ratio of 0.40 at 1.44 air exchanges per hour. This compares fairly closely to the indoor/outdoor ozone concentration ratios of 0.42 to 0.43 measured during July 1993, as shown in Tables 1 and 3.

Procedures for control of ozone concentrations within museums have been studied by Cass et al. (1991). The control methods that are available include reduction in the rate of air infiltration into the buildings from outdoors, installation of activated-carbon air-filtration systems, and localized protection of specific objects in the collections by placement in display cases or by framing under glass.

Often, the least expensive method for indoor ozone control involves careful management of outdoor air infiltration rates. The minimum recommended outdoor air supply rate to a building is often taken to be 8.5 $m^3\,h^{-1}$ $person^{-1}$ occupying the building (American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE), 1985). The west 3rd floor gallery of the Matejko Museum has a volume of 186 m^3. At the 1.26 air exchanges h^{-1} observed during July 1993, there is enough air brought into the small room historically to accommodate a crowd of 27 people. At the higher annual average air exchange rate of 2.3 air changes h^{-1} shown in Table 2, the 3rd floor west gallery at the Matejko Museum could in principle accommodate 50 people. It is hard to envision such a crowd in such a small room. The typical occupancy of that gallery is much smaller than this. If the air exchange rate were reduced to the 0.46 air changes h^{-1} needed to handle an average occupancy of 10 persons within that gallery, Eq. (6) predicts that the indoor/outdoor ozone concentration ratio would fall to 0.17. That value is about the same as the values observed within the other museum galleries in the Krakow area. If the ventilation rate were set for an average occupancy of 5 persons $gallery^{-1}$ (corresponding to about 30 persons at one time for the whole building) Eq. (6) predicts that the indoor/outdoor ozone ratio would fall to 0.094.

Installation of a mechanical ventilation system accompanied by activated-carbon air filtration provides an alternative ozone-control technology. Southern California museums such as the Los Angeles County Museum and the Huntington Gallery that have well-maintained activated-carbon ozone-removal systems, show indoor ozone concentrations in the range of 4–6% of those outdoors (Druzik, 1990). Although it has an activated-carbon ozone-removal system, indoor/outdoor ozone concentration ratios at the National Museum in Krakow are higher than this, having a value of 0.19 as shown in Table 3.

The activated carbon beds within building ventilation systems have a single pass control efficiency of about 95% when fresh (Wadden and Scheff, 1983). This control efficiency thereafter declines over time. As seen in Table 3, the average control efficiency of the activated carbon bed at the National Museum is approximately 77% (i.e., $1 - 0.23 = 0.77$) indicating that its efficiency could be increased if the carbon bed was renewed. However, one can see from Table 3 that indoor ozone concentrations in the National Museum are almost as high as the concentrations immediately downstream of the activated carbon bed which is placed in the air inlet to the building; very little depletion of ozone seems to occur due to reaction with interior building surfaces. This suggests that the air exchange rate for the National Museum must be very high and that air retention time in the building must be low. It should be possible to decrease the air flow rate from outdoors (f_{ox} in Eq. (3)) and increase the internal air recirculation rate (f_{ix} in Eq. (3)). If that is done, then ozone concentrations will decline further.

If indoor ozone concentrations equal to about 20% of those leaving the activated carbon bed are obtained by careful management of air exchange rates, then the indoor ozone concentrations in the National Museum should fall to about 5% of those outdoors. This should be the case even if the activated carbon bed is applied only to the outdoor make-up air and has a single pass removal efficiency of 77% (i.e., $0.2 \times (1-0.77) = 0.046$). Reduction in outdoor air supplied to the air-handling system accompanied by increased recirculation of previously conditioned indoor air also would be expected to reduce building heating and cooling costs. Again, human occupancy is the key factor determining how much outdoor air is needed. There should be at least 8.5 m^3 outdoor air per person h^{-1}; if occupancy is highly variable then dampers can be installed that will permit the outdoor air supply to be increased or decreased to match the variations in occupancy.

Use of display cases or framing of paintings behind glass provides a further means to protect museum collections. Much of the collection in the Matejko Museum is already within display cases. A display case acts as a small room within the gallery space and generally the inside of a display case has a very slow air exchange rate with the room. Eq. (6) can again be applied with C_o being the ozone concentration within the gallery and C_i being the ozone concentration inside the display case. Ozone concentrations about one tenth as high as those in the surrounding room have been measured inside even loosely fitted display cases in California (Cass et al., 1991). This suggests that the ozone exposure for objects inside the tightly fitted display cases in the Matejko Museum are below the 1 ppb ozone exposure target for museum displays, as 10% of the 9 ppb seen indoors in the summer at that site would fall below the 1 ppb level.

Management of the ozone exposure conditions experienced by the Sigismund Augustus tapestries in the Wawel Castle provides an interesting challenge. The castle is far too large to be modeled as a single well-mixed air volume, and it is difficult to envision the installation of a forced ventilation system that would provide tight control over the air flows from room to room. Further, the appearance of the tapestries would be significantly altered if they were encased. We note from Table 3, however, that the indoor/outdoor ozone concentration ratio in the Senator's Hall at Wawel Castle in the summer is about 0.17, which is nearly the same as at the National Museum which already has an activated-carbon air-filtration system.

The reason for such low indoor ozone levels at the Senator's Hall at Wawel Castle is in part found in Table 2, where it is seen that the air exchange rate in the Senator's Hall historically has been fairly low (0.66 h^{-1} during the July 1993 experiments). On average over the 1 yr period beginning from July 1993, the air exchange rate as measured by PFT tracer experiments was only 0.33 h^{-1}. At an air exchange rate of 0.33 h^{-1}, the ozone concentration in the Senator's Hall would probably fall to about 0.09 of that outdoors. The reason for the low ozone level in the Senator's Hall is that it is located at the far end of a long series of connected rooms. All of the windows in the Senator's Hall are closed, and air enters the room from adjacent rooms. The nearest open windows are many rooms upstream in the air circulation pattern for the building. The ozone concentration in indoor air is substantially depleted by interaction with the interiors of upstream rooms before the air reaches the Senator's Hall. Recognizing that this system works fairly well, care should be taken not to increase the outdoor air intake to the building by opening windows in rooms near the Senator's Hall. If a further reduction in ozone exposure in the Senator's Hall is desired, a localized activated-carbon air-filtration system could be installed for that one room with an air inlet through the door area that exists on the balcony at the south end of the room. That small activated-carbon air-filtration system should recirculate air from within the Senator's Hall in order not to have to process 100% outdoor air. However, enough outdoor make-up air should be provided to meet occupancy requirements (8.5 m^3 h^{-1} $person^{-1}$) and to pressurize the room slightly such that untreated air does not flow into the room.

5. Conclusions

Many organic pigments and dyes can be expected to fade if they are exposed for long periods of time to a significant fraction of the ozone content of outdoor air. This potential fading hazard can be managed if the factors that affect the penetration of ozone from the outdoor atmosphere into the interior of museums are understood. Few data have been reported for indoor ozone concentrations in eastern Europe. To bridge this information gap, five museums located in the historic center of Krakow, Poland have been surveyed. Month-long ozone levels outdoors in Krakow in July average 42–21 ppb. Indoor concentrations in those museums studied that have no air-conditioning system and that operate with many doors and windows open to the outdoors have average ozone concentrations indoors that are 43–44% as high as those outdoors. Indoor ozone concentrations are lower, in the vicinity of 20% of those outdoors, in museum facilities that have lower air exchange rates with the outdoors. Equations developed to model indoor/outdoor relationships for ozone show how indoor ozone concentrations can be deliberately controlled to low levels through careful management of outdoor air exchange rates, use of activated-carbon air filtration, or use of display cases.

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