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INDOOR OZONE AND NITROGEN DIOXIDE CONCENTRATION IN TWO MUSEUMS OF THE SÃO PAULO MEGACITY - BRAZIL

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SCIENTIFIC PAPER

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This paper reports and discusses O_3 and NO_2 concentration data collected between 2009 and 2011 in the indoor environments of two important Brazilian museums located in the megalopolis of São Paulo: the University of São Paulo History Museum (*Museu Paulista, MP*) and the São Paulo State Art Museum (*Pinacoteca do Estado de São Paulo, PE*). Two techniques were used to obtain the target information: continuous automatic monitors and passive sampling, the latter being tested as a possible routine approach to the museum monitoring. In the MP, both pollutants are found at concentrations that in the best situation reach 50% of the outdoor concentrations, with some visible differences between more or less internal areas. This confirms that the museum exhibits broad air exchange which leads to potential risks for the collection and ought to be regarded as a priority in the museum environmental management strategies. In the Art Museum, filtration and air conditioning systems do result in improvements in the air quality in terms of O_3 and NO_2, especially in the storage area. Yet, the safety standards for this type of microenvironment are not always maintained especially on account of the close proximity of the museum building to intense traffic roads.

1 Introduction

Ozone (O_3) and nitrogen dioxide (NO_2) are common airborne pollutants in urban centres characterised by large vehicular fleets and intense solar irradiation, as well as geographical and climatic factors unfavourable to pollution dispersion.

Air pollution in urban centres is primarily a matter of general health concern. However, its effects on the stability and durability of materials cannot be underestimated. As an example, a study carried out in 1996 estimated the cost of O_3 damage to materials in the UK in the range of £170- 345 million per year[1].

In the case of the tangible cultural heritage, there is a two-fold problem. Firstly, cultural artefacts are unique and their destruction is always an irreplaceable loss. The natural decay of materials, although inevitable to the long term, can be indefinitely delayed, however some of the airborne pollutants that afflict large cities are also known to contribute for accelerating the degradation process. Secondly, important museums are normally located in large cities. São Paulo is not an exception: it is the liveliest cultural centre of the country and its museums shelter notable works of art, mainly Brazilian and European collections.

The focus on the effect of airborne pollutants in the preservation of cultural heritage gained momentum during the 1990s, after the publication of the milestone paper of Brimblecombe[2] (1990) which followed a number of pioneering works on the subject[3-10].

After that, several studies on the indoor contamination of these compounds in museums were carried out[11-19]. Among them, the study of nine museums in Southern California highlighted the importance of architec-

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tonical and logistical aspects in determining the permeation of outdoor pollutants (in that case, NO_2) in indoor environments[13]. The results of these investigations showed that the indoor concentrations of NO_2 were very close to outdoor levels in all the museums not equipped with air conditioning systems and their fluctuations followed the same pattern. The highest indoor level detected in the study was 120 ppb, that is, considerably higher than the recommended standards for museums (see discussion in the Results and Discussion section).

The Uffizi Museum in Florence, that has no HVAC, also exhibited outdoor dependence on the indoor levels of O_3, as well as several other pollutants investigated[14].

Distinct behaviours among different museums in the same urban context were also reported in London (Museum of London and Bethnal Green Museum with average NO_2 indoor/outdoor levels of 0.19 and 0.84, respectively[15]) and in Krakow (with O_3 i/o ratios of 0.42-0.44 at the National Museum and 0.17-0.19 at the Wawel Castle[16]). Both the Sainsbury Centre for Visual Arts, Norwich, UK[17] and Royal Museum of Fine Arts, Antwerp, Belgium[19] displayed seasonal differences in NO_2 concentrations attributed by Brimblecombe[2] to changes in indoor O_3 concentrations (higher in summer) which acts as an enhancement factor for NO_2 formation by oxidation of NO.

Countermeasures commonly suggested for outdoor pollutants in museums include, in general, the use of activated charcoal either pure or with alkaline impregnation, silica gel, zeolites, permanganate-impregnated alumina[20-22]. Their effectiveness generally depends on the target pollutants, on the support used (pellets, woven fibre matrix, for example), on the volume of air and on the mode of operation, i.e. whether by passive diffusion or mechanical forcing through the sorption media.

A number of studies based on the combination of numerical simulations and site measurements of O_3, NO_2 and NO[23-25] tend to agree with the conclusion that the main factors that affect the indoor levels of ozone are the mechanisms of transport from the outdoor environment and the rate of the deposition process onto surfaces, with less contribution from chemical transformations on the gas phase. In particular, the work of Druzik et al.[23], corroborated by the observations in 11 indoor locations in California, gets to the following ranges for i/o ratios for different air exchange schemes often encountered in museums: 0.7-0.8 (buildings with high rates of air exchange), 0.3-0.4 (buildings with conventional air conditioning), 0.1-0.2 (buildings with slow air exchange and no forced ventilation) and <0.1 (buildings with efficient air filtration and no air infiltration).

The present work adds to the general picture summarised above a discussion based on the results obtained from a series of monitoring campaigns carried out in two of the most important Brazilian Museums located in the city of São Paulo, between 2009 and 2010.

The metropolitan area of São Paulo (MASP) undoubtedly gathers a number of conditions propitious to quite high levels of atmospheric pollutants, among which a population of almost 20 million and a fleet of 6.5 million vehicles[26]. The average monthly air temperature ranges from 15.6 to 23.8 °C, with an average maximum temperature of 31.0 °C (February). The global solar irradiation ranged from 370 (July) to 550 MJ m^{-2} (February) over the 1983-2005 period and its average solar energy incidence (397.4 MJ, based on NASA data) was 16, 48 and 70% larger than in New York City, Paris and Berlin, respectively[27]. Thermal inversions are not uncommon, especially during the dry season, that is, from May to September: typically, between 30 to 45 episodes of thermal inversion with a mixing layer < 200m are experienced every year. In 2010, the Environmental Agency of the São Paulo State (CETESB) reported a peak of 59 days classified as unfavourable to pollution dispersion[26].

The above situation determines in the MASP a level of outdoor pollution whose extent can be depicted on the basis of the information retrieved from the openly-accessible databank of CETESB[28]. The actual lowest and highest annual mean values recorded in 2010 in the official monitoring network were 26 μg m^{-3} (14 ppb, at 23º34'03"S, 46º43'47"W) and 67 μg m^{-3} (36 ppb, at 23º36'57"S, 46º39'47"W) for NO_2[26] and 27 μg m^{-3} (14 ppb, at 23º32'40"S, 46º37'40"W) and 46 μg m^{-3} (23 ppb, at 23º33'41"S, 46º42'07"W) for O_3[28]. Individual episodes can be particularly severe: in 2010, ozone concentrations above 160 μg m^{-3} (81 ppb, 1-hour mean, Brazilian Air Quality Standard) were recorded in 49 days (14% over the total monitored days of the year) and in 23 days (7%) in the stations exhibiting the highest and the lowest annual mean, respectively[28].

2 Experimental

2.1 Sites

Measurements were carried out in the University of São Paulo History Museum (*Museu Paulista, MP*) and in the São Paulo State Art Museum (*Pinacoteca do Estado, PE*). Both museums are located in the central area of the municipality of São Paulo (Figure 1), close to important connecting roads, normally affected by heavy traffic. The PE faces a large avenue within a few metres distance while the MP is settled in the middle of a 1500 m^2 urban park. Yet, the former is housed in a building (originally from 1900) that has been adapted to some extent to function as a modern museum, with substantial control of temperature, relative humidity and light, as well as air filtration (see details in Cavicchioli et al.[29]), whereas the latter has no positive environmental control, being hosted in a 1890 monumental mansion which is bound to legal restrictions for architectural modifications. Therefore, the two sites exhibit distinct features in terms of location, architecture, type of ventilation and exposure to outdoor conditions.

In both museums, there is a clear distinction between the exhibition area and storage rooms. In the PE, there are two storage rooms that comprise a 260 m^2 area located in the ground floor, in the east-facing side of the building. One of them is for paintings and the other contains mainly paper artefacts. There are no windows and environmental control is ensured by a centralised air conditioning system (fan coil units, by Trane), provided with polypropylene filters at the air inlet. In this work, the monitored exhibition room was the *Sala Willys*, on the 2nd floor (windows facing south).

External measurements were carried out in the large balcony situated on the 1st floor on the east side of the building.

In the MP, the storage rooms are located on the 2nd level in the rear side (south) of the two towers (east and west) adjacent to the central block. In this work, the monitored exhibition areas were the *Salão Nobre*, on the 1st floor of the central block (windows facing north) and the east lower level corridor, an area where the air ventilation from the outdoor atmosphere occurs through a little hatch and the staircase connecting it with the main entrance hall at ground level.

It is interesting to note that the collection of the PE includes mainly modern art paintings and sculptures, whereas the MP focuses on furniture and textiles.

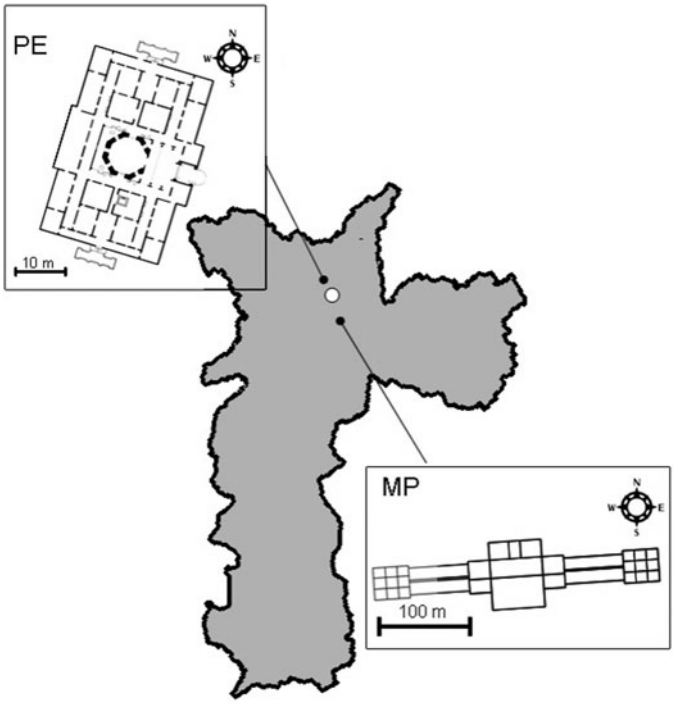

Figure 1: Locations of the monitored sites within the municipality of São Paulo and their plants. MP (geographic coordinates: 23º35'08"S, 46º36'35"W) and PE (geographic coordinates: 23º32'03"S, 46º38'02"W). The white dot indicates the approximate location of the official air monitoring station (23º32'40"S, 46º37'40"W).

2.2 Continuous monitors

Continuous monitoring of O_3 was carried out in the two museums using a Thermo 49i Ozone Analyzer based on a dual cell photometer with UV detector at 256 nm. The equipment, that has a detection limit of 0.5 ppb (ca. 1.0 μg m^{-3}), operates at a flow rate of 1 to 3 L min^{-1} and stores 1-hour average concentration file data (individual measurements are taken every 20 s with a 10 s lag time). The analyser has a precision of at least 1 ppb, according to the manufacturer's specification.

The official data of outdoor concentration were retrieved from the internet site of CETESB, responsible for the air quality monitoring network in the State of São Paulo[28]. In this network, the same Thermo 49i system for ozone and a Thermo 42i NOx Analyzer for NO_2 are employed. To guarantee for accuracy in the measurements, the CETESB instruments are calibrated on a daily basis against precisely-known concentrations of analytes produced in-situ. The O_3 automatic equipment that was deployed in the two museums for this work belongs to the Department of Atmospheric Sciences of the University of São Paulo and is periodically sent to CETESB for a calibration under the same operating conditions, which ensures the comparability of the data.

The official data information reported in this work specifically refers to the O_3 and NO_2 concentrations measured by automatic monitors at the *Parque Dom Pedro* station, located in-between the two monitored sites at 23º32'40"S, 46º37'40"W – that is, at ca. 1 km from the PE and 5 km from the MP.

2.3 Passive sampling and analysis

The O_3 determination by passive sampling was based on the methodology described in Félix et al.[30] (and, subsequently in Garcia et al.[31], among others) which makes use of the reaction between the indigo trisulphonate dye and ozone. The indigo dye reagent, impregnated on the cellulose membrane placed within the passive sampler, undergoes discoloration upon reaction with ozone, thus enabling the determination of average ozone concentration in ambient air during the exposure. For this method, a precision of 8.6% was reported[31]. Furthermore, the correlation between the ozone concentration obtained with this method and with the same Thermo UV analyser described above resulted in a linear relationship with angular coefficient of 0.88 and R= 0.957, thus confirming a very good degree of accuracy.

To this purpose, specific tubular passive samplers assembled in our laboratory (Figure 2) using PTFE and polycarbonate components were employed. The reagent solution was potassium indigo trisulfonate (Sigma Aldrich, 6.5 mmol L^{-1}) in a 1:1 w/w mixture of deionized water (18 MΩ cm grade) and ethylene glycol (Q.M. Ltda.). The amount dispensed onto the filter was 30 μL.

For the NO_2 determination, the target compound was collected in the tubular passive samplers described by Melchert & Cardoso[32] onto cellulose membranes impregnated with the reactive solution proposed by De Santis et al.[33], that is, sodium carbonate (Reagen Ltda., 1% w/w) plus ethylene glycol (1% w/w) in 1:1 water/methanol (Vetec Ltda.).

In both cases, the necessary amount of cellulose membranes (Whatman N. 41) were cut, thoroughly washed with deionised water, dried in a desiccator overnight, impregnated with the reagent solutions and then dried again overnight. To minimize contamination of the filters, desiccators was purged with N_2 for 10 min and then maintained under partial vacuum (blanks were also kept under these conditions for the entire duration of the exposures).

The exposures of the passive samplers in the sites, which took place over typically 5 to 7 days, were always conducted in duplicates. In addition to that, for O_3 measurements duplicates of field blanks were also required to account for dye discoloration due to light irradiation. In this case, the passive samplers were sealed with Parafilm and PTFE tape.

The analysis following the exposures involved soaking the cellulose membranes in deionized water for 30 min under mild shaking, thus allowing the exhaustive extraction of the remaining indigo dye (O_3 tubes) or of nitrite and nitrate (NO_2 tubes). The former was quantified by photometric determination, using the absorbance signal of the indigo dye at 600 nm obtained in a Shimadzu, UV-1650 PC spectrophotometer. The latter were quantified by a 761 Compact IC Metrohm chromatograph with conductivity detection using Metrohm accessories: A-Supp 5 (250×4 mm) separator column (eluent solution of Na_2CO_3 1.8 mmol L^{-1} / $NaHCO_3$ 1.7 mmol L^{-1}, flow rate 1.0 mL min^{-1}) and anion micromembrane suppressor (regenerating solution of H_2SO_4 50 mmol L^{-1}, flow rate 0.8 mL min^{-1}).

In both cases, the Fick's law of diffusion provided a means for estimating the average concentration (mol cm^{-3}) of the ozone and nitrogen dioxide in the gas phase:

$$C_{(g)}=Q\cdot z / D\cdot\pi\cdot r^2\cdot t$$

where r is the diameter (cm) of the diffusion tube, t the exposure time (s), D the diffusion coefficient of O_3 (0.144 cm^2 s^{-1}) or NO_2 (0.136 cm^2 s^{-1}) in air[34], z the diffusion pathway (cm), i.e. the height of the diffusion tube and Q is the amount (mol) of O_3 or NO_2 that reached the reacting membrane over the exposure time. In the case of O_3, Q is assumed to equal the number of moles of indigo dye that undergo discoloration upon 1:1 reaction with ozone and, therefore, it is obtained as the difference in the amount of indigo dye left on the cellulose filter between the exposed samplers and the field blanks (where discoloration results from irradiation). As for NO_2, this value is estimated from the sum of nitrite and nitrate ions extracted from the membranes of the exposed samplers, after discounting the molar amount of the same anions determined in the blanks. Although the original method

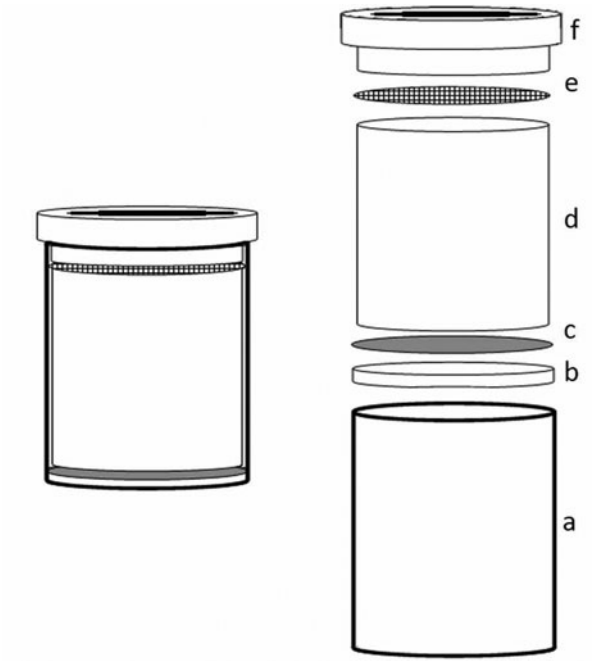

Figure 2 Compact and exploded representation of passive samplers developed for the work, comprising: a) Main tubular body in polycarbonate, 50 mm (h) x 25 mm (d); b) Ring spacer in PTFE, 2 mm (h); c) Impregnated cellulose disk; d) Ring spacer in PTFE, 18 mm (h); e. Polycarbonate protective disk membrane, 10 µm pore size; f. Tight-fitting ring stopper, 4 mm (h).

associates the absorption of NO_2 only with nitrite, in this study both nitrite and nitrate concentrations were employed. This is because unusually high values of NO_3^- were found in the filters after exposure, which could not be accounted for unless nitrite oxidation (following its uptake on the filter's surface) was assumed, a reaction that is known to occur in the presence of ozone (in fact, in an alternative method the quantification of ozone by passive sampling is carried out using nitrite-impregnated substrates[35].

3 Results and discussion

The results of ozone monitoring carried out in the different areas of the two museums are shown in Figures 3 and 4. In the same graphs, the data of an Environmental Agency monitoring station located almost halfway between the two museums are also displayed for comparison. In general, each monitoring phase took place over a period of 7-10 days, in February and March, that is, late summer-early autumn in the southern hemisphere. Typically, this time of the year is characterised by a decrease in rainfall intensity (if compared to mid-summer conditions), but still under strong solar light incidence. This means that during these weeks, although the high photochemical pollution levels distinctive of the late dry season (August-September) are not reached as a rule, significant peaks of ozone concentration are not unusual. Maxima tend to occur at around 3-4pm.

In the PE, the O_3 concentration in the two storage room (Figure 3C and 3D) exhibited over the monitored period almost constant concentrations, with overall mean values of 3.2 ppb (paper storage area) and 2.8 ppb (paintings storage room), within ranges of hourly averages of 0.98-10.9 ppb and 0.71-3.5 ppb, respectively. It is clear that the typical photochemical patterns observed in the outdoor environment do not directly reflect in these indoor areas, unless exceptional high levels of outdoor ozone concentration occur, as was the case of day 1 in the paper storage room, when a 10.9 ppb peak of indoor concentration was recorded corresponding to an external peak of more than 100 ppb at 5pm (Figure 3C). Furthermore, there is a patent difference between the two storage rooms in terms of ozone level, with lower levels in the room (paintings) that receives downstream air precisely from the paper storage (which, in turn, is aspirated from the exhibition area).

In the exhibition area (Figure 3B), only an overall average of 2.8 ppb is recorded, i.e. roughly as low as in the storage rooms. Nonetheless, such a comparison of average figures between different periods must take into account the actual variability of the air quality in external atmosphere: in this case, towards the end of the monitored period, there was a distinct improvement in outdoor air quality which explains the better performance of the indoor environment as a whole (Figure 3B). In fact, the exhibition area is somewhat more vulnerable when compared with the storage rooms, for it experiences peaks higher than 10 ppb (hourly averages) every time the urban environment outside the museum undergoes significant increases in photochemical pollutants, that is, approximately above 25 ppb (Figure 3B). Daily maxima occur simultaneously inside and outside the museum, implying in rapid air exchange. Still, one ought also to pay atten-

tion to the fact that the exhibition location monitored in this work shows a more conspicuous drop in O_3 concentration at the end of each day, whereas the storage rooms (and particularly the paintings depot) tend to maintain a higher background. This might possibly be associated with the fact that the improved air circulation taking place in the exhibition area also contributes to refreshing the indoor atmosphere with external air, precisely at the time when the outdoor levels drop to practically zero ozone concentration (as shown in all the graphs).The monitoring carried out in the balcony of the museum (Figure 3A) resulted in data that were very close to the official station's information, being in this case discrepant only at the end of the monitored period. This tends to confirm that the ozone concentration provided online and in real time by the governmental body can indeed be used as reliable estimate on the amount of the same gas present in the surroundings of the museum.

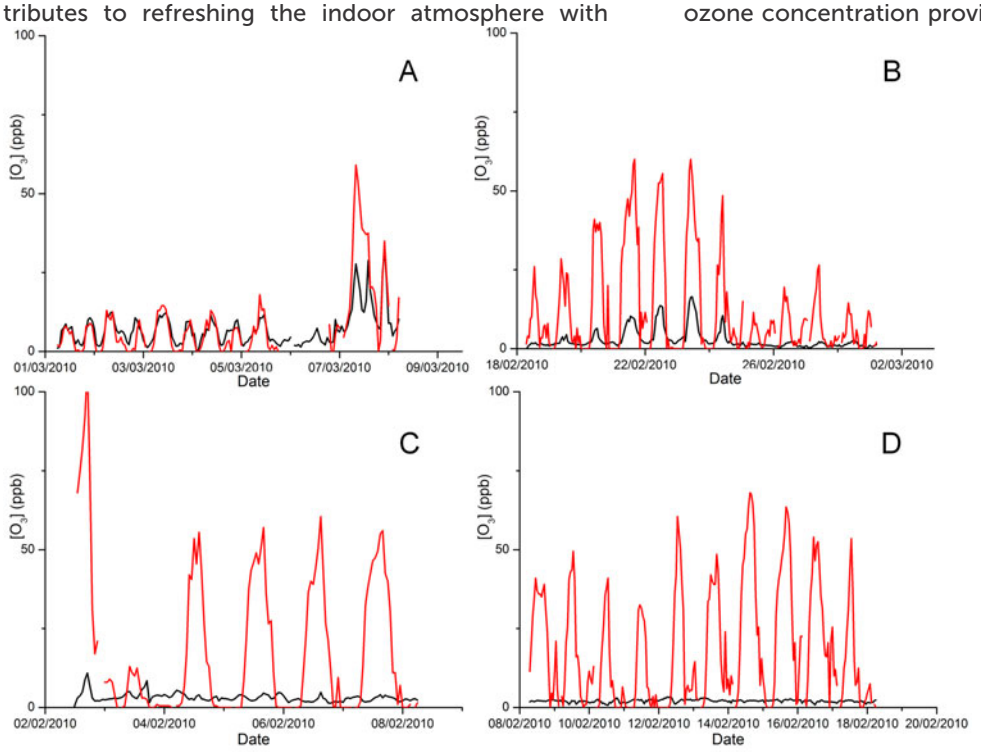

Figure 3: Ozone concentrations by continuous monitoring at the PE (black line): comparison with official urban ozone concentration in a nearby monitoring station (red line) measured simultaneously. External area of the museum (A); exhibition room (*Sala Wyllis*, B); storage area (paper, C); storage area (paintings, D).

The situation in the MP, where there is no gaseous pollutant filtration, is considerably different: in all the four monitored indoor areas of the building the levels of O_3 concentration closely follow the outdoor fluctuations associated with the typical daily pattern (Figure 4). This occurs in both the exhibition rooms (Figure 4a and 4b) and in two distinct storage sectors (Figures 4c and 4d). Here again, the ozone peaks take place, as a rule, simultaneously inside and outside the museum, hence with fast air exchange between the outdoor and the indoor atmosphere.

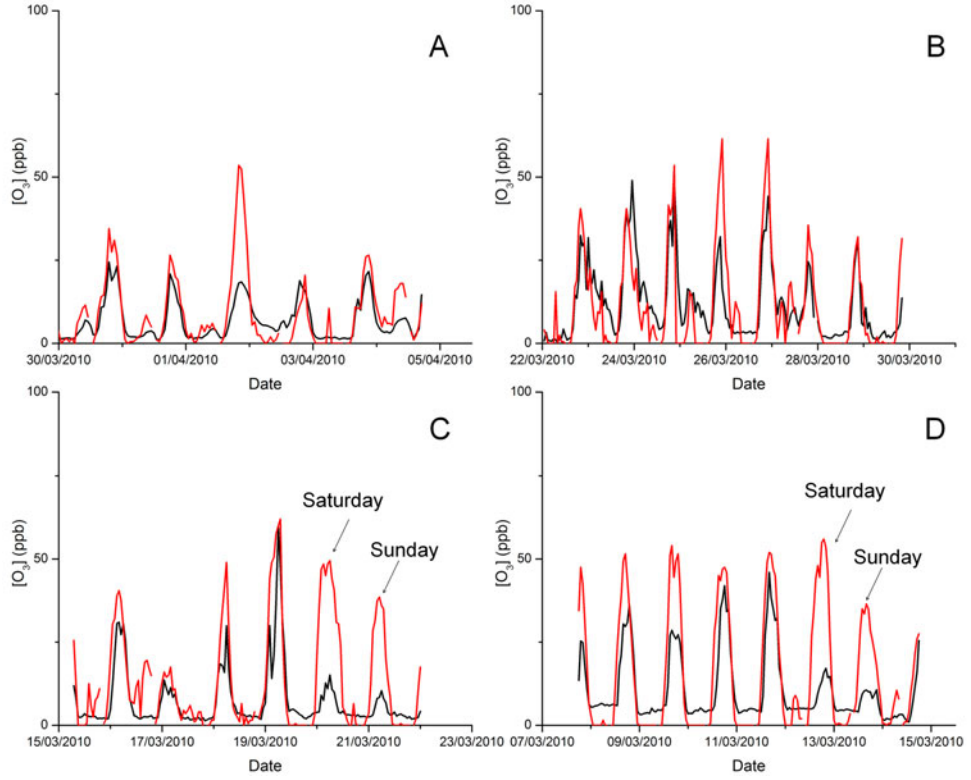

Figure 4: Ozone concentrations by continuous monitoring at the MP (black line): comparison with official urban ozone concentration in a nearby monitoring station (red line) measured simultaneously. Upper level exhibition room (*Salão Nobre*, A); lower level exhibition room (B); storage area (east tower, C); storage area (west tower, D).

In the main exhibition room (upper level, *Salão Nobre*) and in the storage areas (Figures 4a, 4c and 4d) the concentrations indoors are generally quite close to the values measured at the official station, but rarely higher than them. In the storage areas, they drop significantly over the weekends, which is likely to be ascribed to the fact that these sectors are also used for transit to the museum's administrative offices. This finding indicates that mere physical barriers, such closed doors and windows, do impact positively on the concentration of airborne pollutants with an external source. On the other hand, indoor/outdoor (i/o) ratios higher than one are particularly frequent in the lower level exhibition sector of the museum (Figure 4b), especially in late afternoons (see days 23rd,

24th and 25th of March). On average, during the monitored period this area of the MP presented an i/o ratio ca. equal to unity (Figure 5), unlike all the other rooms. On this point, it should be recalled that the official station where the outdoor monitoring was conducted, is located at approximately 5 km from the museum. This means that the MP is likely to experience a different outdoor level of ozone than that showed by the official data – probably even higher, as discussed below – and, therefore, that the real i/o ratios might in fact be lower than those reported in Figure 5. Yet, the distinct behaviour of the lower-level exhibition area deserves some attention. Here, indoor sources are in principle ruled out, even considering that the lower level sector is close to an administrative department where electronic devices are routinely used. For, if ozone sources were present there, one would observe a drop of such phenomenon on weekends when offices are closed, which is not the case. Brimblecombe and coworkers[17-18] believe that unusual high indoor levels of ozone can occur as a result of the shift of the NO/NO_2 redox equilibrium towards NO_2 in poorly illuminated internal spaces, since the backward reaction is predominantly photochemical and favoured by radiation with $\lambda \leq 430$ nm. It is well known that nitric oxide acts as a scavenger for O_3 and, therefore, in this case one of the mechanisms for ozone removal in the indoor atmosphere would be partially inhibited. This could be particularly true for the scarcely lighted room where measurements were carried out in this study.

As a summary of the continuous monitoring campaign so far discussed, Figure 5 shows the average concentration for each location over each monitored period and a comparison with average outdoor ozone level measured by the official agency at the same time. The differences between the two buildings in terms of response to outdoor ozone concentrations can here be clearly seen, as well as distinct behaviours within the same building.

In the case of the PE, the comparison between the indoor environments and the CETESB data must take into account the lower levels of ozone experienced outside the museum (Figure 5), a situation commonly encountered in São Paulo in the proximity to avenues with heavy traffic, as it is the case. This is clearly associated with higher concentrations of primary pollutants, including the ozone scavenger NO. The information on the outdoor O_3 concentration outside the MP could not be obtained in this work, but one may assume to be slightly higher that at the official station, since the MP is located at a certain distance from main roads and within a park. This condition is known to commonly favour ozone accumulation in the city and occurs on regular basis near two other monitoring stations (*Ibirapuera* at 23º35'30"S, 46º39'38"W and *IPEN* at 23º34'03"S, 46º43'47"W) of the same network. This means that part of the higher i/o ratios calculated for the MP on the basis of the official urban O_3 concentrations might indeed be accounted for a higher ozone concentration in the immediately surroundings of the museum. At any rate, the main contribution to this effect is certainly associated with more substantial air exchange on account of the MP own architectural characteristics and management practices. Here, internal differences at the MP are quite evident and show different degrees of penetration of this gas within the premises of the building.

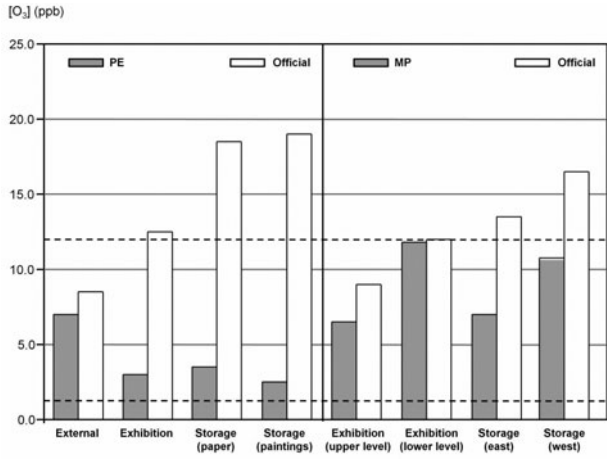

Figure 5: Summary of ozone average concentrations (continuous monitoring) at the PE and MP and official (CETESB) urban ozone data in nearby station.

The same graph (Figure 5) highlights two different commonly proposed threshold limits for ozone, 1 ppb and 13 ppb[12]. It is possible to observe that the second threshold limit was always attended on average, but in fact this is a boundary that was originally devised for paper-based archive records rather than plastic arts. The lowest limit of 1 ppb, which is always overcome in all rooms to different degrees, is a target recommended on a more general basis, on account of the high reactivity of ozone, its accumulative effects and the high life expectancy for works of art. This means that even levels considered safe for human health can result, on the long term, in doses of O_3 that represent a threat for cultural heritage.

It should be emphasised that the campaign hereby described was carried out in a part of the year when only a moderate level of pollution by ozone takes place, but there are seasons in which the concentration of the gas reaches larger values. Considering, for example, the overall outdoor average concentration of 14 ppb measured in the same official station over 2010 and maintaining the i/o ratios calculated during the 2010 campaign for the different rooms in the two museums, the indoor environments would experience the average concentrations shown in Table 1 over the same time span. In order to have a very rough perception of the meaning of such outdoors/indoors influence as far as ozone is concerned, the same table reproduces the number of years that would be necessary for materials to be exposed, in each monitored area, to the same dose of ozone as if they were kept for 12 weeks in a 400 ppb ozone concentration environment. This reference was taken from the study of Cass et al. (1989)[8], that showed this level to be sufficient to promote significant change in a variety of artists' pigments at 22 °C, 50% RH and in the absence of light*.

*Such figures should clearly be regarded as merely indicative and mostly in relative terms, since in a real world the degradation process depends on a series of factors that should be taken into account for a realistic projection, not least the synergistic action of other environmental factors, the fact that different pigments exhibit distinct sensitivity to ozone-mediated degradation and that artistic materials other than pigments undergo ozone attack.

	PE			MP			
	Storage (paintings)	Storage (paper)	Exhibition	Storage (west)	Storage (east)	Exhibition (upper L)	Exhibition (lower L)
Measured i/o ratios	0.10	0.16	0.22	0.65	0.53	0.73	0.99
Average annual indoor concentration in 2010 (ppb)	1	2	3	9	7	10	14
Estimated number of years before damage	92.0	41.2	30.0	10.2	12.4	9.0	6.6

Table 1: Indoor/outdoor O_3 concentration ratios measured during the 2010 February-March campaign in different locations at the two museums and extrapolated average annual indoor O_3 concentrations based on outdoor official data at *Parque Dom Pedro II* station ($[O_3]$ = 14 ppb). The estimated number of years before damage is calculated on the basis of the work of Cass et al. (1989)[8] for a dose of 806400 ppb·h corresponding to 12 weeks at 400 ppb O_3 concentration.

The threshold proposed by Tétreault[36] based on the concept of LOAED (lowest observed adverse effect level) is rather stricter and indicates that the best indoor average ozone concentration (1 ppb, at the paintings storage area of the PE) would guarantee only ten years of minimum damage if RH were kept between 50 and 60%; a result that would cast a gloomy perspective to the other monitored areas, if literally taken.

Undoubtedly, the i/o calculated from the data collected in this campaign are subject to large error due to the fact that just one series of measurement were taken at each site. It seems clear, nonetheless, that the monitoring of the access of outdoor pollutants into the museum should be a preoccupation of these institutions (and in general of museums in this city), as well as the adoption of mitigation measures and means to assess their efficiency.

In this perspective, there is an interest in widening the range of alternatives for monitoring indoor areas in museums, in order to provide not only cheaper options than the automatic equipment employed in this work (which furthermore requires periodic calibration), but also approaches enabling more frequent and simultaneous measurements in different sectors of the same institution. For this reason, passive samplers based on the use of the O_3-sensitive indigo dye were selected as a promising solution and evaluated in the indoor areas of the MP a few months later (Oct-Dec 2010). The more significant results are shown in Figures 6 and 7. In addition to that, Figure 8 presents data on NO_2 monitoring in both museums, also by passive sampling, collected in a separate campaign (Dec 2009-Mar 2010).

The average picture illustrated by Figure 6 indicates that over a total of eleven monitored weeks, the outdoor ozone concentration at the museum is approximately 14% higher than at the site of the official station, as already conjectured. The indoor areas exhibit i/o values of 0.98 (exhibition lower level, average of five weeks), 0.54 (exhibition upper level, average of eleven weeks) and 0.22 (storage west, average of four weeks). The outdoor values used for this evaluation were those obtained from the Environmental Agency network at the *Parque Dom Pedro II* station. Here, apart from the exhibition room at lower level, the passive samplers' data point to a better behaviour of the indoor environments in terms of insulation from the outdoor atmosphere. Now, to this respect, it must be observed that the passive samplers' information is based on an average of different weeks of measurement which do exhibit a certain variability degrees of i/o ratios. This is particularly evident in the graphs of Figure 7 which illustrates the concentrations of O_3

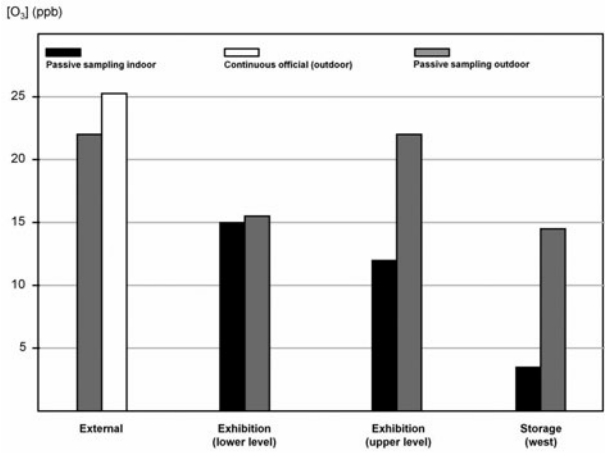

Figure 6: Summary of ozone average concentrations (passive sampling) at the MP and official urban ozone data in nearby station.

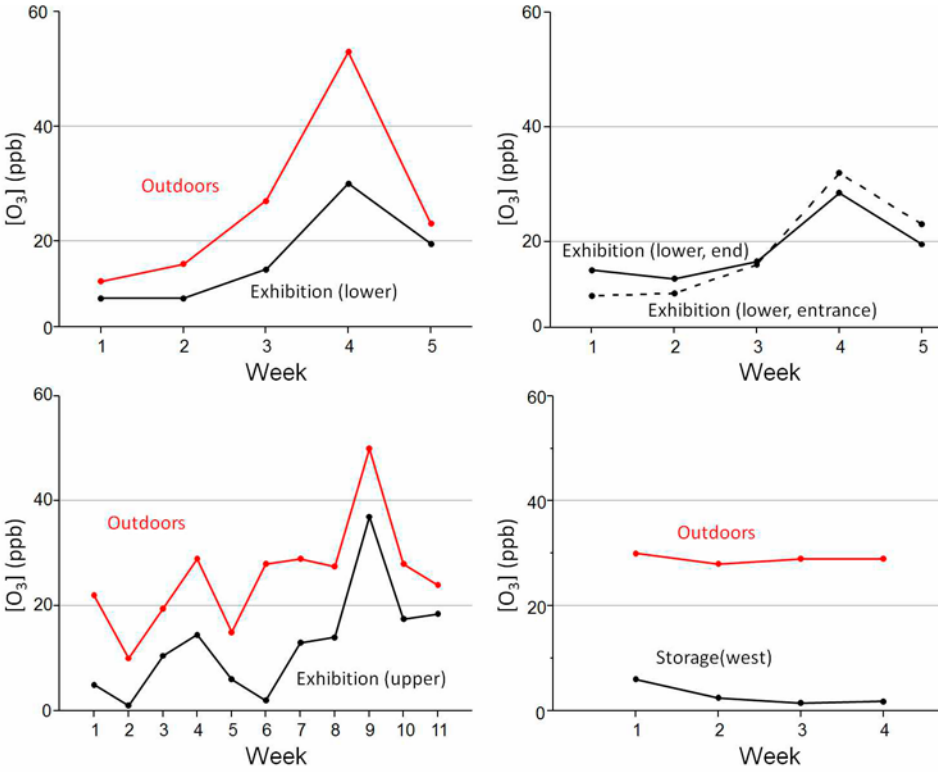

Figure 7 Comparative graphs of ozone average concentrations (passive sampling) in different sampling points at the MP.

measured at the MP indoors and outdoors (unlike Figure 6, in this case the outdoor information refers to measurements carried out by passive sampling immediately outside the museum).

Although all graphs point to similar tendencies in the indoor and outdoor environment (Figure 7), there is a between-week variability in the i/o ratio. This is particularly evident in the case of the lower level exhibition room in the case of weeks 1 and 5 vs. 3 and 4, but to a different degree in perceptible in the other monitored areas. This denotes the fact that ventilation in the several areas of the museum is indeed little controlled, being influenced by a number of factors not necessarily subordinated to a conservation priority, at least not in all rooms.

It must be stressed that the MP has no HVAC system, not least because of legal issues that restrict architectural modifications in the historical building which houses the museum. This implies in the tendency of regulating the indoor climate by naturally enhancing or moderating air exchange with outdoor atmosphere, basically through opening and closing doors and windows. It was observed that this practice is performed by staff persons of different sectors (including cleaning and security) and generally poorly supervised. A further point that should have contributed to the picture above is the fact that measurements were carried out in spring, that is, when the season change favours the alternating occurrence of warmer and cooler weeks.

Finally, Figure 8 presents the results of the NO_2 measurements in both PE and MP by passive sampling, with highlight on the i/o ratios referred to the data of the official monitoring station. Firstly, it can be noted that the NO_2 concentration immediately outside the museums was somewhat lower when compared to official data. This might partly be due to the fact that the monitoring station exhibits one of the highest levels of NO_2 in the whole network with an annual average of approximately 27 ppb (2010). Now, although there might be a certain degree of underestimation in the passive sampling method (that was not hereby quantified, thus making the present discussion only semi-quantitative), it is quite clear that PE is exposed to outdoor levels of NO_2 higher than at MP, a circumstance compatible with the close proximity of the former to a major traffic road. However, the drop in concentration

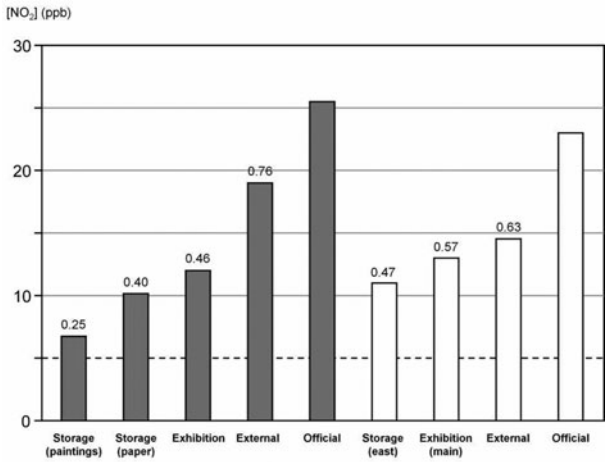

Figure 8: Summary of NO_2 average concentrations (passive sampling) in different sampling points at the PE (grey) and MP (white) and official urban ozone data in nearby station. i/o ratios for indoor locations calculated *versus* the official concentration are highlighted above bars.

between outdoor and indoor atmosphere is more significant in the PE, with reductions of the order of 39 and 67% from external concentrations to exhibition and storage (paintings) areas, respectively, vs. 9 and 25% in the MP for similar sectors. This improved performance of PE moderates the risk associated with the higher levels of this compound in the outdoor environment of this museum, although here, as in the MP, the indoor concentration resulted well above the recommended threshold of 5 ppb in all rooms[36]. This occurred in weeks where (Figure 8) the concentration of NO_2 at the official station was below the annual average of 27 ppb (2010) and, therefore, it is expected to have average levels of this gas above the threshold limit with certain regularity.

In neither case, there were signs of indoor sources of NO_2, hence it is likely that the broader presence of this urban pollutant inside the museums compared to O_3 simply results from its reduced reactivity towards materials.

4 Conclusions

The concentrations of ozone and nitrogen dioxide measured in the indoor areas of the two museums clearly show differences in behaviour between the two buildings and within the same building. Physical barriers seem to contribute to reduce air exchange and, consequently, i/o ratios. However, it is quite evident that, in the light of a substantial outdoor pollution pressure, only efficient air filtration can effectively reduce the indoor concentration of these airborne pollutants to standards considered safe, according to the available literature. Therefore, there should be little doubt about the necessity of this kind of environmental management solution when dealing with valuable collections or collections of objects made of sensitive material.

Yet, it is also clear that, given the extent of outdoor concentrations of pollutants and the fact that indoor environments will always experience deterioration in air quality to some extent, aggravated pollution-related degradation risk is an issue for all institutions involved in conservation in a fast-growing megacity like São Paulo. Owing to this, widespread awareness among all the actors that play a role in the definition and implementation of preventive conservation actions should be the target of increasing efforts.

In this framework, the first step towards the management of indoor air pollution is certainly a thorough understanding of how indoor areas behave against external stress, the dynamics of their performance and the response to mitigative actions. In this sense, the present work has shown that in certain situations simple solutions like the physical segregation of rooms do have a visible effect, even if it might be only partially satisfactory. Furthermore, it could be interesting to relate indoor airborne pollutant concentrations to outdoor levels, especially when – as in the case of São Paulo – real-time data are available.

Air monitoring of selected species by passive sampling is an attractive option for keeping track of the indoor museum performance, though the advantages and potentials of this approach ought always to be weighed against its limitations.

As final remark, it must be observed that the control of indoor areas, though frequently hampered by lack of investments, is especially hard to tackle with due to restraints that go beyond the financial limitation and, in the opinion of many, often concern the general way of thinking conservation and managing human activities inside the museums. The absence of a tradition in conservation science and preventive conservation, the destination of historical, hardly-adaptable buildings for use as museums, bureaucratic internal procedures, poor communication among areas, unsuitable general staff training are some of the issues that should be regarded as preliminary in the approach to the problem.

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