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# Indoor air quality of a museum in a subtropical climate: The Oscar Niemeyer museum in Curitiba, Brazil

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## HIGHLIGHTS

• Analysis of compounds that participate in reactions that damage artwork surfaces.

Aim: assess damage to artwork caused by pollution in hot and humid environments.

• MON has satisfactory air quality when compared to other international museums.

• The situation could improve by using higher efficiency filters in the HVAC system.

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# ABSTRACT

The assessment of damage to indoor cultural heritage, in particular by pollutants, is nowadays a major and growing concern for curators and conservators. Nevertheless, although many museums have been widely investigated in Europe, the effects of particulate matter and gaseous pollutants in museums under tropical and subtropical climates and with different economic realities are still unclear. An important portion of the world's cultural heritage is currently in tropical countries where both human and financial resources for preserving museum collections are limited. Hence, our aim is to assess the damage that can be caused to the artwork by pollution in hot and humid environments, where air quality and microclimatic condition differences can cause deterioration. As a case study, particulate matter as well as gases were collected at the Oscar Niemeyer Museum (MON) in Curitiba, Brazil, where large modern and contemporary works of art are displayed.

NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, Acetic Acid, Formic Acids and BTEX, in the ambient air, were sampled by means of passive diffusive sampling and their concentrations were determined by IC or GC–MS.

The particulate matter was collected in bulk form and analyzed with the use of energy dispersive X-ray fluorescence and aethalometer. The chemical compositions of individual particles were quantitatively elucidated, including low-Z components like C, N and O, as well as higher-Z elements, using automated electron probe microanalysis. The gaseous and particulate matter levels were then compared with the concentrations obtained for the same pollutants in other museums, located in places with different climates, and with some reference values provided by international cultural heritage conservation centers. Results are interpreted separately and as a whole with the specific aim of identifying compounds that could contribute to the chemical reactions taking place on the surfaces of artifacts and which could potentially cause irreversible damage to the artworks.

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# 1. Introduction

The global warming threats can intensify the synergisms between climate and urban air pollution, especially in large parts of South America, where the high humidity and air pollution are a reality. An important

\* Corresponding author. Tel.: +55 41 88569504. E-mail address: rhmgodoi@ufpr.br (R.H.M. Godoi). portion of the world's cultural heritage resides in tropical and subtropical regions, where both human and financial resources for preserving museum collections are limited. Although many museums have been widely investigated in Europe and the United States (Camuffo et al., 1999, 2001; Godoi et al., 2006a, 2008; Kontozova-Deutsch et al., 2008, 2011a, b; Ionescu et al., 2012), studies of the presence and effects of particulate matter and gaseous pollutants in museums of developing countries with non-temperate climates and with different economic realities are still

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lacking. Besides these "longitudinal" threats, physical, biological and chemical factors as pollution and its synergism should be considered in the sense of preservation.

The conservation of typical collections such as woods, papers, leathers, among others, is directly related to the indoor environment of the museums, and it is especially sensitive to high levels of temperature and relative humidity (Brimblecombe et al., 1999; Camuffo et al., 1999; Bencs et al., 2007; Cappitelli et al., 2009; Kontozova-Deutsch et al., 2011a,b; Lankester and Brimblecombe, 2012). When the relative humidity (RH) is high, chemical reactions may increase, just as when temperature is elevated. Many chemical reactions require water; so at high RH, chemical deterioration can proceed more rapidly. High humidity also supports biological activity; for instance, mold growth is more likely as RH rises above 65%, as well as the insect activity (Lefevre, 1974).

For artwork, the best environment is a climatically stable one, where there is only slight variation in temperature and RH and where the air pollution concentration is sufficiently low. The synergism between pollutants, temperature and/or humidity can swell/shrink objects, and the results are destructive (Brimblecombe et al., 1999; Camuffo et al., 1999). The effect is noteworthy because paint might crack on a canvas or pop off from a painted object, wooden veneers might peel away, glued joints on wooden furniture might fail, and wooden objects might be permanently warped (Bratasz et al., 2007).

Looking at the air pollution indoors, where the most vulnerable artworks are stored, it is important to focus on components that have a potential deterioration effect such as some gases (e.g., NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>), particulate matter (PM) including black carbon (BC) (Kontozova-Deutsch et al., 2008). More recently, organic acids as acetic and formic acids (HAc and HFor), as well as volatile organic compounds, like benzene, toluene, ethylbenzene and xylenes (BTEX), have also been considered due to their damage potential (Schieweck et al., 2005; Godoi et al., 2008). These species are also important facing the manifold sources of organic and inorganic pollutants in the indoor environment of museums.

Therefore, this research was conducted to fill this gap in a subtropical climate, by first dealing with the characterization of the indoor air quality of the Oscar Niemeyer Museum (MON) in Curitiba, south of Brazil. Although some specific pollutants have been measured in a few Brazilian museums (Grosjean et al., 1990; Druzik et al., 1990; Costa, 2003; Cavicchioli et al., 2012), to the authors' knowledge, this is the first time that a detailed survey of gases and aerosol pollution has been done systematically in a Brazilian museum.

## 2. Material and methods

#### 2.1. Measurement site

The MON in Curitiba, Brazil, is a modern concrete structure divided essentially in two buildings. The main building is a regular construction, semi-open, adapted to house the art collections in ten exhibit rooms. The modern area of the MON has one tower called "The Eye", designed by the famous architect Oscar Niemeyer, in which is located the museum's major exhibit room. An underground tunnel connects both structures. Almost all parts of the museum are equipped with heating, ventilation and air conditioning systems (HVAC). Besides its own collection of about 2000 pieces of modern and contemporary art, the MON receives art expositions from others Brazilians states, as well as from different parts of the world. Fig. 1 shows the façade of the MON building.

#### 2.2. Sampling and instrumentation

The sampling was carried out at MON in two periods of one week. During the first week, from 30 July to 6 August 2007, the exhibition room of "The Eye" was monitored. This period is in the austral winter when pollutants tend to be mostly concentrated in the atmospheric boundary layer, therefore a critical period for the city air quality. During this week, samples for bulk and individual particle analysis, BC and gases such as SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>, HAc, HFor and BTEX were collected. During the second week, from 20 to 27 August 2007, exhibit rooms from the main building were monitored. During this week, samples of BC and gaseous pollutants such as HAc, HFor and BTEX were collected (IAP, 2008).

The HVAC system is operational throughout the building. The main thermohygrometric parameters analyzed (day and night) were air temperature (T) and RH measured with automatic data loggers.

Aerosol particles for bulk analysis were collected on Nuclepore membranes using a stacked filter unit, with 24 h sampling time and a flow rate of 35 L min<sup>-1</sup>. Information concerning the bulk elemental concentration is provided by energy-dispersive X-ray fluorescence (EDXRF). The measurements of total PM were performed on an Epsilon-5 (PANalytical, Almelo, The Netherlands) high-energy polarized-beam (HE-P) EDXRF instrument having a three-dimensional polarizing geometry with 13 secondary targets (W, CeO<sub>2</sub>, CsI, Ag, Mo, Zr, KBr, Ge, Co, Fe, Ti, CaF<sub>2</sub>, Al) and two Barkla scatter targets (B<sub>4</sub>C and Al<sub>2</sub>O<sub>3</sub>). The X-ray characteristic radiation was detected by a Ge detector (PAN 32) with a full-width at half-maximum (FWHM) resolution of 165 eV, performing non-destructive quantitative analysis of elements, starting from Al.

Microanalysis is a very useful technique to identify the simultaneous presence of particular elements in an individual particle, which allows a better discrimination between specific particle types. In the present research, an electron probe microanalysis method, called low-Z EPMA, is applied to characterize quantitatively the composition of individual particles, including low-Z components like C, N and O, as well as higher-Z elements using a common EPMA unit (Godoi et al., 2004, 2006a,b; Avigo et al., 2008). For EPMA, aerosol particles were sampled on Ag foil using two stages of a May cascade impactor, with aerodynamic diameters ranging from 0.5 to 2.0 µm and from 2.0 to 8.0 µm for stages 6-4 and 4-2, respectively, at a 20 L/min sampling flow to separate primarily the size fractions of interest. Low-Z EPMA was performed on a JEOL (Tokyo, Japan) 733 EPMA unit equipped with an Oxford detector with an atmospheric ultra-thin window of 0.2 µm. An accelerating voltage of 10 kV, a beam current of 1.0 nA and a measuring time of 20 s were used. In order to avoid additional absorption and spectral interference, no conductive coating was applied on the samples. It was possible to cool the sample stage to liquid-nitrogen temperature (about -196 °C), which mitigated beam damage to the sample. Computercontrolled X-ray data acquisition for individual particles was carried out automatically in point analysis mode, i.e. the electron beam was focused on the center of each particle, and X-rays were acquired while



Fig. 1. Façade of the Oscar Niemeyer Museum (MON), in Curitiba, Brazil.

the beam remained fixed on this single spot. The data from these estimated X-rays were used as input parameters for the quantification procedure. Approximately 400 particles were measured in each stage, so in this way almost 800 individual aerosol particles were analyzed in one sample set; in total, the complete analysis included more than 4000 particles. Carbonaceous particles can be separated in three different groups of species: biogenic, soot and organic particles (Godoi et al., 2004). Particles are identified to be biogenic when the concentrations of C and O are similar and they also contain some N, P and/or S contents (>10 % wt), which are characteristic elements for biogenic species. When C content is about three times higher than the O content (or more), the particle is identified as soot. Particles are considered to be organic when they do not match the criteria above for biogenic or soot particles. Organic particles can act as a medium for the adsorption and incorporation of damaging gases, such as SO<sub>2</sub>, and allow them to participate in a possible weathering process. Particles were identified as  $CaCO_3$  when the stoichiometry ratio of Ca, O and C was kept > 70 % wt; similarly, particles with more than 70 % wt of Ca, O and S were identified as CaSO<sub>4</sub>. Particles with high sulfur content, more than 70 % wt, were identified as S-rich. If these particles have 10-15% of Cl, the particle was classified as S-Cl-rich. Particles that contain more than 50 % wt of Cl are considered as Cl-rich particles. Fe-containing particles are also encountered and two different types of Fe-containing particles were identified: Fe<sub>2</sub>O<sub>3</sub> and Fe metal. Most of Fe metal particles contain 70-80% of Fe with some C and O, due to surface oxidation. In this work, all Fe-containing particles are denoted by "FeO". Many distinctive particle types were identified, according to their chemical composition. Since this technique can determine the chemical species at least semiquantitatively, some individual particles were identified as internal mixture particles, which are composed of two or more chemical species. However, it is somewhat difficult to clearly determine if particles are composed of only one chemical species or more, especially for aluminosilicate species. These types of particles were identified as mixed.

The gaseous compounds BTEX, SO<sub>2</sub>, NO<sub>2</sub>, HAc, and HFor were sampled on two types of cartridges in parallel and continuously (24 h for seven consecutive days) by means of radiello® diffusive passive samplers from Fondazione Salvatore Maugeri (Padova, Italy). The adsorbing cartridges for BTEX consist of 60 mm length stainless steel net cylinders, with 100 mesh grid opening and 5.8 mm diameter, packed with  $530 \pm 30$  mg of activated charcoal with a particle size of 35–50 mesh (Cocheo et al., 1996). For O<sub>3</sub>, the samplers are chemiadsorbing cartridges, consisting of a microporous polyethylene cylinder (5.8 mm diameter, 60 mm height), impregnated with triethanolamine (Campos et al., 2010).

After desorption with carbon disulfide ( $CS_2$ ), BTEX were analyzed with a gas chromatograph (Varian GC–MS, Walnut Creek, CA, USA). The analytical methodology can be found elsewhere (Godoi et al., 2009). SO<sub>2</sub>, NO<sub>2</sub>, HAc, and HFor were determined by means of ion chromatography (dual column Dionex DX-120), with conditions previously established (Stranger et al., 2009). Ozone was sampled using homemade analyzed by ion chromatography as stated by Campos et al. (2010). BC was monitored by an aethalometer (Magee Scientific, model Ae-10) (Hansen and Schnell, 1991; IPCC, 2001). Table 1 describes the locations, the type of analysis done and the date/duration of the samplings performed.

# 3. Results and discussions

Comparing the mean temperature and humidity values obtained at MON to values obtained by studies in other museums, one may observe that the mean temperatures ("Eye" building: 18 °C, Room 1: 18 °C, Room 2: 18 °C, Room 3: 19 °C) are similar to the ones obtained in sampling campaigns performed in winter time in different museums, as the Correr Museum (CM), Italy, with a mean temperature of 15.3 °C (Camuffo et al., 1999), the Kunsthistorisches Museum (KHM), Austria, 19 °C (Camuffo et al., 2001), the Sainsbury Centre for Visual Arts (SCVA), England, 20 °C (Brimblecombe et al., 1999) and of the Royal Museum of Fine

Arts (RMFA), Belgium, with a mean temperature of 21 °C (Gysels et al., 2004). However, when comparing the mean RH rates (MON: "Eye": 68%, Room 1: 62%, Room 2: 62%, Room 3: 59%) to the ones obtained in the European museums (CM: 41%, KHM: 60%, SCVA: 45%, RMFA: 40%), one notices that the values in the Brazilian museum are relatively high. The higher RH rates are characteristic for tropical and subtropical climates. The microclimatic homogeneity cannot be discussed in this work because the thermo-hygrometric equipment used does not have high resolution and fast response.

#### 3.1. Particulate matter

Although we do not have a time series to describe at high resolution the diurnal variability of PM, it is reasonable to propose that the indoor concentrations of total PM are expected to depend on aerosol transport from outdoors and also on the transit of people in and into the indoor environment.

The EDXRF results obtained inside and outside of the MON are presented in Table 2. The accuracy of the applied EDXRF method and of the obtained calibration curves can be found elsewhere (Avigo et al., 2008).

No elements were detected at concentrations higher than 100 ng m<sup>-3</sup>. Intermediate concentrations ranging from 100 to 10 ng m<sup>-3</sup> were identified for S, Cl and K, and Ca, Fe and Zn were detected at concentrations below 10 ng m<sup>-3</sup>.

One of the main anthropogenic sources of some of the pollutants mentioned above is vehicle traffic, whereby Cr, Ni, Zn and Fe are normally emitted by vehicle exhaust, Cr, Fe and Zn originate from brake wear and tear, and Fe and Zn originate from the wearing of tires (Yi et al., 2001; Hildemann et al., 1991).

The high S-abundance in urban air particles could be attributed to secondary reactions on anthropogenic emissions of  $SO_2$  (Wolf and Hidy, 1997). The particulate S-, Cl- and Si-concentrations were comparable to the findings of Gysels et al. (2004) and co-workers who studied the Royal Museum of Fine Arts in Antwerp, Belgium. However, in the Correr Museum in Venice, Sainsbury Centre for Visual Arts, Norwich and Kunsthistorisches Museum, Vienna, higher concentrations of those elements were observed (Camuffo et al., 2001).

Element depositions on glass or metals can result in the formation of complex salts (patinas and mineral crust) enhancing the corrosion process. Frequently, these salts increase the absorption of water and gases, facilitating the continuity of degradation process, as in the case of the hygroscopic sulfate particles. In addition, these newly formed minerals on the glass can lead to changes in the optical qualities of the glass (opacification and partial discoloration). For instance, it is well known to glass technologists that Fe, Mn as well as Sb can act as a decolorizing

Table 1	
Sampling	description.

Date	Sampling site	Description	Type of analysis	Sampling period
30/07 to 06/08	1	"Eye" building (HVAC system)	Gases PM (bulk) SPA (EPMA) BC	7 days 7 days 3 days 1 1/2 h/day
	2	"Eye" building (HVAC system)	Gases	7 days
	3	2nd floor of "eye" building (naturally ventilated)	Gases	7 days
	4		Gases	7 days
		Outside	PM (bulk) SPA (EPMA)	7 days
20/08 to 27/08	5, 6, 7	Room 1 — main building (HVAC system)	Gases	7 days
	8, 9, 10	Room 2 – main building (HVAC system)	Gases	7 days
	11, 12	Room 3 — main building (HVAC system)	Gases	7 days
	13	Corridor (naturally ventilated)	BC	1 1/2 h/day

|--|

Results of the EDXRF bulk analysis (ng m<sup>-3</sup>) of total PM inside and outside of "The Eye" tower - MON - first week sampling (DL: Detection Limit).

Sampling date	sampling place	Al	Si	S	Cl	К	Ca	Ti	Fe	Zn	Pb
31/07	Inside "Eye" Tower	<dl< td=""><td><dl< td=""><td><math display="block">29\pm5</math></td><td><math>10\pm2</math></td><td><math>14 \pm 1</math></td><td><math>5\pm1</math></td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><math display="block">29\pm5</math></td><td><math>10\pm2</math></td><td><math>14 \pm 1</math></td><td><math>5\pm1</math></td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	$29\pm5$	$10\pm2$	$14 \pm 1$	$5\pm1$	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	Outside	<dl< td=""><td><math>24 \pm 4</math></td><td><math>49 \pm 7</math></td><td><math>35\pm2</math></td><td><math>32 \pm 1</math></td><td><math>22 \pm 1</math></td><td><math>2 \pm 1</math></td><td><math>22 \pm 2</math></td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	$24 \pm 4$	$49 \pm 7$	$35\pm2$	$32 \pm 1$	$22 \pm 1$	$2 \pm 1$	$22 \pm 2$	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
01/08	Inside "Eye" Tower	<dl< td=""><td><dl< td=""><td><math>50\pm5</math></td><td><math>12 \pm 2</math></td><td><math>61 \pm 1</math></td><td><math>6 \pm 1</math></td><td><dl< td=""><td><dl< td=""><td><math>2\pm 2</math></td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><math>50\pm5</math></td><td><math>12 \pm 2</math></td><td><math>61 \pm 1</math></td><td><math>6 \pm 1</math></td><td><dl< td=""><td><dl< td=""><td><math>2\pm 2</math></td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	$50\pm5$	$12 \pm 2$	$61 \pm 1$	$6 \pm 1$	<dl< td=""><td><dl< td=""><td><math>2\pm 2</math></td><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><math>2\pm 2</math></td><td><dl< td=""></dl<></td></dl<>	$2\pm 2$	<dl< td=""></dl<>
	Outside	$115 \pm 4$	$167 \pm 3$	$149 \pm 6$	$48 \pm 2$	$244 \pm 1$	$214 \pm 1$	$21 \pm 1$	$206 \pm 2$	$7\pm3$	<dl< td=""></dl<>
02/08	Inside "Eye" Tower	<dl< td=""><td><dl< td=""><td><math>72 \pm 5</math></td><td><math>10 \pm 2</math></td><td><math>122 \pm 1</math></td><td><math>10 \pm 1</math></td><td><dl< td=""><td><math>7 \pm 1</math></td><td><math>3\pm2</math></td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><math>72 \pm 5</math></td><td><math>10 \pm 2</math></td><td><math>122 \pm 1</math></td><td><math>10 \pm 1</math></td><td><dl< td=""><td><math>7 \pm 1</math></td><td><math>3\pm2</math></td><td><dl< td=""></dl<></td></dl<></td></dl<>	$72 \pm 5$	$10 \pm 2$	$122 \pm 1$	$10 \pm 1$	<dl< td=""><td><math>7 \pm 1</math></td><td><math>3\pm2</math></td><td><dl< td=""></dl<></td></dl<>	$7 \pm 1$	$3\pm2$	<dl< td=""></dl<>
	Outside	$55 \pm 4$	$100 \pm 4$	$113 \pm 7$	$56 \pm 2$	$154 \pm 1$	$211 \pm 1$	$12 \pm 1$	$124 \pm 2$	$7\pm3$	<dl< td=""></dl<>
03/08	Inside "Eye" Tower	$33 \pm 3$	$53 \pm 2$	$57 \pm 4$	$8\pm1$	$37 \pm 1$	$69 \pm 1$	$4 \pm 1$	$40 \pm 1$	$3\pm2$	<dl< td=""></dl<>
04/08	Outside	<dl< td=""><td><dl< td=""><td><math>88 \pm 9</math></td><td><math>24\pm3</math></td><td><math>151 \pm 1</math></td><td><math>17 \pm 1</math></td><td><dl< td=""><td><math>11 \pm 2</math></td><td><math>5\pm4</math></td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><math>88 \pm 9</math></td><td><math>24\pm3</math></td><td><math>151 \pm 1</math></td><td><math>17 \pm 1</math></td><td><dl< td=""><td><math>11 \pm 2</math></td><td><math>5\pm4</math></td><td><dl< td=""></dl<></td></dl<></td></dl<>	$88 \pm 9$	$24\pm3$	$151 \pm 1$	$17 \pm 1$	<dl< td=""><td><math>11 \pm 2</math></td><td><math>5\pm4</math></td><td><dl< td=""></dl<></td></dl<>	$11 \pm 2$	$5\pm4$	<dl< td=""></dl<>
	Inside "Eye" Tower	$47 \pm 3$	$67 \pm 2$	$86 \pm 4$	$30 \pm 1$	$150 \pm 1$	$118 \pm 1$	$6 \pm 1$	$74 \pm 1$	$4\pm 2$	<dl< td=""></dl<>
05/08	Inside "Eye" Tower	<dl< td=""><td><dl< td=""><td><math>85 \pm 14</math></td><td><math>24 \pm 5</math></td><td><math>120 \pm 1</math></td><td><math>8 \pm 2</math></td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><math>85 \pm 14</math></td><td><math>24 \pm 5</math></td><td><math>120 \pm 1</math></td><td><math>8 \pm 2</math></td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	$85 \pm 14$	$24 \pm 5$	$120 \pm 1$	$8 \pm 2$	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	Outside	$138 \pm 7$	$200\pm5$	$151 \pm 10$	$49\pm3$	$270 \pm 1$	$358 \pm 1$	$21 \pm 1$	$187 \pm 3$	$7\pm4$	$22 \pm 1$
06/08	Inside "Eye" Tower	<dl< td=""><td><dl< td=""><td><math>13 \pm 5</math></td><td><math>10 \pm 2</math></td><td><math>12 \pm 1</math></td><td><math>8 \pm 1</math></td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><math>13 \pm 5</math></td><td><math>10 \pm 2</math></td><td><math>12 \pm 1</math></td><td><math>8 \pm 1</math></td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	$13 \pm 5$	$10 \pm 2$	$12 \pm 1$	$8 \pm 1$	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
	Outside	$28 \pm 5$	$48 \pm 4$	$38 \pm 7$	$16 \pm 2$	$59 \pm 1$	$89 \pm 1$	$5 \pm 1$	$47 \pm 2$	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>

agent in the silicate glass. In the leached layer on the glass surface Fe and predominantly Mn can lead to a brown discoloring of the surface layer due to an oxidation process of Mn(II) oxide to manganese dioxide (Schreiner, 1991).

The indoor/outdoor ratio (I/O) points out the lower amount of bulk particles inside of the Eye Tower, suggesting that the HVAC system is able to retain a significant part of the total PM (Van Grieken et al., 2000; Godoi et al., 2008; Camuffo et al., 2001; Gysels et al., 2004).

## 3.2. Single particle analysis

The single particle analysis (SPA) results from MON, presented in Table 3, show the relative abundance of individual particle types obtained inside and outside of the museum. For all samples collected inside and outside, 6 major types of aerosol particles based on their chemical compositions are significantly encountered: biogenic, calcium carbonate, calcium sulfate, soil dust, organic and soot.

Calcium sulfate particles can be released by the plastered wall indoors and others may be introduced from the outdoor urban atmosphere. In Table 3, overall relative abundances of those particle types are shown for the 4 samples. The overall relative abundance is calculated by dividing the encountered number of the specific type of particles by the total number of analyzed particles for each sample. The results obtained for SPA show the abundance of various particle clusters.

Two types of clusters that contain Ca species were found: calcium carbonate (CaCO<sub>3</sub>) and calcium sulfate (CaSO<sub>4</sub>). There are some theoretical possibilities for the origin of CaSO<sub>4</sub>, such as crustal sources and the atmospheric conversion of CaCO<sub>3</sub> species reacting with SO<sub>2</sub>. Gas-particle adsorption to produce CaSO<sub>4</sub> is known to occur under conditions of high relative humidity (Camuffo et al., 2001), especially in a polluted urban area. An additional process that can take place

Table 3

Relative abundance of the obtained particle types (combined groups) observed in the eight samples.

Cluster %	Inside		Outside	
	0.2–2.0 (μm)	2.0–8.0 (µm)	0.2–2.0 (µm)	2.0-8.0 (µm)
Biogenic	18	13	4	17
Organic	17	13	10	15
Soil dust	16	15	50	21
Soot	13	0	15	27
S-rich	6	11	6	13
S–Cl-rich	2	8	0	0
Cl-rich	0	5	0	0
CaSO <sub>4</sub>	17	23	0	0
CaCO <sub>3</sub>	8	10	14	9
FeO	1	1	0	1
Mixed	0	2	0	0

is the absorption of  $SO_2$  by the plastered walls. Both particles may originate from the degradation of museum plaster walls.  $CaSO_4$  has also a damaging potential for the artwork, causing the darkening of the surfaces when it adsorbs e.g. soot. The deterioration process of the walls and consequent re-suspension of the  $CaSO_4$  produced can also be an internal source of gypsum, although the walls of the MON are in very good condition.

Particles that are produced by living organisms are called biogenic aerosols such as pollens, fungi spores, bacteria and viruses. However, vegetation fires can also be considered another source of biogenic aerosols. The high amount of biogenic particles present inside the museum may be associated with large green area that surrounds the museum.

The indoor to outdoor concentration ratios revealed a significant enrichment of organic particles at most of the indoor sample locations, especially in the fine fraction, indicating an accumulation process due to chemical reactions taking place in the micro-environment and/or the infiltration due to the unsealed condition of the museum. This is in agreement with previous research, where the pollutant composition in museums using HVAC was found to be mainly due to organic carbonaceous particles and soil dust (Godoi et al., 2008). Organic particles with a high S-content were observed abundantly inside of the museum. These small size fraction particles can stay in the air for a longer time than the coarse fraction particles and at high humidity, potential S-incorporation from the air may result. These particles are of particular importance with regard to conservation and preservation of artifacts (Brimblecombe et al., 1999; Camuffo et al., 1999). For instance, the oxidation of S-rich particles to sulfuric acid can cause discolouration of paintings.

Table
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Results obtained in the first sampling week (07/30 to 08/06/2007) at Point 1, in the "Eye" Tower.

Sampling site	Day	Mean (ng m <sup>-3</sup> )	Maximum (ng m <sup>-3</sup> )	$\begin{array}{c} Minimum \\ (ng \ m^{-3}) \end{array}$	
Point 1 ("Eye" Tower)	07/30	2900	23150	102	
	07/31	9400	25120	7	
	08/01	5900	30340	8	
	08/02	7700	78610	17	
	08/03	8300	24880	286	
	08/04 (morning)	6000	25110	3	
	08/04 (afternoon)	7100	27740	31	
	08/05 (morning)	5800	42560	28	
	08/05 (afternoon)	4700	22008	35	
	08/06	6500	57800	185	
	Total average concentration: 6580				
Point 13 (main building)	08/23	9000	36950	87	
	08/24	8900	29260	1	
	08/25	12000	44780	169	
	Total average concentration: 9960				
Outside	08/27	16400	48740	437	

# Table 5

Results obtained for gases in the first sampling week (07/30 to 08/06/2007).

Sample location	$NO_2\mu g\;m^{-3}$	${\rm SO}_2~\mu g~m^{-3}$	$O_3\mu g\ m^{-3}$
Point 1	6.8	0.2	1.6
Point 2	6.7	0.2	0.8
Point 3	11	1.3	4.3
Point 4 (outdoor)	24	1.9	21

#### 3.3. Black carbon

In the field of cultural heritage, BC mainly causes soiling and blackening of surfaces, causing undesirable esthetic effects as black crust formation and material decohesion (Brimblecombe, 1990; Camuffo, 1998). The results obtained for BC at the MON are displayed in Table 4.

It is clear from Table 4 that the concentration of BC is significantly higher outside than inside. It is also interesting to notice that the two lowest average BC concentrations occurred in periods of low vehicular traffic in the museum area, being the concentration of 4700 ng  $m^{-3}$ registered on a Sunday afternoon (08/05/2007) and the concentration of 2900 ng m<sup>-3</sup> on a Monday (07/30/2007) on which the museum was closed. This confirms that the main source of BC to the atmosphere can be attributed to the vehicular traffic. Besides, when comparing the BC concentration obtained at Points 1 and 13, it can be seen that the main building presented higher average indoor concentration than the "Eye" building, which can be attributed to the fact that the main building presents more points of natural exchange of air, allowing a greater rate of transport of BC to the building interior.

The indoor concentration values obtained by the present study are similar to those of studies carried out in American museums by Ligocki et al. (1993) and Nazaroff et al. (1993). These museums do not present specific filtering for PM, similarly to the MON. However, museums which use the filters acting on BC (Norton Simons Museum and Scott Gallery) present much lower indoor concentrations of BC (Nazaroff et al., 1993; Ligocki et al., 1993). A positive result is the relative low amount of black carbon (soot) particles inside of the MON. The deposit of these types of particles on works of art is recognized as being the main reason for the soiling and chemical degradation of collections.

## 3.4. $NO_2$ , $SO_2$ and $O_3$

Table 5 displays the concentrations obtained for NO<sub>2</sub>, SO<sub>2</sub> and O<sub>3</sub> gases in the first sampling week.

One may notice that the concentration values of NO<sub>2</sub>, SO<sub>2</sub> and O<sub>3</sub> outside of the building (Point 4) are considerably higher than the ones obtained in the indoor environment. It was also observed an important concentration gradient between Points 1 and 2 with respect to Point 3. The I/O ratio for these pollutants indicates that there are no significant sources placed indoors. The concentration of NO<sub>2</sub> is usually high in an urban atmosphere, due to its emission by automobiles. Since MON is located close to streets of heavy vehicular traffic, it is expected to obtain higher concentration of NO<sub>2</sub>.

Usually, for naturally ventilated buildings, the indoor concentration values of O<sub>3</sub> are approximately half the outdoor values (Shaver and Cass, 1983). At MON, however, the indoor concentration is much lower than that, which can be due to high rates of deposition of O<sub>3</sub>,

Table 6 Results obtained for HAc and HFor in the first sampling week (07/30 to 08/06/2007).

Sample location	HAc $\mu g \ m^{-3}$	HFor $\mu g \ m^{-3}$	
Point 1	5.7	13	
Point 2	5.7	7.7	
Point 3	2.4	1.7	
Point 4 (outdoor)	2.2	2.4	

Table 7

Table 8

Point 4 (outdoor)

Results obtained for HAc and HFor in the second sampling week (08/20 to 08/27/2007).

Sample Location	HAc $\mu g m^{-3}$	HFor $\mu g \ m^{-3}$
Point 5	2.8	<dl<sup>a</dl<sup>
Point 6	2.7	<dl< td=""></dl<>
Point 7	2.7	<dl< td=""></dl<>
Point 8	3.4	<dl< td=""></dl<>
Point 9	3.8	<dl< td=""></dl<>
Point 10	2.4	<dl< td=""></dl<>
Point 11	2.6	<dl< td=""></dl<>
Point 12	2.6	<dl< td=""></dl<>

< DL: Under the detection limit (0.2 µg m<sup>-3</sup>).

08

F	Results obtained for BETX in the first sampling week (07/30 to 08/06/2007).							
	Sample location	$\substack{\text{Benzene}\\ \mu g \ m^{-3}}$	$\begin{array}{c} Toluene \\ \mu g \ m^{-3} \end{array}$	Ethyl benzene $\mu g \ m^{-3}$	$\begin{array}{l} m + p \text{ xylene} \\ \mu g \ m^{-3} \end{array}$	o-Xyler µg m <sup>-3</sup>		
	Point 1	<dl< td=""><td>2.3</td><td>1</td><td><dl< td=""><td>0.9</td></dl<></td></dl<>	2.3	1	<dl< td=""><td>0.9</td></dl<>	0.9		
	Point 2	<dl< td=""><td>&lt; DL</td><td>1.6</td><td><dl< td=""><td>1.4</td></dl<></td></dl<>	< DL	1.6	<dl< td=""><td>1.4</td></dl<>	1.4		
	Point 3	0.2	1.5	2.4	<dl< td=""><td>2.6</td></dl<>	2.6		

<DI

mainly in the floor carpets (De Santis et al., 1992), or due to reactions with other pollutants in the indoor atmosphere of the museum.

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The US National Bureau of Standards defined guidelines for atmospheric pollutants inside museums, in order to preserve the artworks exposed. The  $SO_2$  and the  $O_3$  pollutions detected in the MON are below the limits defined by the US National Bureau of Standards, but the NO<sub>2</sub> concentration values are slightly higher. However, when considering the guidelines defined by the Museum Environment, NO<sub>2</sub> concentration attends the defined limits (Blades et al., 2000).

The mean concentration values for NO<sub>2</sub> and SO<sub>2</sub> obtained in the present research are in general lower than the mean concentrations obtained in European museums (Camuffo et al., 1999, 2001; De Saints et al., 2003; Godoi et al., 2004). For SO<sub>2</sub>, this difference can be explained due to the fact that in Brazil there is much higher use of ethanol as automobile fuel, which emits no SO<sub>2</sub>, than diesel, which is largely used in Europe and still constitutes a (minor) source of SO<sub>2</sub> to the urban atmosphere.

#### 3.5. HAc and HFor

Tables 6 and 7 display the concentrations obtained for HAc and HFor in both sampling weeks.

For both pollutants, the indoor concentration values were in general higher than the outdoor values, indicating the presence of indoor sources of HAc and HFor. This pattern is most likely due to the presence of few plywood boards, which were used as a support for the art expositions in the sampling locations and are known as an important indoor source of both acids. The concentration of HAc and HFor inside the MON is very low compared with that inside the other

Table 9	
Results obtained for BTEX in the second sampling week (08/20 to $\ensuremath{c}$	08/27/2007).

Sample location	$\substack{\text{Benzene}\\ \mu g \ m^{-3}}$	$\begin{array}{c} Toluene \\ \mu g \ m^{-3} \end{array}$	Ethyl benzene $\mu g \ m^{-3}$	$\begin{array}{l} m + p \text{ xylene} \\ \mu g \ m^{-3} \end{array}$	o-Xylene µg m <sup>-3</sup>
Point 5	<dl< td=""><td>2</td><td>13.6</td><td>8.1</td><td>20.4</td></dl<>	2	13.6	8.1	20.4
Point 6	<dl< td=""><td>2.6</td><td>19.2</td><td>12.4</td><td>29.5</td></dl<>	2.6	19.2	12.4	29.5
Point 7	1.2	5.5	11.3	12.3	29.4
Point 8	<dl< td=""><td>2.5</td><td>11.7</td><td>8.3</td><td>20.9</td></dl<>	2.5	11.7	8.3	20.9
Point 9	<dl< td=""><td>0.7</td><td>11.2</td><td>7.9</td><td>20.1</td></dl<>	0.7	11.2	7.9	20.1
Point 10	<dl< td=""><td><dl< td=""><td>8.4</td><td>5.3</td><td>14.4</td></dl<></td></dl<>	<dl< td=""><td>8.4</td><td>5.3</td><td>14.4</td></dl<>	8.4	5.3	14.4
Point 11	<dl< td=""><td>2</td><td>15</td><td>16.3</td><td>37.8</td></dl<>	2	15	16.3	37.8
Point 12	0.6	1.1	17.4	17	39.3



Fig. 2. Comparison between average BTEX concentrations obtained at the MON, the Rubens House and the Lower Saxony State Museums.

museums worldwide. For instance, in the galleries and in the outdoor air of Metropolitan Museum, high concentrations of organic acids were found, with average concentrations of 50  $\mu$ g m<sup>-3</sup> of acetate and 10  $\mu$ g m<sup>-3</sup> of formate (Kontozova-Deutsch et al., 2011b).

There are still no guidelines for these pollutants in museum indoor environments, but it is expected that concentrations below 10.5  $\mu$ g m<sup>-3</sup> are found (Blades et al., 2000). Even though the results in the present research are below this value, it is important to notice that the exposure of the museum's collections to HAc and HFor for a long period of time, even at low concentrations, may cause irreversible damage.

#### 3.6. BTEX

Tables 8 and 9 display the concentrations obtained for BTEX in both sampling weeks.

When comparing both tables, it is clear that the BTEX concentration is lower in the "Eye" building than in the main building. This happened most likely because an exposition room at the main building, near the ones where the sampling was taking place, was being painted, and paints are known to represent one of the greatest sources of BTEX, since these substances are used as solvent in them.

It can be noticed that only 3 of the indoor locations indicated the presence of benzene, two of these are close to openings, where natural exchange of air takes place (Points 3 and 7) and the other one is close to the room which was being painted (Point 12). Thus, it suggests that the most important sources of benzene are outdoors (exhaust of automobiles), and this pollutant is being carried to the indoor environment. The other pollutants were not found outdoors, but were found indoors, indicating that they have emission sources placed in the indoor environment. At the time of the sampling, there were potential sources of these pollutants placed in the "Eye" building, such as wood structures and glass recently painted, while in the main building there was a room being painted, as already mentioned.

Compared to MON, the Rubens House Museum, Belgium (Godoi et al., 2008) and the Lower Saxony State Museum, Germany (Schieweck et al., 2005) presented higher average concentration of benzene and toluene, as shown in Fig. 2. However, when analyzing the average concentrations of ethyl benzene, m + p xylene and o-xylene, the Brazilian museum showed higher levels of pollution, mainly at the main building. Again, this result is most likely due to the painting process that was taking place at the room near the sampling locations.

It is known that BTEX are potentially corrosive. Besides, benzene and toluene act on inorganic pigments (Agelakopoulou et al., 2007) and ethyl benzene and xylenes, being solvents, can also act on pigments used in paints, altering the coloration of the artworks.

## 4. Conclusions

When comparing the air quality of the MON, characterized in the present study, to the air quality of other international museums, one can conclude that the MON has a satisfactory air quality, which may be favoring the conservation of its art collection.

 $SO_2$  and  $O_3$  presented low indoor concentrations, below the limits defined by both the US National Bureau of Standards and the Museum Environment (Thomson, 1986), while  $NO_2$  attends the guidelines only for the last one.

Acetic acid was detected at low concentrations in both studied buildings, while formic acid was detected only at the "Eye" building, also at low concentrations. Regarding BTEX concentrations, the values obtained at the main building were significantly higher than the ones obtained at the "Eye" building. This trend was due to the painting of an exposition room close to the sampling sites at the main building, which was happening at the time of the sampling period.

The elemental analysis of total PM showed values which, when compared to other studies, were low, especially for the most damaging elements to the artworks, such as S and Fe. The element found at the highest concentrations was K, which presents no damage potential to the artworks.

In the SPA, a relatively high abundance of biogenic and organic particles was found. The percentage of the most harmful particles to the artwork was low in comparison with the findings of other studies.

The BC concentrations were directly related to the intensity of the vehicle traffic in the surrounding area. The values obtained in the present study are similar to the values reported by other studies.

From the point of view of conservation, it became clear that the artworks are not directly threatened by particulate pollution. Still, the situation could be improved by employing filters with higher collection efficiency in the HVAC system, especially for small particles.

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