PARTICULATE MATTER IN THE INDOOR ENVIRONMENT OF MUSEUMS IN THE MEGACITY OF SÃO PAULO

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Atmospheric pollutants can have serious impacts on the preservation of São Paulo's tangible cultural heritage. The purpose of this paper is to report the results of a monitoring campaign focussed on particulate matter (PM) that was conducted in three of the most important museums of the São Paulo megacity (Brazil): the *Museu de Arqueologia e Etnologia* (MAE-USP), the *Museu Paulista* (MP-USP), and the *Pinacoteca do Estado de São Paulo* (PE). These museums exhibit indoor PM and black carbon (BC) concentrations consistent with their urban locations and their specific methods for managing the indoor environment.

Keywords: cultural heritage; indoor environment; particulate matter.

INTRODUCTION

In recent years, the scientific community has shown considerable interest in the presence of particulate matter (PM) in the atmosphere and its impact on air quality. This reflects the intensification of concern for a problem that shows no significant sign of improvement. According to the official environmental agency of São Paulo State (Companhia Ambiental do Estado de São Paulo, CETESB),1 in the Metropolitan Area of São Paulo (MASP) "the annual average concentrations of PM_{25} are quite high if compared with the quality standards of the USA or the World Health Organization (WHO). Overdoses have reached levels that are 48% higher than the annual American standard or 100% above the WHO reference value on an annual basis." CETESB also stated that "there is no sign of a reduction trend in the levels of PM_{25} considering that since 2004, that is, over the last four years, the average concentrations remained unaltered." This quote refers to the 2003-2006 period. However, similar figures were confirmed in more recent years at MASP stations that monitor this parameter.²

In general, PM contamination studies focus on outdoor environments where the primary sources of this pollutant are found (vehicular and industrial emissions, soil resuspension). As a result, indoor pollution remains an area of study of relatively minor interest. The composition of indoor air depends on a series of factors, such as the level of atmospheric contamination in the outdoor surroundings, internal sources of contaminants and the processes that govern the transport, physical–chemical transformations and the deposition of substances. In this context, the type of air exchange used and practices for indoor air quality management play a special role.³

This issue requires attention, not only on account of human health considerations, but also with regard to the deterioration of materials. In areas specifically devoted to the preservation of tangible cultural heritage (museums, archives, galleries, libraries, among others), the degradation of artistic and historic artifacts resulting from PM depends on particle size, concentration and composition.^{4,5}

The importance of undestanding the factors that affect PM penetration in indoor environments, its sinks and possible countermeasures were the focus of a 1992 study in which internal sources were also emphasised.⁶ Similarly, Nazaroff *et al.* assessed both indoor and outdoor concentrations of PM, levels of black carbon (BC) and rates of deposition in five California museums.7 According to that study, museums with natural ventilation exhibited fine particulate concentrations almost as high as outdoors, thus highlighting the potential risk of impacts in urban museums without indoor environmental control systems. Similarly, indoor concentrations of BC ranged from 50% to 100% of the outdoor concentrations versus 20% to 50% in buildings with heating, ventilation and air conditioning (HVAC) systems. The circulation of visitors and its role in PM penetration, as well as the effect of meteorological factors, was stressed in a study focussed on the Sainsbury Centre for Visual Arts.8 In London, two museums were assessed in terms of rate of particle deposition on vertical and horizontal surfaces as a function of particle size, temperature (T), relative humidity (RH) and number of visitors.9 Schmidt et al. studied PM concentrations in the National Museum of Copenhagen, a facility located in the city centre and, therefore, surrounded by heavily travelled streets.10 In areas with HVAC systems in place, the rate of PM removal was as high as 98%. However, the study found that the efficiency of removal was lower for fine particles, associated with BC.

The collection of 30 samples from different locations in the Archaeological Museum of Thessaloniki enabled the comparison of indoor fine PM concentrations and with outdoor PM levels.¹¹ According to the authors, the findings point to similar temporal fluctuations in fine PM concentrations inside and outside (I/O ratio) the museum. This is typical of buildings with high rates of air exchange, as is the case where windows are kept open most of the time. A study of the air quality in a historical archive in Milan, Italy, highlighted different tendencies for fine PM accumulation in distinct locations within the building, with underground areas exhibiting higher I/O ratios.¹²

In Brazil, the first comprehensive study of indoor air quality was conducted in 1993 by the *Laboratório de Apoio ao Desenvolvimento Tecnológico* (LADETC), followed by a second phase in 1995-96. The study focussed primarily on the presence of formaldehyde, acetal-dehyde, benzene, toluene and xylenes (BTX) in offices, restaurants, kitchens, museums, schools, libraries, graphic workshops, homes and airports.¹³ Later studies of indoor air quality covered a range of large,¹⁴ medium and small urban centres.¹⁵⁻¹⁷

In Brazil, studies of indoor air quality were conducted in public libraries in São Paulo¹⁶ and Curitiba.¹⁷ In the São Paulo study, average PM_{10} concentrations inside the two libraries ranged from 166.7 to

334.6 μ g m⁻³, whereas the mean value for PM_{2.5} ranged from 132.4 to 303.6 μ g m⁻³. In the outdoor atmosphere, PM₁₀ concentrations were in the range of 129.5-141.9 μ g m⁻³ and PM_{2.5} concentrations were in the range of 101.2-196.6 μ g m⁻³. As a result, I/O ratios were higher than the unity, on average.

With regard to its chemical composition of PM, the coarse fraction tends to be more heterogeneous. However, because it originates primarily from the resuspension of soil particles, it is generally richer in Si, Al, Ca, Mg and Fe, while also incorporating combustion ashes and pollen particles.¹⁸ In the fine mode, sulphate, nitrate, ammonium, some heavy metals, PAHs and BC predominate. BC, a typical marker of combustion processes, is composed of organic and inorganic structures (particularly elemental carbon), and is mainly defined in terms of its optical properties.¹⁹⁻²¹

The literature is unanimous in emphasising that the impact of PM on materials is more specifically associated with fine mode particles. These can cause physical and chemical damage resulting from: i) the catalytic action of heavy metals (e.g. Fe and Mn) in the degradation of organic compounds or by favoring the oxidation of S-rich species into H_2SO_4 ; ii) the presence of substances specifically harmful for materials, as is the case of $(NH_4)_2SO_4$ in the blooming of varnishes; iii) the deposition of hygroscopic material, hence promoting the uptake of water molecules that can accelerate a number of degradation processes (hydrolysis); and iv) the impregnation of fine particles like soiling or ghosting.^{4,5} Furthermore, even when the visual alteration of works of art can be reversed, the repeated action of cleaning triggers decay and is considered a long-term impact.⁴

Owing to the fact that objects exposed or preserved in museums are unique, precious and vulnerable, detailed studies on the microenvironmental conditions of their indoor areas become extremely important for the adoption of preventative conservation measures. Yet, investigations are still quite scarce. With this goal in mind, this paper will illustrate and discuss the results of the monitoring of PM concentrations and its content of black carbon conducted in three important museums located in the municipality of São Paulo, Brazil, São Paulo is the largest and possibly most polluted of Brazilian cities. However, it is perhaps the liveliest in terms of cultural activities and the richest in the quantity of artistic and historic artifacts. Institutions in which monitoring was conducted included the archaeology museum of the University of São Paulo (Museu de Arqueologia e Etnologia MAE-USP), the historical museum Museu Paulista (MP-USP), also part of the University of São Paulo, and Pinacoteca do Estado de São Paulo (PE-SP), one of the richest plastic arts museums in Latin America.

EXPERIMENTAL

Locations

The three museums selected for study are all important institutions for conservation that exhibited substantial differences in location, architecture, type of exposed material, and probable mechanism for the exchange of air between indoor and outdoor environments, and availability of HVAC systems. Two of the museums were also the subject of further measurements of indoor air quality that are reported elsewhere.^{22,23}

The location of the museums within São Paulo and simplified floor plans of each building are shown in Figure 1. It shows the sectors (highlighted with capital letters) within which samplings were conducted. However, because they are multistorey buildings (with the exception of MAE-USP), sampling sites can be more easily identified if the information in Figure 1 is crosschecked with the data in Table 1, which identifies the collection points on each floor. The photographs and satellite images in Figure 2 show more clearly the three buildings, their surroundings and their location within the urban context.



Figure 1. Location of the three museums within the municipality of São Paulo: Pinacoteca do Estado de São Paulo (PE-SP, geographic coordinates: 23°32'03"S, 46°38'02"W), Museu Paulista (MP-USP, 23°35'08"S, 46°36'35"W) and Museu de Arqueologia e Etnologia (MAE-USP, 23°33'35"S, 46°44'28"W). These simplified plans of the museums are presented to scale and with their actual spatial orientation. The black dots indicate the position of the main entrances. In the case of MAE-USP, the grey highlights show the built parts of the museum, with the rest being open-air areas. Capitalised letters indicate the sectors where sampling was conducted (no reference is given in this figure as to the actual floor of each sampling point)

PE-SP is located on *Avenida Tiradentes*, in the city centre, at the southeast corner of *Parque da Luz*, opposite the homonymous railway station. The three-floor building, erected in 1900, has a rectangular base and is oriented in such a way as to have its major sides facing the street on the southeast and the park on the northwest. There are entrances on the two minor sides (the visitor's entrance being the on the south) and several windows, the majority of which remain permanently closed. The central part of the building is comprised of two large patios covered by a glass roof that provides natural light in those areas and a limited degree of air exchange.

Five sampling points were selected (Table 1 and Figure 1): i) a storage room used for paintings (RT 1, sector C, ground floor); ii) a storage room located in close proximity to RT 1, used primarily for paper artifacts, but containing other objects such as sculptures (RT



Figure 2. Photographs and satellite images (from Google Earth, Google Inc.) showing a 1.5 km area around the museums. All images of the three museums are oriented as in Figure 1. From top to bottom: Museu Paulista (view from the northeast), Pinacoteca do Estado de São Paulo (view from the east), and Museu de Arqueologia e Etnografia (view from the southwest)

2, sector C, ground floor); iii) an exhibition room facing the street (*Sala Willys*, EX 1, sector A, second floor); iv) an exhibition room facing the park (*Sala Retratos*, EX 2, sector B, second floor); and v) the balcony (*Belvedere*, EXT, sector C, first floor) facing the street.

With regard to environmental controls, the exhibition areas are acclimatised by means of a fan coil system (Trane) in which outside air is captured at roof level and filtered through polypropylene/nylon membranes, adjusted to the desired T and RH and pumped into the internal galleries. The storage area, where T and RH are precisely controlled by dedicated equipment, receives air from an indoor inlet (exhibition area) and this is subsequently filtered in a fashion similar to other sectors of the museum. All internal rooms are provided with a system of passive exhaust ducts.

The MP-USP is situated inside a park called the Parque da Independência. The park is surrounded by large avenues that connect the city centre with the southeast suburbs. The main edifice is a few hundred metres from these avenues. The building was erected at the end of the 19th century in a sumptuous style, with its main entrance on the north side and large doors and windows all around. The museum consists of four levels: the lower level (basement), ground floor, first floor and second floor. Here, it was possible to carry out sampling at eight points distributed in the museum as follows (Table 1 and Figure 1): three storage areas situated in the central tower (RT 1, sector A; RT 2, sector B; and RT 3, sector B), the latter comprising the textile collection; four exhibition areas (EX 1, sector C) in the mezzanine of the main staircase that leads from the main entrance to the first floor galleries; EX 2, sector A, Sala Rostos e Roupas; EX 3, sector D, Sala Mobiliário; EX 4, sector C, in the lower level); and an external point that corresponds to the external gallery on the first floor facing the park (EXT, sector E).

In the MP-USP, there are no rooms with environmental controls apart from the physical barriers represented by doors and windows. In general, doors (and sometimes windows) are kept open, facilitating the exchange of air between the between indoor and outdoor environments. The storage areas (RT1, RT2 and RT3) are enclosed spaces within corridors that lead to the administrative offices. They have no windows and doors are mostly closed. In RT 3, a fan is kept on permanently to minimise air stagnation.

Constructed in 1989, MAE-USP occupies an area of approximately 12,000 m² on the main campus of the University of São Paulo. The museum consists of two main single-storey areas: the larger one used for administration and storage and a smaller one for permanent exhibitions (Figure 1). The building's immediate surroundings are covered mostly by vegetation; the campus bus parking and the busy *Marginal Pinheiros* are slightly more than 1 km distance.

Five sampling sites were selected at the MAE-USP: i) a point in the middle of the storage area (RT 1, sector B); ii) a point next to the entrance door (RT 2, sector B); iii), a point near the door in the ethnographic exhibition building (EX 1, sector C); iv) a point in the inner part of the ethnographic exhibition building (EX 2, sector D); and v) an outdoor sampling location next to the guard post (EXT, sector E).

The MAE-USP has no air conditioning, but other forms of air circulation exist. In the exhibition area, external air is provided mechanically (without filtration); an exhaust system is provided in the storage sector.

It is worth noting that, following the sampling described in this paper, all three museums underwent some degree of structural alteration (the MAE-USP will soon move to a new building). Therefore, some of the sampling areas described above no longer exist.

Sampling

During the study, 152 samples of fine and coarse PM were collected. A portion of the samples was obtained during the wet season

Points (Floor) Site Description Main Characteristics	Forced Inlet	Air	Forced
		Filters	Exhaust
RT 1 A (0) Storage area (next to the door)	No	No	Yes
RT 2 B (0) Storage area (inner point)	No	No	Yes
MAE-USPEX 1D (0)Exhibition area "África" (inner point)Painted wall, floor covered with syn ber, main exhibit materials: feather	thetic rub- rs, natural Yes	No	No
EX 2 C (0) Exhibition area " <i>Brasil</i> fibres, ceramics, textiles, wood, gla Indígena" (next to the door)	ss, metals Yes	No	No
EXT E (0) Guard post (external)	-	-	-
RT 1 A (+2) Storage area (West) Painted wall, wooden floor, main	exhibit No	No	No
RT 2 B (+2) Storage area (East) materials: paintings, porcelain, woo metals, paper	d, textiles, No	No	No
RT 3B (+2)Storage area (textile)Painted wall, floor covered with syn ber, main exhibit materials: tex	thetic rub- No	No	No
EX 1 C (+1) Main staircase Painted walls, floor covered with tiles, main exhibit materials: metal, marble	ceramic paintings, No	No	No
EX 2 A (+1) Exhibition area "Sala Rostos e Roupas" Painted wall, wooden floor, main	exhibit No	No	No
EX 3 D (+1) Exhibition area "Sala metals, paper materials. Paintings, porcerain, woo	No	No	No
EX 4 C (-1) Lower level exhibition area Painted wall, wooden floor, main materials: paintings, porcelain, s	exhibit No metals	No	No
EXT E (+1) Open-air gallery (external) -	-	-	-
RT 1 C (0) Storage area (paintings) Painted wall, granite floor, main extra rials: paintings	nibit mate-Yes	Yes	No
RT 2 C (0) Storage area (paper) Painted wall, granite floor, main extra rials: paintings, metal, chalk, p	nibit mate-Yes	Yes	No
PE-SP EX 1 A (+2) Exhibition area "Sala Wyllis" Painted wall, carpeted floor, main materials: paintings, metal	s exhibit Yes	Yes	No
EX 2 B (+2) Exhibition area "Sala Retratos" Painted wall, carpeted floor, main materials: paintings, metal	s exhibit Yes	Yes	No
EXT C (+1) Balcony Belvedere (external) -	-	-	-

Table 1. Sampling Sites: Location and Characteristics

*For the sectors codes, see Figure 1 (in brackets, the floor level in relation to entrance level).

(December 2008 to February 2009, and November 2009). Other samples were obtained during the dry season (April 2009 to September 2009). Sampling was carried out randomly from Monday through Friday. Sampling on Mondays, the day on which all the museums are closed, was not expected to bias the sampling results in the exhibition areas because visitor volume on weekdays is not particularly high. Furthermore, on days off there are always a number of maintenance activities that involve the circulation of a substantial number of people and the opening of doors and windows in all the rooms.

The PM sampling was performed using a lab-made Low Volume Sampler (Mini-Vol), developed and assembled according to the design proposed by Hopke *et al.*.²⁴

The equipment has two units: pumping and inlet/sampling. A pump is comprised of a diaphragm pump (Gast, model DOA V722-AA), a valve for coarse flow control, a rotameter (Dywer, model MMA, 5-25 L min⁻¹ range) and a conventional hourmeter. Inlet/sampling includes a PVC/polyethylene impactor and a polycarbonate stacked filter unit. The impactor, which restricts the access of particles with diameter larger than 10 μ m, was lathe-turned in accordance with the original design. The filter unit, acquired from the Norwegian Institute for Air Research (NILU, Norway), supports two stacked 47-mm membranes (polycarbonate IsoporeTM Membrane Filters), with porosity of 8 μ m (collecting the coarse mode, i.e. 8–10 μ m particles) and 0.4 μ m (collecting the fine mode, i.e. 0.4–8 μ m particles). Each round of sampling was performed for 24 hours at

a flow rate of 18 L min⁻¹ with the inlet mounted on a 1.60 m-high tripod. Some measurements in PE-SP and MAE-USP were carried out with an automatic DustTrak Aerosol Monitor (TSI Inc., USA) provided with a PM_{10} impactor kit.

Quantification

PM concentrations were obtained by relating the amount of collected material, determined by gravimetry, and the volume of air aspirated over the entire sampling time. The gravimetry procedure involved measuring the mass of the polycarbonate membranes before and after sampling, after the acclimatisation of filters for 24 h at 22 °C e 42% RH, on plastic petri dishes. Weighing was performed in triplicate on a balance with a readability of 1 μ m (Mettler Toledo, MX5 model).

The quantification of BC was obtained using a Smoke Stain Reflectometer (Diffusion Systems Model M43D) following a well--established methodology.²⁵

RESULTS AND DISCUSSIONS

The results of the sampling program conducted in the three museums are reported in Table 2 and illustrated, in terms of average PM concentration in the fine and coarse modes, in Figure 3. When considering these data, it must be stressed that the number of indoor

Table 2. Summary of the PM concentrations, indoors and outdoors at the three museums: number of samples (n); standard deviation (sd); mean; n	median;
respective ratios between average indoor and outdoor values; (I/O); maximum concentration (max.); minimum concentration (min.); BC mean concent	trations
and mass percentage contribution for PM	

	MAE-USP					MP-	USP		PE-SP			
	Fine		Coarse		Fine		Coarse		Fine		Coarse	
	In.	Out.	In.	Out.	In.	Out.	In.	Out.	In.	Out.	In.	Out.
n	19	5	19	5	28	4	28	4	16	4	16	4
sd (µg m-3)	1.7	1.4	4.8	6.2	2.4	3.0	3.2	2.8	2.6	2.3	2.3	9.4
Mean (µg m-3)	3.5	6.2	5.1	13	5.8	6.8	5.4	7.4	5.1	8.4	3.6	21
I/O	0.56		0.39		0.85		0.72		0.61		0.17	
Median (µg m-3)	3.0	6.2	3.8	9.4	5.8	7.2	5.0	7.4	4.6	8.7	3.7	22
I/O	0.48		0.41		0.80		0.67		0.53		0.17	
Max (µg m ⁻³)	5.9	8.1	20	25	11	10	15	11	12	11	7.8	30
Min (µg m ⁻³)	1.2	4.0	0.80	8.4	1.4	2.5	1.0	3.8	1.9	5.0	0.40	7.8
BC (µg m ⁻³)	0.8	1.5	0.20	0.40	1.3	1.5	0.20	0.30	1.1	1.9	0.20	0.80
BC (%)	23	24	4.0	3.0	23	22	4.0	3.0	21	23	6.0	4.0

samples was, as a rule, quite larger than that of the outdoor samples. This is because the focus of the investigation was on the indoor microenvironments and there was a specific interest in mapping differences in distinct areas of each museum. However, in every museum the outdoor atmosphere was sampled for the same number of days as each individual indoor room (the only exception being RT2 in MAE that was monitored over four days *versus* five days for the outdoor environment), so that every group of data was equally representative of one type of environment in statistical terms.

The PE-SP had the highest outdoor contribution of PM (particularly the coarse mode, with an average concentration of 20.6 μ g m⁻³). This is attributable to the museum's close proximity to primary sources of PM, mainly car and motorcycles (burning petrol and ethanol), and buses and lorries (burning diesel). The MAE-USP ranked second in PM concentrations, exhibiting an average of 13.1 µg m⁻³. It must be remembered that the external measurements at the MAE-USP were taken just outside the main building, at ground level and at a few metres distance from the parking area. This, together with the proximity to the university's bus depot just behind the museum, should explain the somewhat higher level of PM_a at that location. The MP-USP, on the other hand, displayed lower outdoor PM_e concentrations (average of $7.4 \,\mu\text{g}\,\text{m}^{-3}$, half the MAE-USP outdoor levels). The outdoor PM_c values of standard deviation, maximum and minimum concentrations of 2.8, 11.1 and 3.8 µg m⁻³, respectively, did not differ significantly from the PM_f concentrations at the MP-USP. Unlike the other two museums (Table 2 and Figure 3), this data reflect stable environment conditions. This is likely due to the fact that at the MP-USP, the measurements were taken directly outside the museum and the park around the building served as a buffer zone, at least for the PM.

For PM_r, the concentrations varied within narrower intervals, with averages ranging from 6.2 (MAE-USP) to 8.4 (PE-SP) μ g m⁻³, minima from 2.5 (MP-USP) to 5.0 (PE-SP) μ g m⁻³ and maxima from 8.1 (MAE-SP) to 11.0 (PE-SP) μ g m⁻³. This indicated, again, the least favorable conditions outside the PE-SP. These results are perfectly compatible with the fact that indoor PM_r concentrations are less influenced by variables like traffic intensity and meteorological conditions, as already observed in a recent review on this topic.⁴

It is interesting to note that, in all the external measurements, the PM_{10} concentrations (sum of fine and coarse modes, also denominated inhalable particles) were significantly below the thresholds defined in the air quality standard (150 µg m⁻³) for PM_{10}^2 . They exhibited average, minimum and maximum figures of 20.7, 6.3 and 41.1 µg m⁻³, respectively. These values were not fully representative of the bulky outdoor concentration of PM_{10} in the in the São Paulo city centre. For



Figure 3. Fine (PM_f) and coarse (PM_c) particle material mass concentrations (average and standard deviation) in the three monitored museums from December 2008 to November 2009

example, at the Faculty of Medicine of USP in the central area of the town, Castanho recorded PM₁₀ average concentrations of 77 µg m⁻³ in winter and 32 µg m⁻³ in summer by using a Tapered Oscillating Monitor (TEOM).²⁵ Bourotte et al. confirmed similar levels using the methodology employed in this study, with an average winter PM₁₀ concentration of 62.7 µg m^{-3.26} Also, according to CETESB²⁷, the average annual concentrations of PM_{10} in 2009 were 32 and 34 µg m-3, respectively, at the Pinheiros and Parque Dom Pedro air quality monitoring stations. These stations were the closest to the three museums. On the other hand, some nonsystematic measurements were performed with the automatic DustTrack instrument at peak hours at the external sampling points of MAE-USP (on 3/3/10, for 15 min) and PE-SP (on 1/3/10, and 4/3/10, for 10 min). Those measurements provided PM₁₀ concentrations of, respectively, 15 23 and 55 µg m⁻³ that were consistent with the averages reported in Table 2. This means that, although some underestimation of PM₁₀ concentrations provided by the sampling device is quite likely, the external values generated were affected by a certain degree of abatement in PM concentration that took place between the source area (vehicular traffic) and the sampling points. These were located either distant from primary sources (MP-USP) or in locations that provided, to some extent, sheltering or reduced access by particles. Nonetheless, what should be considered is the actual concentration in the immediate vicinity of each museum.

Table 3 shows average PM concentrations (fine and coarse modes) measured in all indoor areas of the two museums in the dry and wet seasons, as well as rainy and nonrainy days (information retrieved from the authors' own records, corroborated by the literature).²⁷

To demonstrate how the data is representative, the number of samples (n) used for the calculation of each average is also reported.

The data shows that, at MAE-USP, the change from the wet to dry season provoked an overall increase in both PM_f and PM_e , consistent with the worsening of urban air quality. The fact that three of the wet-season measurements were taken during holidays, when visitation and vehicle traffic around the museum is reduced, may contribute to the difference in average values. In fact, if those three values are excluded from the calculation, the difference in PM_e between the wet season and dry season falls from +30% to +4%. As for the effect of atmospheric precipitation, which is expected to wash PM from the air, the results indicate again that the indoor area is quite strongly affected by the outdoor particulate concentration, particularly the coarse mode that experiences a 50% decrease on rainy days *versus* a 37% reduction recorded for PM_f.

Despite the larger amount of measurements, the situation at the MP-USP, is less clear because of the broader variety of indoor environments sampled. The change of season is evident in the increase of mean PM_c concentration (+26%), but has no marked effect on PM_r . On the other hand, the decrease in rainfall does have an impact on PM_r (+9%) and almost no effect on PM_c . This observation and the fact that all the wet-season measurements were taken during holidays when this museum receives far less visitors (mainly students), appears

to indicate that the presence of larger particles are less influenced by changes in outdoor atmospheric PM concentration and more by the movement of people in the exhibition areas, as will be further described below.

Conditions at the PE-SP can only be analysed in terms of wet and dry season because the number of samples obtained on rainy days is limited to two. This was considered insufficient for a reliable assessment. Here, the differences between PM concentration at the beginning of the wet and dry seasons amount to decreases on the order of -5% (PM_c) and -18% (PM_t), notwithstanding the fact that, over the last years, average PM₁₀ in São Paulo has been 22% higher in April/May than in November.²⁷

This occurrence can be explained by the combination of three effects: the close proximity of the museum to the primary source of both coarse and fine PM; sampling periods corresponding to the transitional rather than full seasons; and the existence of an environmental control system in the PE-SP. The first two effects imply that atmospheric conditions typical of the dry season, which tend to favour the accumulation of pollutants in the urban context (thermic inversions and overall reduced precipitation events and intensity), were less significant in the case of the indoor area of the PE-SP. Data from CETESB²⁷ confirm that, of the wet season days when the measurements were taken (November 3rd, 4th, 5th, 9th, 10th and 11th, 2009), there was rain only on 11/9/2009. Therefore, substantial differences in the data between the two periods would not be expected. On the other hand, one should consider that with a centralised HVAC system for the control of the indoor environment and the increase in outdoor temperature and relative humidity, the flow of air from outdoors in November is likely to be artificially intensified in relation to natural ventilation, and possibly stronger in April/May. Furthermore, enhanced mechanical air mixing in a partially enclosed environment is expected to maintain suspended particles to a greater extent, an aspect particularly supported by Nazaroff et al.7 and Camuffo et al.28 The more distinct increase of PM_f in November, as opposed to April/May, is consistent with this view since various authors agree that filtration in conventional air conditioning systems is not sufficient to retain fine particulate matter.4,7,17,28

With regard to indoor concentrations, Table 2 presents a general picture of the overall efficiency of each museum in terms of average indoor/outdoor concentration ratio (I/O). In contrast, Figure 3 highlights differences between separate areas in each building. In the PE-SP, the I/O ratios were 0.17 (PM_c) and 0.61 (PM_r), with better performance in the two storage rooms and the exhibition sector located on the park side of the building. These results show that, in the PE-SP, the more isolated the areas (storage, where inlet air was sucked from indoors) or more distant from the main street (exhibition west, less exposed to the direct influence of vehicular traffic), the more successful the reduction of PM_f concentrations. Yet, fine mode particles were not addressed with equal efficiency and, in fact, the average PM_f concentrations outside the building, or even slightly higher (Figure 3). In almost all

Table 3. Average PM concentration (µg m⁻³) in the fine and coarse fraction in samples (n) collected during the wet season (WS) and dry season (DS) in MAE--USP (Dec-Feb, Aug-Sep), MP-USP (Jan, May) and PE-SP (Apr-May, Nov) and measured in rainy (R) and non rainy days (NR) in both seasons

	MAE	E-USP			MP-	USP		PE-SP				
Fine Coarse		Fi	ne	Co	arse	Fi	ine	Coarse				
WS (n=11)	DS (n=8)	WS (n=11)	DS (n=8)	WS (n=14)	DS (n=14)	WS (n=14)	DS (n=14)	WS (n=8)	DS (n=8)	WS (n=8)	DS (n=8)	
3.1	3.9	4.5	5.9	5.8	5.7	4.7	6.0	5.6	4.6	3.7	3.5	
R (n=8)	NR (n=11)	R (n=8)	NR (n=11)	R (n=15)	NR (n=13)	R (n=15)	NR (n=13)	R (n=2)	NR (n=14)	R (n=2)	NR (n=14)	
2.9	3.9	4.0	5.9	5.6	6.1	5.4	5.3	2.6	5.4	0.75	4.0	

cases, with exception of RT2, PM_f had higher concentrations than PM_c . This fact might be ascribed to the use of air filters that were only effective against larger particles, whereas finer particles could enter the museum through both improperly sealed doors and windows and the filters themselves. Furthermore, leakage of air though cracks in the building should not be disregarded in the case of particles in the 1–5 µm diameter range and where the optimum penetration efficiency/ deposition velocity ratio was reached.⁴

In the MP-USP, although the external contribution of PM was significantly reduced compared to the PE-SP, the I/O (0.72 and 0.86) was considerably less favorable. The vulnerability of the MP-USP to outdoor factors such of temperature and humidity, solar light and airborne pollutants has already been highlighted and discussed in earlier papers.^{22,23} In the case of PM, it is worth observing that fine particles tend to penetrate inside the museum with enhanced ability, being more concentrated than coarse particles in all areas. Exceptions were the main staircase point (EX1), where the large volume of visitors certainly contributed to the resuspension of PM, and the lower level gallery (EX4) that probably suffered from its proximity to larger particles in suspended soil. The difference between the two first floor exhibition rooms follows the same pattern, particularly with lower PM_f in EX2 (Roupas e Rostos) than in EX3 (Mobiliário). This difference is likely due to a door and a window facing the open-air terrace that are normally kept open EX2, whereas EX3 is linked to another indoor area and is maintained with doors and windows permanently closed. Fine particles were almost as concentrated in the storage rooms as in the outdoor atmosphere, although with coarse particles at the lowest indoor levels. A drop in PM_f level was observed in RT3 (textile storage room), where constant mechanical ventilation was used as a form of environmental management. This positive result is consistent with previous observational and modeling studies that conclude it is an efficient way to address indoor PM₆.⁷

In the MAE-USP, indoor contamination from PM was associated more with the coarse mode. This was possibly due to much larger outdoor concentrations of this PM fraction (twice more concentrated than fine faction) and to the fact that the entire museum is located at ground level, thus receiving larger contributions of suspended particles. The fact that fresh air was injected into the exhibition area without filtering should further affect PM concentrations in this sector. Interestingly, the fact that housekeeping personnel conduct intensive cleaning does not appear to positively affect the levels of coarse PM in this area. In the storage area, an exhaust system is installed, which is likely to explain a somewhat lower overall concentration of the two PM modes. It should be observed that the larger average coarse concentration in RT2 was outweighed by the fact that one of the measurements occurred on a day on which general house cleaning was conducted. This involved access by a somewhat larger number of staff, the movement of furniture and objects, vacuuming and dusting. This likely caused the resuspension of an unusual quantity of coarse PM. The concentration was maintained, but induced a larger standard deviation within this set of data. Its exclusion would result in the reduction of the average PM_c from 6.30 to 2.82 µg m⁻³, which is lower than RT1 (3.97 µg m⁻³). This is a reasonable result if one considers that the exhaust system should be more efficient in this part of the storage room (inner section) than close to the door (RT1).

Figures 4 and 5 and Table 2 show the concentration of BC in both fine and coarse mode particles. To minimise the effect of potential outliers that were identified among the concentration values, the BC data were clustered in three categories: external concentrations, exhibition areas and storage rooms. The suspect concentrations were not eliminated. However, a simulation (not shown) confirmed that their exclusion would not qualitatively alter the scenario illustrated in Figures 4 and 5. In absolute terms, the BC concentrations followed the same patterns as the overall PM concentrations, with always larger levels in the outdoor environment, followed by the exhibition areas (generally more exposed to the outdoor environment) and finally the storage areas. The average indoor PM_f concentrations ranged from 0.57 (RT-MAE-USP) to 1.36 μ g m⁻³ (EX-MP-USP). That is, levels comparable with previous published concentrations in this field can be regarded as intermediate.^{7,29} The MP-USP exhibited distinct characteristics with the highest BC concentrations in the storage area than the exhibition area, but consistent with trends in the overall levels of PM.

As expected, BC is found at higher concentrations in fine PM, consistent with the fact that they were generated by fossil fuel combustion, possibly with a significant contribution of diesel-based engines. Although data on PM smaller than 2.5 μ m are not available, BC concentrations of smaller particles are expected to be even higher according to well-established literature information.^{4,7,28}

In relative terms, BC represented 23% of the overall mass concentration of PM_f and 3% of PM_c in the outdoor environment, essentially



Figure 4. Average and standard deviation Black Carbon (BC) concentrations in fine and coarse PM in the three museums, from December 2008 to November 2009



Figure 5. Mass percentage contribution of Black Carbon (BC) in fine and coarse PM

with no difference among the three sites. This is in agreement with literature data, although the sampling point in this case was particularly important.^{21,25} On average, indoor proportions do not deviate from these values, although Figure 5 shows interesting enrichment for PM_f in the storage areas of the PE-SP and MP-USP apart from almost all cases of PM_c. This may be due to the fact that, in the PE-SP, the filtration system was indeed effective in reducing overall PM concentrations in the inner parts of the museum. However, efficiency was reduced in the case of BC particles, possibly because of their reduced dimensions that make them less prone to retention in filtering membranes. BC particles are particularly more concentrated in the finer fractions of PM. In this respect, Worobiec et al. confirmed in a previous study at the Wawel Castle in Crakow, Poland, that BC was more abundant in the fine fraction in winter and the most internal part of the building (45% in 2nd floor rooms vs. 34% outside, 27% on the 1st floor and 13% on the ground floor); when air circulation was enhanced, the BC variations followed that of the PM concentrations.30 In the MP-USP, the proportion of BC in the storage area was the same as outdoor PM. However, it dropped in the exhibition rooms, likely because of the greater contribution of larger noncarbonaceous particles at lower levels in the building. That is, the proportion of BC seems to increase in areas where some kind of restriction to access by PM was promoted (unless specific measures for very fine BC particles were implemented) and where typical resuspension particles became less abundant.

CONCLUSION

This study addressed the distribution of PM concentrations in the indoor environment of three of the most important Brazilian museums. The overall levels of particles in exhibition and storage areas, although always significantly below the safety standards defined for the human population, exceeded the threshold for safe conservation (10 µg m⁻³ in stores and archives) in 46% of all measurements. Of those, 76% were in the exhibition rooms and 28% were in the storage areas.³¹ The current safety guidelines for cultural heritage are based on an estimate of the time it will take, under average environmental conditions, for some degradation to be observed. For example, Tétreault estimated that 10 μ g m⁻³ is the maximum concentration of PM_{2.5} for a preservation target of one year before the appearance of the lowest observed adverse effects.32 In this sense, the lowest level of aggressive airborne pollutants, including PM, should always be the goal in order to guarantee the longest life time of a valuable artifact and to reduce the drawbacks and economic costs associated with recurrent interventions. This implies a continuous and organised deployment of efforts to characterise microenvironments in a museum or any other conservation institution. Along with a thorough understanding of all the factors governing the presence of harmful species in the indoor atmosphere and their effects on materials, the conservation scientist should contribute to strategic planning and decision-making for the protection of indoor air quality and preventive approaches to conservation.

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