

## Measurements for indoor air quality assessment at the Capodimonte Museum in Naples (Italy)

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**ABSTRACT:** The state of works of art exhibited inside museums can be strongly influenced by indoor air quality, due to chemical activity of gaseous pollutants and particulate matter. For that reason it is important to carry out periodic air quality controls to check if the concentration levels of air pollutants comply with the limits specified by the national laws. In this work we show results obtained in a monitoring campaign carried out at the Museum of Capodimonte in Naples, one of the most important museums in Southern Italy. Results concern indoor monitoring of inorganic and organic gaseous pollutants and PM<sub>10</sub> and PM<sub>2.5</sub> fractions; moreover we also present the comparison between indoor and outdoor particulate matter concentration. From this analysis emerged a satisfying indoor condition with respect to gaseous pollutants, without any limit exceedance; in contrast particulate matter exhibits high concentration levels with frequent exceedances. Comparison with outdoor concentrations demonstrates the influence of dust and organic matter transported from the park surrounding the museum due to wind and visitors stamping.

**Key words:** Indoor Pollution, Cultural Heritage, Indoor monitoring, Gaseous pollutants, Particulate matter

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### INTRODUCTION

The state of works of art in museums is strictly affected by physical and chemical conditions, i.e. relative humidity, temperature, illumination, noise, vibration and atmospheric pollutants concentration. Relative humidity fluctuations can cause the deterioration of much kind of materials, for example sculptures, paintings, objects made by bronze, ivory or wood. Bones and cloths can change in size and shape as well as in consistency and fragility. The absorption or release of moisture can determine material deformation with the appearance of cracks and breaks (Pavlogeorgatos, 2003). It is also well known that high relative humidity can damage organic materials because it favors mould development and growth of fungi and microorganisms colonies on material surfaces. Even metals can suffer deterioration, particularly they can show superficial corrosion, due to high humidity exposure (Thomson, 1986). Temperature and illumination (natural or artificial)

can determine similar effects on works of art: they can accelerate chemical processes (as for example degradation of cellulose), cause material expansion and painting discoloring (Camuffo, 1998; Pavlogeorgatos, 2003; Thomson, 1986). Other physical parameters, noise and vibration, can affect the state of materials stored in museums; particularly they can cause destruction or cracking of crystals or other fragile objects, for example old paints can suffer detachment (Thomson, 1986). However the assurance of satisfying physical conditions is not sufficient to ensure a good conservation of works of art. It is now well known that chemical composition of indoor and outdoor air can damage the state of exhibits stored in museums (Brimblecombe, 1990; Pavlogeorgatos, 2003; Thomson, 1965; Van Grieken *et al.*, 1998); particularly, atmospheric pollutants can play an important role in the deterioration of works of art. Many substances

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induce chemical reactions on exhibits and, for this reason, are considered pollutants for museums. Substances typically considered as pollutants for cultural heritage are: sulphur dioxide, nitrogen oxides, ozone and particulate matter. Other substances (nitric and nitrous acids, hydrogen sulfide, hydrogen dioxide, formaldehyde, organic acids, other organic matter, ammonium sulphate) can contribute to chemical deterioration of works of art as well, but they are usually present at low concentrations, or are produced by chemical transformation of primary pollutants and do not directly contribute to deterioration processes (Brimblecombe, 1990). For example, nitric and nitrous acids are produced by heterogeneous reactions between nitrogen oxides and water (Jenkin *et al.*, 1988); nitric acid (HNO<sub>3</sub>) is a very aggressive species in contrast with nitrous acid (HNO<sub>2</sub>). The latter is not particularly active by itself, even if it is an important source of OH radicals, one of the most important atmospheric oxidants. However, because of its formation by reaction from nitrogen dioxide and water, nitrous acid can be considered an indicator of weathering conditions favoring acidification (De Santis *et al.*, 1992); for this reason the use of nitrous acid as indicator is preferred because of its lower reactivity and longer persistency in the atmosphere with respect to the more aggressive nitric acid (Katsanos *et al.*, 1999). Sulphur dioxide (SO<sub>2</sub>) can directly determine material fading or, more importantly, it may be catalytically converted, in high moisture conditions and in presence of hydrosoluble radicals or metallic ions, to sulphuric acid with high corrosive power. Also nitrogen oxides (NO<sub>x</sub>) contribute significantly to metals corrosion and cellulose degradation, after their transformation in acid forms. Ozone (O<sub>3</sub>) is another very active species in the deterioration of exhibits; ozone is a secondary pollutant, typically produced in urban areas under photo-oxidants pollution conditions. Ozone acts as a powerful oxidant, so it determines the fading of many types of materials such as textiles or organic materials, as cellulose, also for long exposition to low concentrations (Salmon *et al.*, 2000). Mineral pigments containing lead, iron or copper oxides can greatly suffer exposition to high ozone concentrations (Vuerich *et al.*, 2008). Different effects may be due to high concentration of suspended particles, whose accumulation onto works of art surfaces can determine soiling; also chemical characteristics of particulate matter play an important role in deterioration processes, particularly in association with high moisture, with the formation of a liquid phase (Gysels *et al.*, 2002). In this medium, particles can accelerate chemical reactions, as for example oxidation of compounds containing sulphur with the formation of sulphate ion or sulphuric acid; on the other hand the organic fraction of solid

phase can act as medium for the absorption of atmospheric sulphur dioxide or as substrate for microorganism development. The effects of all these phenomena are pigments fading, metals corrosion, blackening of exhibits.

For all these reasons it is important to determine pollutants concentration to which works of art are exposed, to make hypothesis on their sources and suggest control strategies. Particularly it is important to control that pollutant levels were always below limits established by law making *ad hoc* monitoring campaigns (Brimblecombe *et al.*, 1999; Camuffo *et al.*, 1999; Camuffo *et al.*, 2001; Costanzo *et al.*, 2006; Gysels *et al.*, 2004; Leysen *et al.*, 1987). Limits currently used as references in Italian law (MIBAC, 2001) are showed in Table 1.

**Table 1. Limit values as indicated in the Italian Law (MIBAC 2001)**

Pollutant	Limit values
Sulphur dioxide (SO <sub>2</sub> )	< 1 µg/m <sup>3</sup> [1]
Nitrogen dioxide (NO <sub>2</sub> )	< 5 µg/m <sup>3</sup> [1]
Ozone	< 2 µg/m <sup>3</sup> [1]
PM <sub>10</sub>	20-30 µg/m <sup>3</sup> [1]

[1] Values must not to be exceeded, even in the case of instantaneous measurements.

In this paper we present results obtained in a monitoring campaign carried out in several rooms of the Capodimonte Museum in Naples, one of the most important museums of the Campania Region and Southern Italy.

This museum is close to the urban area, surrounded by a big park and interested by the transit of airplanes from and to the Capodichino Airport. Interests of this campaign were focused on monitoring of typical pollutants, such as SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, particulate matter and on substances indicating acidification conditions (HNO<sub>2</sub>) as well as gaseous organic substances.

## MATERIALS & METHODS

The Palace of Capodimonte was founded in 1738 by *Charles of Bourbon* to hold the works of art inherited from the mother *Elisabetta Farnese*. The building had the dual function of royal residence and royal family private museum. The palace was mildly used as a residence by the *Bourbon Family*; the same *Farnese Paintings collection* short-lived, because, from the beginning of XVIIIth century, and for over a century, the art collections were exhibited in the *Building of Studies* (now the National Archaeological Museum) together with other archaeological finds. Just

after World War II, with the Savoy exile, the structure becomes definitively a state-owned property. Thanks to Bruno Molajoli, the public museum was opened on May 5, 1957, and the Farnese collection is now located in the large halls of the Palace. The Museum is now organised on three floors and two mezzanines. The first floor (Fig. 1). contains the *Farnese Paintings collection* (rooms 1-30) with masterpieces of Italian Renaissance, the Borgia collection (Room 7), the “Gallery of rare things” (room 14), the Historic Apartment (rooms 31-37, 42-44 and 51-60) and the Armoury (rooms 45-50).

The second floor is almost entirely occupied by the Neapolitan Gallery, exhibiting paintings from ‘200 to ‘700. The third floor is divided into three sections: art Contemporary Gallery; Photo Gallery and Gallery of the ‘800 Neapolitan. The Museum is located on the Capodimonte hill, surrounded by a park, without nearby industrial activities, but close to a highly urbanized areas, characterized by intense road traffic; moreover

it is located in correspondence of the airplane trajectories from and to the *Capodichino Airport*. For these reasons, works of art in the Capodimonte Museum may be exposed to typical urban pollutants and also to pollutants due to airplane crossing, determining the interest on periodic monitoring campaigns. The consequences of biogenic activities favored by emissions of park plants and visitors breathing could be also monitored. The monitoring campaign discussed in this work was conducted with the aim of establishing:

- the state of air quality in museum rooms,
- the contribute of external sources (road traffic and the park) to particulate matter concentrations,
- the contribute of external sources (biogenic and road traffic emissions and emissions due to airplanes crossing) to gaseous organic pollutants,

To these purposes we monitored the parameters listed in Table 2.

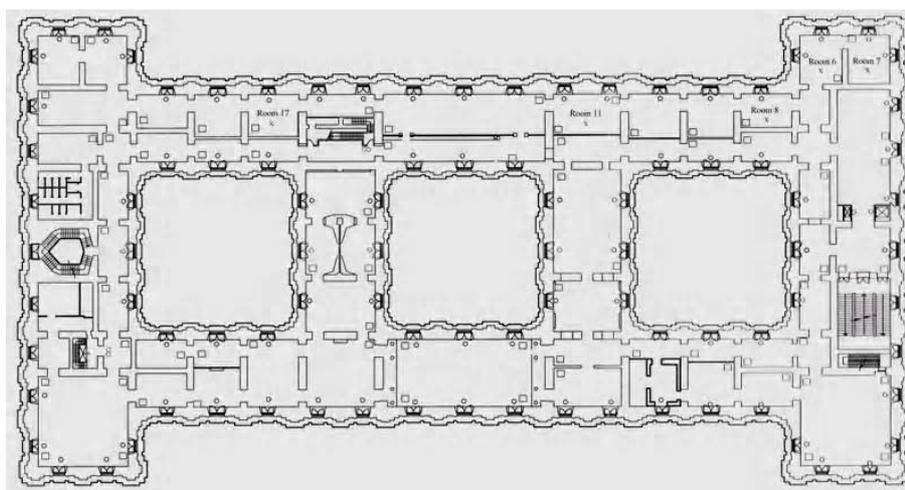


Fig. 1. Capodimonte Palace, first floor plan

Table 2. Monitored parameters and relative sampling and analysis methods

Monitored parameter	Sampling and analysis methods	Room	Period
Benzene, toluene, xylenes, ethylbenzene, benzoic acid, naphthalene and limonene	Radiello and Gas Chromatography	8 (indoor-outdoor comparison), 11, 17	December 2007- January 2008
SO <sub>2</sub> , HNO <sub>2</sub> , O <sub>3</sub> , NO <sub>x</sub>	Analyst and Ion Chromatography	8, 11, 17	March 2007- May 2007
PM <sub>2.5</sub> , PM <sub>10</sub>	Dust Scan Scout, Aerosol monitor	8 (indoor-outdoor comparison), 11, 17, 7	March 2007- June 2007

The rooms were chosen for their dimensions and for the presence of noticeable works of art, determining the stationing of many visitors; we also considered the presence of balconies with the aim to perform a comparison between indoor and outdoor concentrations for particulate matter and organic pollutants. In these rooms Analyst and Radiello samplers (for inorganic and organic gaseous pollutants, respectively) and a particulate matter monitor were positioned.

Room 8 was selected because of its small size (90m<sup>2</sup>) and because of the presence of particularly important works of art as “*La Trasfigurazione di Cristo*” by Giovanni Bellini and the “*Ritratto del Vescovo De’ Rossi*” by Lorenzo Lotto, determining frequent visitors stationing; in this room we also performed the comparison between indoor and outdoor conditions for organic pollutants and particulate matter, by positioning Radiello samplers and the Dust Scan Scout Aerosol Monitor on the balcony.

In Room 11, larger than room 8, the works of art “*Danae*” by Tiziano and the “*Soflon*” by El Greco are exhibited; in this room Analyst and Radiello samplers and particulate matter monitor were used. In Room 17, with the same size of room 8, the valuable “*Parabola dei Ciechi*” by Bruegel il Vecchio is hosted; in this room gaseous pollutants (by means of Analyst and Radiello samplers) and particulate matter were also monitored. Inorganic pollutants and particulate matter were monitored in the period from March to May, 2007, gaseous organic pollutants were monitored in the period from December 2007 to January 2008.

Organic compounds (benzene, toluene, ethylbenzene, o-xylene and (m+p)-xylene, benzoic acid, naphthalene and limonene) were collected using passive diffusive Radiello® samplers, patented by the Salvatore Maugeri Foundation. The exposition time for each sampler was one month. The samplers are constituted by a stainless steel net cylinder with a 100-mesh-grid opening and containing 530 mg of activated charcoal (Bruno *et al.*, 2005). After the exposition, the samplers were sealed and transferred to laboratories for analysis. The analyses were carried out at the Department of Environmental Sciences, Second University of Naples, using a Perkin Elmer GC-MS instrument, model Clarus 500, equipped with a thermal desorption apparatus, model TurboMatrix ATD. A stream of helium of 80 mL min<sup>-1</sup> at 320 °C for 10 min was applied to the exposed cartridges to extract the analytes. These were condensed in a trap at 2 °C and then released by heating at 290 °C for 1 min.

The column used for the GC separation was an Elite-5MS fused silica capillary, 30 m x 0.25 mm, 0.25 µm film thickness (Perkin Elmer Instruments). The oven

temperature program was 35 °C for 5 min, to 120° at 8 °C min<sup>-1</sup> and to 200 °C at 15 °C min<sup>-1</sup>. The carrier gas was heated at a flow rate of 1 mL min<sup>-1</sup>. The mass spectrometer scanned from 35 to 300 a.m.u. every 0.1 s, in the electronic impact (70 eV) mode. The ion source temperature was 180 °C and the multiplier voltage 350 V. The calibration method involved the injection of a standard liquid mixture onto an adsorbing cartridge (Kim *et al.*, 2001). To determine blank value, batches of unexposed samplers (six cartridges) were analyzed 1 day and 15 days after conditioning, with storage at 4°C. The resulting analyses showed very low levels of all compounds and there was no significant difference between the two storage durations. The detection limits for each compound, defined as three times the standard deviation of blank values, were relatively weak (0.03 µg/m<sup>3</sup> of benzene, 0.02 µg/m<sup>3</sup> of toluene, 0.03 µg/m<sup>3</sup> of ethylbenzene, 0.02µg/m<sup>3</sup> of m/p-xylene, 0.03 µg/m<sup>3</sup> of o-xylene for 7 days exposure). Sampling capacity and extraction efficiency of the tubes, as well as stability of the compounds in the tubes, were tested in earlier studies; repeatability tests for benzene, toluene and xylenes were comparable with data reported in literature (Meybeck *et al.*, 2000).

Gaseous inorganic pollutants (ozone, nitrogen oxides, sulphur dioxide and nitrous acid) were collected by means of passive samplers Analyst, developed by CNR-Institute for Atmospheric Pollution and certified by the Italian law DM60 04/02/2002. Analyst are based on the molecular diffusion principle: substances diffuse and are absorbed on specific substrate, whose composition depends on pollutant chemical characteristics; for each species two analyst were exposed, one of which closed and used as blank; in each room analysts were positioned at about 1m from the ground, in a corner of the room, to avoid breakage due to visitors contact.

The exposition period can vary from few days to some months; for this work, an exposition time of one month was chosen for a sufficient sampling.

After exposition each sampler was treated with 5 ml of solution made by NaHCO<sub>3</sub> (1mM) and Na<sub>2</sub>CO<sub>3</sub> (3.2mM) with the addition of 0.03% H<sub>2</sub>O<sub>2</sub> for the sulphur dioxide analyst, to ensure the complete oxidation to sulphate ion; solutions were analysed for anion contents (nitrite ion for nitrogen oxides determination, sulfate ion for sulfur dioxide determination, nitrite ion for nitrous acid determination and nitrate ion for ozone determination) by ion chromatography using standard procedures (Alexandrov, 1996; Chalmers, 1975; Duneman *et al.*, 1994; Sarzarini, 1998; US EPA, 1999; Weiss, 1999). The amount of anion was used for the determination of related inorganic pollutant by means of the equation:

$\text{pollutant (}\mu\text{g)} = k \times \text{anion concentration (}\mu\text{g)} / \text{exposition time (h)}$

where  $k$  is a constant depending on pollutant.

Anion determination was carried out at the *Department of Chemistry, University "Federico II" of Naples*, using a Metrohm chromatographic system, based on a 733 IC separation centre, 754IC dialysis suppression unit, 853 CO<sub>2</sub> suppressor and a double detection system (819 IC conductivity detector and Lambda 1010 UV detector).

Separation column was a Metrohm Metrosep A SUPP5 250 column (4,0 mm x 250 mm), packed with a styrene/divinylbenzene resin with quaternary ammonium group, particle size 10 $\mu\text{m}$ , used with chemical suppression of conductivity; a column guard (Metrohm METROSEP ANION SUPP1 GUARD) was used, made of the same material. Eluent was standard carbonate eluent (1,0 mM sodium hydrogen carbonate + 3,2 mM sodium carbonate) with 2% added acetonitrile to prevent bacterial growth.

Standard flow of 0,7ml/min was adopted to separate major inorganic ions with good resolution, from fluoride to sulphate in ca. 32 min. The volume of the loop was 20 $\mu\text{L}$ , pressure 12.0 MPa.

All samples and eluents were degassed before use, by applying vacuum for at least 10 min and then micro filtered (0,45  $\mu\text{m}$  filter).

Analytical reagent grade chemicals were used throughout this study. Stock grade 1000ppm anion solutions, certified for anion and impurities content, were from ROMIL Ltd Cambridge, and from Metrohm CH. Standards were prepared for each day of analysis by appropriate dilution of the stock solution with ultrapure water. No differences above the experimental sensitivity were observed in the absorbance values. All the glassware and plastics used in the analysis were washed, rinsed with distilled and deionised water and then dried. Ultrapure anion-free water from a Helix and Milli-Q Millipore system was employed. The water and other reagents used in this study were shown to have negligible values for the major ion analysed. Linear calibration graphs were obtained using a series of calibrating standards. The average recoveries were in the range 98.9- 101.5%.

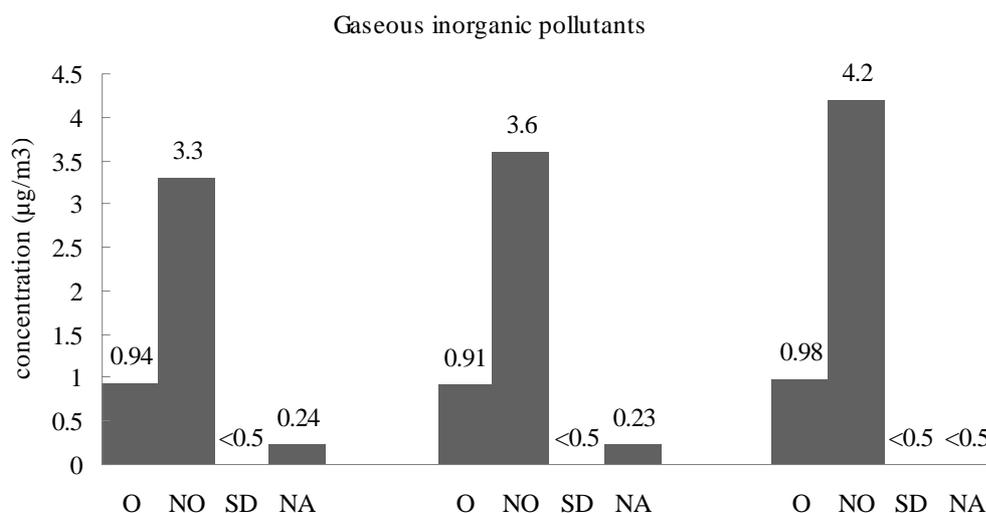
The Dust Scan Scout Aerosol Monitor is a continuous dust analyzer whose measurement method is based on light scattering: air flows, with a rate of 2 L/min, through the sampling head analyzer, with a filter for PM<sub>10</sub> or PM<sub>2.5</sub>. After the sampling head, the flow enters in the detection chamber where particles travel orthogonally to a laser light source (670 nm) and to the corresponding receiving system, consisting in an optical sensor. The amount of light scattered at 90°,

determined by the analyser, is directly proportional to the concentration of the particles, expressed as  $\mu\text{g}/\text{m}^3$ . The range of measurement sampling corresponds to 0-0.5  $\text{mg}/\text{m}^3$ , with an accuracy of  $\pm 10\%$  and a precision on a single measure of 0.002  $\text{mg}/\text{m}^3$ ; the sampling time step used in this work was 30 sec. Data obtained from the instrument were organised in a file text, with the indication of data, time for each concentration value recorded, average concentration (calculated over selected time intervals), minimum and maximum concentrations (referred to each time interval) and time at which minimum and maximum concentrations occurred. These data were used to obtain information on temporal profiles and on concentration levels.

## RESULTS & DISCUSSION

Concentrations of gaseous inorganic pollutants are showed in Fig. 2. it is clear that all gaseous inorganic pollutants show very low concentration levels, with values always below limits (see Table 1). The museum is far away from any industrial sources, though it faces an intensely travelled road; for that reason, concentrations of sulphur dioxide in all rooms are below the detection limit corresponding to 0.5  $\mu\text{g}/\text{m}^3$  and well below the limit indicated by law (1  $\mu\text{g}/\text{m}^3$ ). Low concentrations registered for sulphur dioxide are consistent with the usually low emission rate, as a consequence of reduction of sulphur content in fuels, and the high deposition velocity and oxidation rate for that pollutant.

The Italian law establishes a limit for nitrous acid; anyway its concentration is below the detection limit (0.2  $\mu\text{g}/\text{m}^3$ ) in room 17 and very low for all other rooms; for that pollutant, De Santis (1992) and Katsanos (1999) reported much higher concentrations for *Galleria degli Uffizi* in Florence (with a value ranging from 4 to 12  $\mu\text{g}/\text{m}^3$  in the daytime) and the *Museo della Civiltà Romana* (with values ranging from 2.5 to 5  $\mu\text{g}/\text{m}^3$ ), respectively. Also, ozone shows low concentration levels with an average concentration corresponding to 0.94  $\mu\text{g}/\text{m}^3$ ; that value is lower than the maximum acceptable concentration (2  $\mu\text{g}/\text{m}^3$ ) and lower than ozone levels typically recognised in indoor environments (Salmon *et al.*, 2000; Vuerich *et al.*, 2008; Worobiec *et al.*, 2007). Ozone has no inner source, so its presence must be attributed to the transport from outside; in this case the absence of close pollution sources explains the low levels registered. Moreover a sink for ozone may be via the reaction with organic materials associated with wood materials hosted in the museum, as frames or sculpture (Pavlogeorgatos, 2003). Finally nitrogen oxides show values higher than other gaseous pollutants, with an average concentration of 3.7  $\mu\text{g}/\text{m}^3$ ; all values are below limit (5  $\mu\text{g}/\text{m}^3$  reported as NO<sub>2</sub>) and below values usually reported in the



**Fig. 2. Inorganic gaseous pollutant concentrations expressed as  $\mu\text{g}/\text{m}^3$  (O= ozone, NO= nitrogen oxides, SD= sulphur dioxide, NA= nitrous acid)**

literature, typically ranging from  $3 \mu\text{g}/\text{m}^3$  (Worobiec *et al.*, 2007) to  $28.5 \mu\text{g}/\text{m}^3$  (Cappitelli *et al.*, 2009). It should be outlined that values obtained by analyst extraction are reported as  $\text{NO}_2$  concentration, but they actually correspond to a mixture of  $\text{NO}_x$ ;  $\text{NO}_2$  concentration should be considered lower than 5-10% of the total nitrogen oxides concentration.

Results on concentrations of gaseous organic pollutants extracted by Radiello® samplers and determined with Gas Chromatography (benzene, toluene, ethylbenzene and xylenes) are showed in Figs 3 and 4. Outdoor concentrations are very high; Italian law set a limit for benzene outdoor concentration of  $5 \mu\text{g}/\text{m}^3$ , referred to safety of human health, since it is known as a carcinogenic compound; xylenes, toluene and ethylbenzene are toxic but not carcinogens and there are no limits for them. Concentrations of BTEX are high also in museum rooms; data published in the literature for the same period, and referred to indoor air quality in schools, indicate a much lower concentration for benzene, toluene, ethylbenzene and xylenes, of  $1.54 \mu\text{g}/\text{m}^3$ ,  $5.23 \mu\text{g}/\text{m}^3$ ,  $1.46 \mu\text{g}/\text{m}^3$  and  $4.77 \mu\text{g}/\text{m}^3$  respectively (Stranger *et al.*, 2008). Though indoor benzene concentration is lower than outdoor concentration, its level does not comply with the maximum acceptable limit in rooms 8 and 11. In rooms 8 and 11 toluene and xylenes also achieve significant concentrations, while room 17 shows the lowest concentration values and a benzene level below the limit.

BTEX have no known effects on cultural heritage but they were monitored because are emitted principally by road traffic and so indicate the effects of that source on air quality inside the museum; data show that even their indoor concentrations are significant, usually above the maximum acceptable outdoor limits.

Moreover the constant ratio among concentrations probably indicates a unique source for indoor and outdoor BTEX; these results are consistent with observations made in the Naples urban area in previous works (Iovino *et al.*, 2009). Radiello® analysis also revealed the presence of limonene, benzoic acid and naphthalene, whose values are showed in Fig. 4. The first one is produced by biogenic activity from the plants in the park surrounding the museum; outdoor, as well as indoor, concentration was in the range of typical levels for that substance (IPCS, 1998; Moukhtar *et al.*, 2005). Limonene inside the museum decreases significantly with a reduction of 75% for rooms 8 and 11 and a reduction of 89% for room 17. Naphthalene has been found in areas interested by the passage of airplanes (Chen *et al.*, 2006) but it is also a metabolite of certain tropical plants (Krauss *et al.*, 2005); benzoic acid was recognized in indoor and outdoor urban aerosol in comparable concentrations (Mirivel *et al.*, 2009) as well as in the gas phase of urban areas (Kawamura *et al.*, 2000). Benzoic acid is produced by oxidation of toluene and photochemical degradation of aromatic compounds in engine exhausts (Rogge *et al.*, 1993), as well as by photochemical degradation of benzoic acid esters used as fragrance ingredients (Shibamoto *et al.*, 1995). Indoor limonene and naphthalene concentrations decrease significantly with respect to outdoor concentrations, while benzoic acid achieves its outdoor levels; this can be due to different molecular weight, being limonene and naphthalene the heaviest ones. The presence of these compounds confirms the influence of outdoor sources of primary and secondary organic substances on air quality inside the museum, indicating the influence of transport emissions (road traffic but also airplanes passage) and of biogenic sources.

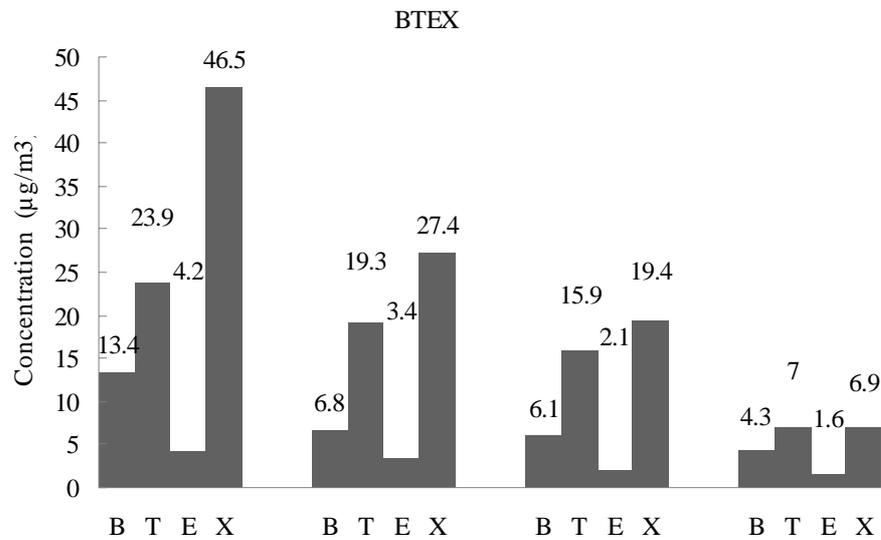


Fig. 3. Benzene (B), toluene (T), ethylbenzene (E) and xylenes (X) concentrations, expressed as  $\mu\text{g}/\text{m}^3$

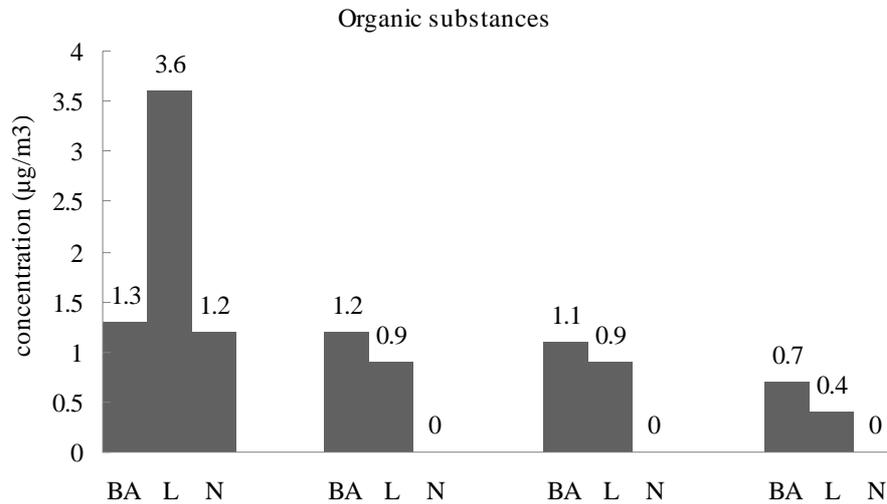


Fig. 4. Benzoic acid (B.A.), limonene (L) and naphthalene (N) concentrations, expressed as  $\mu\text{g}/\text{m}^3$

Particulate matter concentration was monitored with a continuous analyzer which calculates mean concentration (referred to a selected time interval) from instantaneous values; measurements were performed in the period from March to May 2007 and in June, 2007. Italian standards establish several limits for  $\text{PM}_{10}$  particulate matter fraction, based on the observation of mechanic effects, that is superficial deposition and consequent material soiling (Owen and Ensor, 1992); nevertheless it is well known that  $\text{PM}_{2.5}$  fraction is also important because of small particle dimensions and of its anthropic origin, determining a complex and dangerous chemical composition (Nazaroff *et al.*, 1990). Moreover finer particulate matter has a relatively long residence time and contains the great part of carbonaceous fraction and sulphate ions present in the aqueous/solid atmospheric phase (Cappitelli *et al.*, 2009). For these reasons we monitored atmospheric

concentration of both fractions, measuring diurnal average, maximum and minimum concentrations and percentage of limit exceedances. Data on  $\text{PM}_{10}$  monitoring are showed in Table 3. Average  $\text{PM}_{10}$  concentrations are very high during the monitoring period, particularly for room 8 where the highest maximum concentration also occurred; in that room the highest percentage exceedances are relevant, even for the  $30 \mu\text{g}/\text{m}^3$  limit. Minimum concentrations were always registered during days of closure to public, indicating that the presence of visitors can contribute to indoor particulate matter concentration, (from vehicular traffic or from the park) due to opened doors, or determining the resuspension of dust deposited on the floor. It should be noted that concentration of coarse particulate fraction decreases going from room 8 to room 17 as well as in the case of gaseous organic substances. Data on  $\text{PM}_{2.5}$  concentrations are showed

in Table 4. average concentrations indicate that PM<sub>2.5</sub> constitutes a significant fraction, underlying the anthropic origin of particulate matter. As in the case of PM<sub>10</sub> fraction, maximum and minimum PM<sub>2.5</sub> concentrations decrease going from room 8 to room 17 with minimum concentrations always registered during days of closure to the public. For the finer fraction limit values are not available, so we considered the limits used for PM<sub>10</sub> fraction for comparison; it should be noted from Table 4 that concentration is usually above the 20 µg/m<sup>3</sup> limit. Particulate matter monitoring was repeated in the summer period (June 2007), performing also outdoor measurements (on the balcony of room 8) with the aim to compare indoor and outdoor

concentrations; data are showed in Table 5. Concentrations are generally higher than those registered in the previous monitoring campaign, with average and maximum concentrations reaching very high values for both fraction.

Outdoor and indoor average concentrations are well above the limits established for PM<sub>10</sub> in outdoor (corresponding to 40 µg/m<sup>3</sup>) indicating an important anthropic impact; also PM<sub>2.5</sub> average concentration exceeds that value. The ratio between indoor and outdoor concentrations for PM<sub>10</sub> has a value of 0.59, while for PM<sub>2.5</sub> it is 0.64; these values indicate the importance of external sources for particulate matter concentration inside the museum.

**Table 3. Data on PM<sub>10</sub> concentrations during the spring period**

	<b>Room 8</b>	<b>Room 11</b>	<b>Room 17</b>
Average concentration (µg/m <sup>3</sup> )	30.0±1.2	27.3±1.1	22.4±1.4
Maximum concentration (µg/m <sup>3</sup> )	38±0.3	37.8±0.9	32.1±1.5
Minimum concentration (µg/m <sup>3</sup> )	15.1±0.2	12.1±0.3	12.2±0.4
Percentage of exceedances (referred to 20 µg/m <sup>3</sup> )	97	93	84
Percentage of exceedances (referred to 30 µg/m <sup>3</sup> )	62	33	3

**Table 4. Data on PM<sub>2.5</sub> concentrations during the spring period**

	<b>Room 8</b>	<b>Room 11</b>	<b>Room 17</b>
Average concentration (µg/m <sup>3</sup> )	23.3±1.2	20.7±0.8	16.7±1.0
Maximum concentration (µg/m <sup>3</sup> )	30.1±0.6	31.0±3.2	26.5±2.8
Minimum concentration (µg/m <sup>3</sup> )	9.2 ±1.4	6.4±0.3	10.3±0.2
Percentage of exceedances (referred to 20 µg/m <sup>3</sup> )	86	75	25
Percentage of exceedances (referred to 30 µg/m <sup>3</sup> )	0.01	-	-

**Table 5. Data on PM<sub>10</sub> and PM<sub>2.5</sub> concentrations for indoor-outdoor comparison in the summer period**

	<b>PM<sub>10</sub> indoor</b>	<b>PM<sub>10</sub> outdoor</b>	<b>PM<sub>2.5</sub> indoor</b>	<b>PM<sub>2.5</sub> outdoor</b>
Average concentration (µg/m <sup>3</sup> )	47±0.8	79±9.1	40±1.2	62.2±6.1
Maximum concentration (µg/m <sup>3</sup> )	51±1.1	96±0.2	41±1.3	73±0.8
Minimum concentration (µg/m <sup>3</sup> )	38±0.5	60±1.4	35±1.4	50±1.3
Percentage of exceedances (limit of 20 µg/m <sup>3</sup> )	100	100	100	100
Percentage of exceedances (limit of 30 µg/m <sup>3</sup> )	100	100	100	100

## CONCLUSION

There has been many monitoring campaigns in museum rooms and halls dedicated to the assessment of particulate matter or gaseous pollutants or microclimatic parameters. In this work we monitored several chemical atmospheric species using non-invasive instruments, to study pollution conditions due to different kind of substances: particulate matter (fine and coarse), organic and inorganic, primary and

secondary gaseous substances and indicators of weathering condition favouring works of art corrosion due to atmospheric acidification. The application of that methodology allows the study of museum atmosphere without prejudice the enjoyment of the structure.

Inorganic substances were present in low concentrations, always below limits; this is also true for classic atmospheric pollutants as nitrogen oxides,

sulphur dioxide and ozone, as well as for nitrous acid for which there are no limits established by law but whose concentration is low compared with concentration levels reported in literature. Low levels registered for nitrous acid are related to low levels of its precursors (nitrogen oxides) and the absence of conditions favouring precursor transformation. Organic substances present a different behaviour with BTEX registered in high concentrations outside as well as inside the museum, indicating the transport from outside due to visitors transport and opened doors; levels of these pollutants, from vehicular emissions, are decreasing along the path from room 8 to room 17. Benzoic acid, limonene and naphthalene were also monitored. The first is a secondary atmospheric pollutants, often found in gaseous and solid phases of polluted areas; its concentration is not very high, nevertheless it is transported inside the museum where it can contribute to develop other reaction. Limonene is a product of biogenic activities from the park surrounding the building, registered inside and outside the museum at its typical concentration levels; it may be very important for the oxidation capacity of the atmosphere inside the museum, because its contribution to secondary reactions. Naphthalene was registered with samplers positioned outside the museum; for that substance two sources can be hypothesized: biogenic production due to tropical plants (present in the park) or airplanes passage over the building. It is not found inside the museum, because of its low outdoor concentration and its molecular weight favouring deposition, but its presence may indicate a potential impact of airplanes passage on museum air quality. Finally particulate matter indicates a poor air quality inside the museum: both fine and coarse fractions show significant concentration levels, often above limits for all the rooms monitored. The comparison between  $PM_{10}$  and  $PM_{2.5}$  fractions indicate that fine fraction is the most relevant part, while the comparison with outdoor concentrations indicate the transport from outside as principal source. These observations allow affirming that particulate matter registered inside the museum is mostly of anthropogenic origin; this problem may be probably attenuated with the introduction of an air circulation system with filters. To ensure the maintenance of optimal conditions for works of art exposed, it should be preferable to repeat periodically similar campaigns, introducing also the study of particulate matter chemical composition and microbiological analysis.

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