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Chemical–physical and Microbiological Measurements for Indoor Air Quality Assessment at the Ca' Granda Historical Archive, Milan (Italy)

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Abstract In a few cases, atmospheric particulate matter characterization was taken into account together with aerobiological monitoring but never in an archive. The aim of this study was to estimate the air quality, by means of both chemical–physical and microbiological studies, at the Ca' Granda Historical Archive (Milan, Italy) that houses an important collection of documents from the 12th century. Temperature and relative humidity were measured in the rooms. Particulate matter (PM2.5) concentrations were quantified and the chemical composition, in terms of ionic components, elements, and carbonaceous fraction (total, organic, and elemental carbon) determined. The gaseous pollutants NO_2, SO_2, and O_3 and indoor acidity were also measured. Aerobiological monitoring (aerobic heterotrophic bacteria and fungi) was performed as volumes stored in the Archive were composed of organic materials, a potential energy and carbon source. In this paper, we present our findings and propose some guidelines for a better preservation of the documents.

Keywords Archive indoor air · Particulate matter · Energy dispersive X-ray fluorescence (ED-XRF) · Carbon analysis · Aerial microbiological contamination

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1 Introduction

Libraries and archives have been used for centuries to preserve a wide variety of materials and to store precious information. The effect of air pollution on objects stored in museums and archives has recently received an increased awareness from museum and conservation staff. Actually, numerous studies have been carried out to assess the complexity of the risks, which can be chemical, physical, and biological, in museums, galleries, and all the environments where works of art are exhibited and stored (Brimbecomble 1990; Van Grieken et al. 2000; Camuffo et al. 2001).

Atmospheric pollution is one of the most relevant threat to the preservation of cultural heritage. Studies comparing libraries under different environmental pollution conditions (urban sites and rural areas) demonstrated that degradation is more significant in polluted areas (Pavlogeorgatos 2003). Looking at indoor air quality from a chemical point of view, it is important to focus on components that have a potential deterioration effect on the building interiors such as some gases (e.g., NO_x, SO_2, and O_3) and particulate matter (PM). Indoor pollution can be due to external penetration. Outdoor particles are brought indoor via ventilation or, on the contrary, indoor sources might be present. The indoor sources are numerous and can be ascribed to different processes such as room heating, soil dust, dust from visitors, human bio-effluent, cleaning materials, deterioration of the walls, etc. One of the main problems caused by indoor aerosols is soiling, i.e., particle deposition on surfaces (Owen and Ensor 1992) or the chemical damage (Nazaroff et al. 1990) depending on their size and chemical composition.

Few studies have been carried out in libraries for the assessment of total dust concentration together with indoor exposure to volatile organic compounds (Fantuzzi et al. 1996; Righi et al. 2002; Schieweck et al. 2005). The latter, potentially hazardous for both stored materials and libraries users, could have been generated from products used in previous conservation treatments (Schieweck et al. 2005; Mills and White 1994). Particulate matter in the indoor atmosphere can also be generated by photo-oxidative processes (Brimblecombe 1990). In addition, hydrocarbons from outdoor air can be oxidized contributing to the amount of dust deposited on indoor surfaces.

It has been demonstrated that the environmental parameters temperature and relative humidity are critical for organic material preservation. When organic material-based objects—like paper and parchment—release humidity, they become fragile and the fibers are easily broken (Pavlogeorgatos 2003). In contrast, high temperature and relative humidity favor microbial growth. Actually, as with other objects, documentary heritage is susceptible to biological damage (Cappitelli and Sorlini 2005). Biodeterioration is any irreversible alteration that implies changes of the material properties caused by microorganisms and/or organisms belonging to different systematic groups (Giacobini et al. 1987). Biodegradable materials are those which, because of their chemical structure, are susceptible to being assimilated by microorganisms such as fungi and bacteria. Since the 1950s, a close similarity between the airborne microflora and the library and archival materials biodeteriogens has been noted (Kowalik and Sadurska 1956; Gallo 1964).

In the year 2004, a major program of improvements in conservation, access, and collections management was begun at the Ca' Granda Historical Archive (Milan, Italy) that houses an important collection of documents (e.g., parchments, maps, and codes) dealing with the local hospital administration, and dated from the 12th century, together with other precious objects such as paintings. Two different locations were monitored: the Archive's main hall or Capitolo d'Estate, a 9-m-high frescoed room where ancient documents are stored up to 7 m, and the 3-m-high basement where the oldest historical documents are retained. The Archive's hall was less frequently attended by visitors than typical museum rooms and re-suspension was likely a minor source of particles. Consequently, we chose to sample PM2.5, i.e., particles with aerodynamic diameter smaller than 2.5 μm, because it easily penetrates in the hall from outdoor (where traffic is the major local source), its residence times in ambient air are high, and it is mainly composed of acidic substances and black carbon (Seinfeld and Pandis 1998), which can affect the stored documents and the visitors as well.

Air quality monitoring was included in the framework of this diagnostic investigation project whose major goal was the total restoration and functional recovery of the building (investigations on mortars, plasters, and wooden parts; thermography of the vaults and topography relieves were also planned).

Although some joint chemical–physical and microbiological studies aiming at air quality monitoring have been carried out in museums (Camuffo et al. 1999, 2001; Gysels et al. 2004), case studies considering all these investigations in archives and libraries have been carried out in few researches (Mandrioli et al. 2003).

The aim of this work was to study indoor pollutants and microbial contaminants at the Ca' Granda Historical Archive and to assess the relationship between the indoor and the outdoor environment in order to plan sound preventive strategies.

2 Materials and Methods

2.1 Monitored Site and Sampling Location Description

The Historical Archive of Ca' Granda is located in the center of Milan (Italy) near major traffic axes. Milan is a large city characterized by a high density of residential and commercial premises and a very high volume of vehicular traffic.

Physical–chemical samplings were carried out indoor and outdoor in parallel during an intensive field campaign in 2004, April 21st–30th (just before the beginning of refurbishment works in the Archive) aiming at the characterization of particulate matter concentration and composition as well as at the assessment of criteria gaseous pollutants levels. All the rooms have a tile floor and painted walls covered with wooden or metal bookcases.

Passive samplers (Passam®) were used for the determination of integrated concentration levels of SO_2, NO_2, and O_3 (CEN 1997). These diffusive monitors were located in parallel outdoor and at the ground floor for 1 week for O_3 measurement and for 2 weeks for SO_2 and NO_2 (monitoring with passive samplers needs longer times to collect a detectable quantity of the latter investigated gases).

The PM sampler location for outdoor measurements (see Fig. 1) was in the garden of the Archive next to the main hall. Owing to the large difference in traffic intensity on this road on Sundays, it was decided not to sample on April 25th.

Indoor particulate matter samplings were performed for four consecutive days (April 21st–24th) in the Capitolo d'Estate room and subsequently in the basement (April 27th–30th). The samplers were moved from the ground floor to the basement on April 26th so that measurements are not available for that day.

The choice of collecting PM2.5, i.e., the fine aerosol fraction, was motivated by the fact that it has been recognized as an important fraction in case of deposition on vertical surfaces. Literature data on estimations of the deposition flux indicate that deposition velocity has a minimum for particles with aerodynamic diameters of about 1–2 μm (Zhang et al. 2001) and the soiling per unit time and unit surface is maximum for sub-micrometric particles (Camuffo et al. 1999). Fine particles have a long residence time in atmosphere thus reaching also high elevations (the Capitolo d'Estate hall is three floors high and wooden bookcases cover the walls). Furthermore, carbon fractions (which cause the soiling and blackening of the cultural heritage) and soluble acid aerosols, like sulfates, are generally abundant in fine particulate matter.

Twenty-four-hour (from 00:00 to 24:00) PM2.5 samplings have been performed using CEN-equivalent samplers (CEN=Comité Européen de Normalisation) operating at a flow rate of 2.3 m^3/h and equipped with a size-selective inlet to collect particles with aerodynamic diameter smaller than 2.5 μm. The samplers were checked for comparability during previous campaigns showing a fair agreement. Particles have been collected on pre-fired quartz fiber filters and on PTFE filters every other day. The use of both PTFE and quartz fiber filters was requested to achieve the full chemical characterization of the sample. According to the European norm EN12341 (CEN 1998), before and after the samplings, the filters were exposed for 48 h on open but dust-protected sieve trays in an air-conditioned weighing room (T=20±1°C and R.H.=50±5%). The gravimetric determination of the mass was carried out using an analytical microbalance (precision 1 μg), which is installed and operates in the weighing room. PM2.5 concentration values here reported have been normalized to standard conditions (0°C and 101.3 kPa). Relative humidity and temperature were also monitored using the sensors integrated with the PM samplers (the absolute uncertainty was 10% and 1°C on R.H. and T, respectively).

Air samples were collected for microbiological analyses from eight locations in the Capitolo d'Estate (main hall), 13 locations in the basement, and two locations outdoor on 23rd April 2004 (Figs. 1 and 2). In the Archive, no forced ventilation or air-conditioning systems were present; nevertheless, during the winter season (from October to March), the rooms were heated. No assessment of the exchanged volumes of air was performed in this work.

The main hall has many windows and two doors for access from the garden close to a main road, characterized by large volumes of traffic especially during daylight hours. Capitolo d'Estate is also close to a courtyard. In the main hall for each position, one

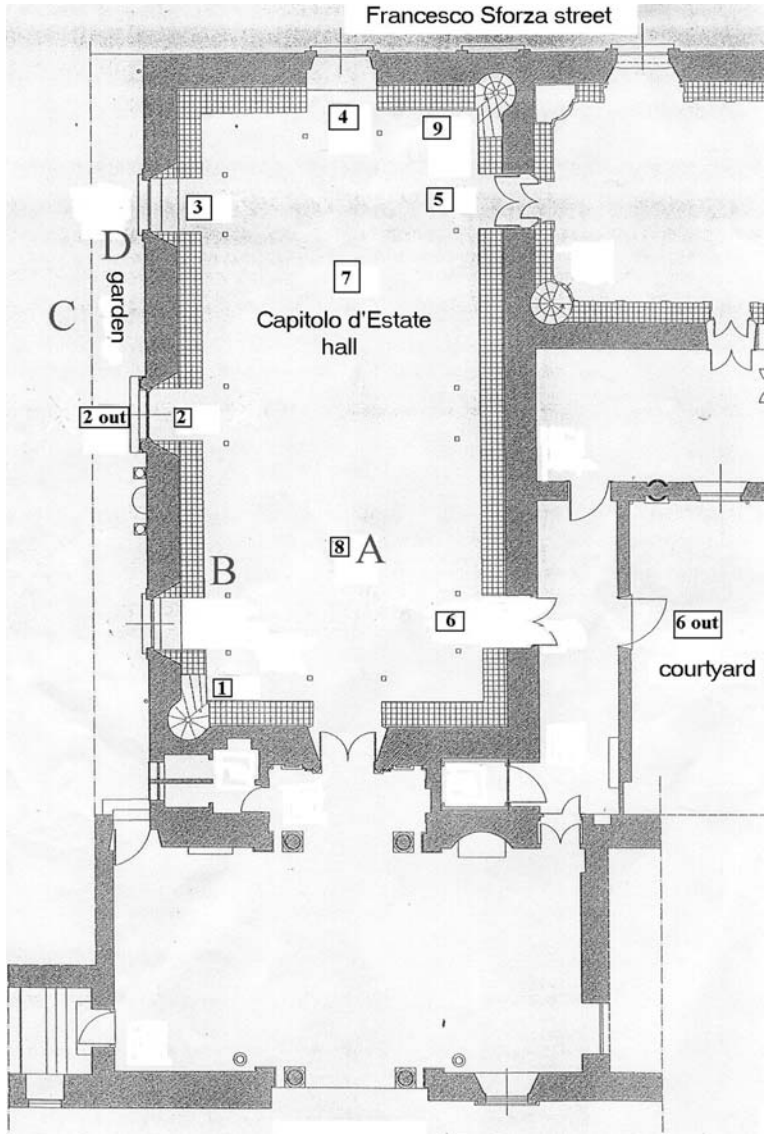

Fig. 1 Capitolo d'Estate plan. *Numbers* indicate where the aerial sampling was carried out. *A* and *C* are the PM sampler locations and *B* and *D* the passive sampler locations

aerobiological sampling was carried out in the morning (before doors and windows were opened) and one in the afternoon (after doors and windows were opened). In the basement, the two small windows were always open to help air exchange and therefore samplings in the basement were carried out at one time only. One outdoor aerobiological sampling was carried out in the garden close to position 2 (see Fig. 1, location 2 out) and one outdoor sampling in the inner courtyard close to the position 6 (see Fig. 1, location 6 out). Overall, three replicas were considered for each location.

2.2 Aerial Microbiological Contamination

Microbial groups examined were aerobic heterotrophic bacteria and fungi. The growth media were plate count agar (Merck) for bacteria and Rose Bengal chloramphenicol agar (Oxoid) for fungi. Incubation was carried out at 25°C for 2 days. Viable heterotrophic microorganisms in the Archive air were sampled using the MAS-100 microbial air sampler (single-stage sieve impactor, Merck, Switzerland) for standard 100-mm Petri dishes to collect a 60-l (outdoor) or 120-l (indoor) air sample in agreement

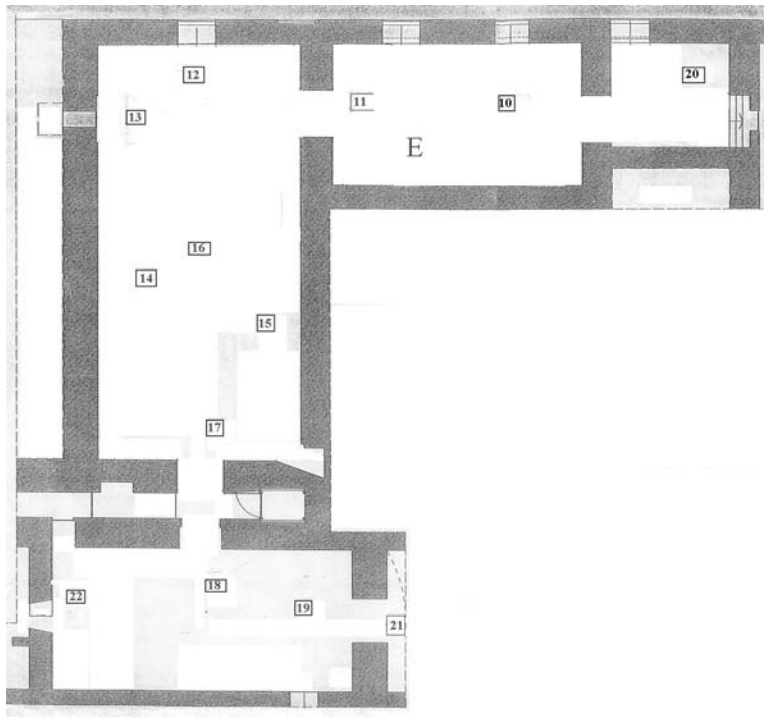

Fig. 2 Basement plan. *Numbers* indicate where the aerial sampling was carried out. *E* is the PM sampler location

with the Italian guidelines Normal 39/93 (1994). The numbers of colony forming units (CFU) in samples were calculated referring to the whole conversion table for the MAS-100 as per manufacturer's instructions.

The comparison of relative CFU/m^3 values for the heterotrophic bacteria and fungi counts in the morning (windows and doors are close) and in the afternoon (windows and doors are open) was conducted using Student's pairwise *t* test. ANOVA (one-way and post hoc double comparison tests, $p=0.05$) was used to determine the significance of the means among the microbiological contaminations in each location in the basement, in the Capitolo d'Estate hall and outdoor.

2.3 Analytical Techniques

2.3.1 Elemental Analysis

Elemental concentrations were determined by energy dispersive X-ray fluorescence (ED-XRF) technique that allowed the simultaneous detection of Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, and Pb in all samples. Minimum detection limits, at 3σ level, ranged between 2 and 20 ng cm^{-2} (for elements with $Z>22$) and between 200 and 300 ng cm^{-2} (for elements with $11<Z<22$), corresponding to about 1–10 ng m^{-3} and 100–150 ng m^{-3}, respectively for a standard 24-h sampling. The ED-XRF system, irradiation conditions, and calibration are described in detail elsewhere (Marcazzan et al. 2004). Experimental overall uncertainties were estimated to be about 10%.

2.3.2 Analysis of the Carbonaceous Fraction

Aerosol organic carbon (OC) and elemental carbon (EC) were determined by means of a thermal–optical transmittance (TOT) instrument.

The TOT instrument is a carbon analyzer by Sunset Laboratory Inc. More details on the methodology can be found in Birch and Cary (1996). The technique detection limit is 0.15 μg C/cm^2 and the precision is 5%.

The analyses were carried out on pre-fired quartz fiber filters. During the pre-firing procedure, blank filters are heated for 1 h at 700°C in order to obtain a clean support for organic carbon sampling.

2.3.3 Analysis of Ionic Components

The water-soluble inorganic fraction was determined by ion chromatography (IC). Major ionic species (NO_3^-, SO_4^{2-}, F^-, Cl^-, NO_2^-, Br^-, $C_2O_4^{2-}$, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) were quantified.

The solutions for the analysis were obtained after extraction of inorganic ions from particulate matter in an ultrasonic bath. Half of each quartz fiber filter (Pall, 2500QAO-UP) was submitted to three subsequent extractions using Milli-Q (MQ) water in order to obtain good recoveries. All the solutions (samples, standards, blanks, and eluents) were prepared using MQ water. Calibration curves were constructed for each ion. Reagent and filter blanks were analyzed for quality assurance.

More details on analysis and sample preparation are given in Fermo et al. (2006) where technique precision and detection limits were also evaluated.

3 Results and Discussion

3.1 Physical–chemical Analyses

During the sampling campaign, the values of temperature (*T*) and relative humidity (R.H.) were evaluated for a better interpretation of the physical–chemical and microbiological analyses. In the basement, the average temperature was 22°C and R.H. ranged between 46% and 50%; in the Capitolo d'Estate hall, the average temperature was in the range 19–21°C and R.H. was 35–36%.

The legislation in force in Italy (MIBAC 2001) referring to total suspended particulate and PM10 limit values in museums suggests that these values should be in the range 20–30 μg/m^3. Results obtained during PM monitoring campaigns carried out in Milan (Marcazzan et al. 2001) gave an average PM10-to-PM2.5 ratio of 0.6–0.8 (depending on the season). In this work, only PM2.5 was measured because of its longer residence times in air. In the Historical Archive, many documents, like books, are stored at the upper levels and can be damaged by chemically aggressive components of PM2.5 (e.g., acidic substances and EC). PM2.5 average mass concentration values and standard deviations (here representing the variability of the data) were 18.2±3.6 μg/m^3 and 31.3±4.2 μg/m^3 in the main hall and in the basement hall, respectively (outdoor concentration was 37.4±10.6 μg/m^3); indoor mass concentrations were generally lower than those registered outdoor. In particular, in the main hall PM2.5 concentration was about one-half than the values registered outdoor, while in the basement PM2.5 levels were high and comparable to outdoor ones. Considering these experimental results, it was possible to make the hypothesis that the limit value was likely exceeded in the basement while in the Capitolo d'Estate the particulate matter concentration was near the limit.

As can be seen in Fig. 3, the PM2.5 composition indoor was dominated by organic carbon which accounted for 42.8% and 25.6% of the mass measured in the main hall located at ground floor and in the basement, respectively. The higher OC concentration measured in the Capitolo d'Estate was likely due to the presence of archival materials made of paper. The unaccounted mass, also reported in Fig. 3, was likely explained by minor components, water, and uncertainties. The role of water was highlighted by the higher percentage of unaccounted mass in the basement (15.9%) where high relative humidity levels

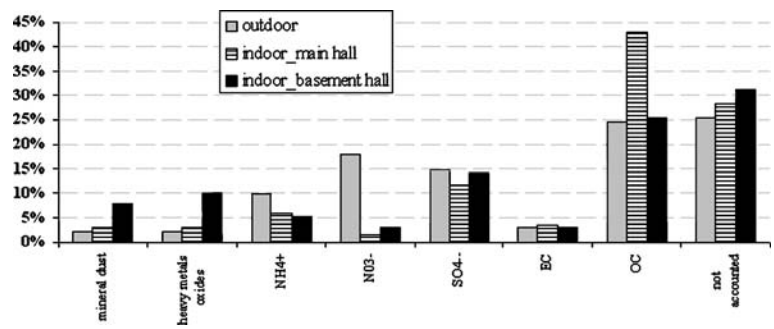

Fig. 3 Chemical mass balance related to indoor (basement and main hall) and outdoor PM2.5 measurements

were registered. Another contribution to the chemical composition taken into account was elemental carbon (EC), which was 3.9% in the main hall and 2.9% in the basement hall. EC percentage was therefore comparable in the two halls and it was also similar to the outdoor concentration. In urban environments during summertime when domestic heating is switched off, EC, generally emitted by combustion processes, can be considered a good marker for traffic. Therefore, it has a prevalent outdoor source and represents a potential pollutant for environments such archives since it contributes to the blackening of surfaces (Bonazza et al. 2005; Ghedini et al. 2006).

Important contributions to indoor PM2.5 were due to ions like SO_4^{2-} (11.8% in the main hall and 14% in the basement hall) and NH_4^+ (5–6% in both rooms); in contrast, indoor NO_3^- concentrations were generally low, accounting for 1.5% of the PM mass in the main hall and 3.2% in the basement hall. The ionic component represented one of PM major fractions. Interestingly, indoor concentrations of the mineral component (i.e., oxides of elements with mineral origin like Al, Si, Ca, and Ti) and of the heavy metal oxides component were not negligible. Together, these two components explained another 18% of the PM2.5 mass in the basement hall while their contribution in the main hall was limited to 6% (Fig. 3).

Looking at the indoor composition of traffic-related pollutants, it seemed that pollutants were transported from outdoor and subsequently accumulated indoor. In the basement hall, two small windows at street level are kept open to help air penetration and this allows entrance of pollutants from outdoor. It is worth noting that metals such as iron and copper showed higher concentrations indoor (in both halls) than outdoor. It is reported in the literature (Shahani and Wilson 1987) that trace concentrations of metal catalysts, such as copper and iron, can decompose peroxide groups due to O_3 and initiate oxidation reactions that can lead to cellulose chain scission.

Unlike the other components, nitrate concentration did not increase in the basement hall; this result might be due to the abundance of coarse (2.5 μm$<d_{ae}<$ 10 μm) nitrate particles instead of fine particles. In the coarse mode, nitrate generally originates from the reaction on pre-existing particles (e.g., reaction of HNO_3 and $CaCO_3$ as described in Yao et al. 2003). Moreover, the high humidity level measured in the basement hall might also cause the hygroscopic increase in the size of particles containing NO_3^-; thereby, if nitrate particles, after their increase in size, are included in the coarse mode, they are not anymore detected in PM2.5 (only PM2.5 fraction was measured in this work).

PM ionic component has been recently deeply studied in an archaeological museum (Mouratidou and Samara 2004) where sulfate was also found to be the dominant ion. In our case, high SO_4^{2-} indoor concentrations were probably due to external penetration because the indoor concentrations are lower than the outdoor ones (see Fig. 3). Comparing chemical indoor and outdoor composition, the largest differences were observed for nitrates, whose percentage in PM2.5 outdoor mass was 17.9%.

The elemental concentrations in the main hall were lower than those measured outdoor in agreement with the mass concentration behavior. In the basement hall, both absolute and relative elemental concentrations in ng/m^3 were enriched in respect to the outdoor environment (Table 1).

Sulfate concentrations determined by IC were compared with sulfur determined by XRF. For this purpose SO_4^{2-}, XRF S values were converted into SO_4^{2-} concentrations. Taking into account both technique limits and standard deviations (here representing the variability among the samples) the mean values were in good accordance suggesting that, in these PM samples, sulfur was present as a soluble species.

Recently, the U.S. Environmental Protection Agency (EPA) has evaluated the possibility of listing acid aerosols as criteria pollutants. For each criteria pollutants, it has been established a maximum concentration above which adverse effects on human health may occur. EPA criteria pollutants such as nitrogen dioxide, ozone, and particulate matter as well as indoor pollutants (such as, for example, tobacco smoke and combustion products of biomass fuels) can increase risk for respiratory virus infections (Ciencewicki and Jaspers 2007). Acids, together with other catalysts that can be present in particulate matter (i.e., metal ions), can mediate ionic reactions of hydrolytic nature, hastening paper deterioration (Shahani and Wilson 1987). As regards libraries, some scientific investigations aimed at highlighting how the technology used to produce paper can also influence its conservation (Shahani and Wilson 1987). Actually, a paper formulated for stability should contain an alkali

Table 1 Elemental concentration (average, min–max values in ng/m^3) in PM2.5 sampled indoor (main hall, basement) and outdoor

	Outdoor ng/m^3	Indoor—main hall	Indoor—basement
Al	46 (36–55)	29 (29–30)	54 (43–65)
Si	180 (100–320)	92 (90–94)	520 (420–620)
S	1,400 (800–2,000)	900 (650–1,100)	1,400 (1,000–1,800)
Cl	53 (29–110)	14 (11–16)	18 (9–27)
K	160 (110–280)	100 (90–110)	500 (400–600)
Ca	100 (80–120)	130 (120–140)	250 (100–400)
Ti	9 (3–22)	7 (4–11)	56 (46–66)
Cr	3 (2–4)	2 (2–3)	5 (2–8)
Mn	55 (8–180)	13 (10–15)	330 (210–440)
Fe	500 (200–1,000)	300 (290–310)	1,680 (1,200–2,100)
Cu	22 (11–26)	12 (10–12)	48 (41–55)
Zn	80 (47–110)	60 (52–67)	120 (73–150)
Br	5 (3–7)	4 (3–5)	4 (4–5)
Pb	27 (19–36)	20 (19–21)	56 (41–70)

filler, such as calcium carbonate, in order to neutralize acidity. Together with other pollutants, this acidity can favor the degradation of the paper. In order to evaluate PM acidity, it was verified if ammonium concentration (expressed in nmol in 1 mg of PM) was enough to neutralize both nitrate and sulfate. The correlation curve obtained considering all the filters is shown in Fig. 4. The high slope indicated that there was some acidity not neutralized by ammonium. For each single filter, the outdoor PM samples were characterized by higher acidity values than PM indoor.

Gaseous pollutants concentration indoor (main hall, ground floor) and outdoor are reported in Table 2. Pollutants, such as O_3, NO_x, and SO_2, are hazardous for cellulose-based materials since they can cause

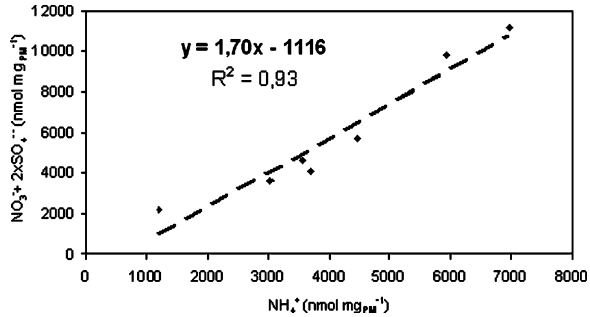

Fig. 4 Correlation between NH_4^+ and (NO_3^-+2SO_4^-) to assess acidity in PM2.5 samples

embrittlement and discoloration (Shahani and Wilson 1987). The gaseous pollutants measured in this campaign were the same suggested as indicators of the air quality in the museums (MIBAC 2001). Outdoor concentration (average 1.6 μg/m^3) as well as indoor concentration was very low in agreement with literature data claiming that European anthropogenic sulfur emissions have been steadily decreasing over the last 25 years (Vestreng et al. 2007). It is well known that NO_2 outdoor emissions derived from combustion processes and in urban areas mainly from traffic (Seinfeld and Pandis 1998). In our study, outdoor concentration was 71.3 μg/m^3. NO_2 concentrations were three times lower indoor. In contrast to SO_2, NO_2 exceeded the provisional threshold limit set at 5–10 ppb for indoor environments. This fact might be explained by the presence of an additional indoor source due to the decomposition of pyroxylin in book bindings (Brimblecombe 1990). As regards nitrogen oxide and sulfur oxide, with the presence of humidity they can easily turn into the powerful nitric acid and sulfuric acid, which are both responsible for cellulose hydrolysis.

In spite of outdoor quite high concentrations, O_3 indoor concentrations were very low in the main hall. An explanation for this result is that, within buildings,

Table 2 Gaseous pollutants concentration (μg/m^3) indoor (main hall, ground floor) and outdoor

Gaseous pollutant	INDOOR (μg/m^3)	OUTDOOR (μg/m^3)	Sampling period (days)
NO_2	28.5	71.3	14
SO_2	<0.4	1.6	14
O_3	<2	32	7

ozone is rapidly destroyed by contact with organic materials (Pavlogeorgatos 2003) such as the constituents of books and parchments stored in the Ca' Granda Archive. Ozone is a powerful oxidant and is deleterious for paper since it induces the formation of peroxide groups in the presence of moisture. Ozone can break any double bond in every carbon chain causing the formation of vertical cracks on a wide range of materials (Pavlogeorgatos 2003).

3.2 Aerial Microbiological Contamination

Table 3 shows the results related to the airborne bacteria and fungi recovered from the Capitolo d'Estate, when the doors and windows were open and close, from the basement and from outdoor locations. In the Capitolo d'Estate hall, after the windows and doors were opened, both the bacterial and fungal counts duplicated. This increase in the number of microorganisms was supported by statistical differences evidenced by the *t* test related to the two groups, morning and afternoon. The peaks might also be correlated to human saprophytes. In the Capitolo d'Estate, human activity due to both the staff and visitors is present. Thus, the increase of the number of airborne microorganisms in the Capitolo d'Estate can be explained by a morning of work and human activity. In the basement, working activity is reduced or absent. This would explain similar data obtained in the morning and afternoon.

In the afternoon, the ANOVA test showed no statistically significant differences among the nine

Table 3 Microbiological counts (CFU/m^3) in each location in the basement, in the Capitolo d'Estate hall and outdoor (garden and courtyard)

	Sampling location	Bacteria (CFU/m^3 mean±SD) Morning	Range of variability	Bacteria (CFU/m^3 mean±SD) Afternoon	Range of variability	Fungi (CFU/m^3 mean±SD) Morning	Range of variability	Fungi (CFU/m^3 mean±SD) Afternoon	Range of variability
Outdoor garden		1,290±342	921–1,596	2,733±424	2,284–3,126	1,139±335	772–1,430	2,567±236	2,338–2,809
Outdoor courtyard		1,467±482	993–1,957	2,444±564	1,830–2,940	1,117±257	898–1,399	2,444±787	1,621–3,189
Capitolo d'Estate hall	1	475±22	458–500	1,400±321	1,116–1,750	633±44	600–683	1,108±57	1,041–1,141
	2	783±38	750–825	1,358±159	1,175–1,466	522±55	475–583	1,050±50	1,000–1,100
	3	666±87	583–758	1,358±130	1,241–1,500	666±22	650–691	1,000±58	933–1,041
	4	708±65	633–750	1,191±136	1,075–1,341	658±108	550–766	1,141±30	1,108–1,166
	5	500±170	308–633	1,116±409	675–1,483	491±28	458–508	1,133±8	1,125–1,141
	6	833±112	725–950	1,025±106	933–1,141	700±88	633–800	1,266±378	841–1,566
	7	433±14	416–441	1,033±38	1,000–1,075	558±50	508–608	991±270	683–1,191
	8	433±82	366–525	1,016±414	725–1,491	608±38	575–650	1,008±109	908–1,125
	9	916±82	850–1,008	1,100±287	816–1,391	775±43	750–825	1,216±88	1,150–1,316
Basement	10	833±60	883–766			666±44	616–700		
	11	816±57	783–883			1,000±101	933–1,116		
	12	783±132	683–933			566±76	500–650		
	13	633±225	416–866			566±150	416–716		
	14	816±145	716–983			400±104	316–516		
	15	550±66	483–616			350±125	233–483		
	16	650±92	566–750			650±150	500–800		
	17	450±109	350–566			583±33	550–616		
	18	866±44	833–916			850±152	683–983		
	19	1,750±404	1,316–2,116			850±28	833–883		
	20	1,300±16	1,283–1,316			1,216±88	1,116–1,283		
	21	1,450±450	983–1,883			1,416±208	1,200–1,616		
	22	650±275	366–916			666±225	483–933		

SD standard deviation

locations of sampling of the Capitolo d'Estate hall; on the contrary, in the morning, there were statistically significant differences both for bacteria and fungi. Statistically significant differences both for bacteria and fungi were also evidenced by ANOVA test in the basement. Considering the two groups microbial counts in the hall in the morning and the basement, the *t* test value showed no statistically significant differences, whereas for the hall in the afternoon and the basement, the *t* test value indicated a statistically significant difference.

Fungal and bacterial counts outdoors (locations 2 out and 6 out) were statistically similar both in the morning and in the afternoon, and in the afternoon microbial counts were approximately double than in the morning. In addition, outdoor contamination was higher than indoor contamination in the morning. Finally, outdoor counts were statistically different from both the indoor morning and afternoon measurements for both bacteria and fungi.

In the museum standards by the Italian Ministry of Cultural Heritage (MIBAC 1998), section related to the museum indoor microflora, the following conditions are recommended: heterotrophic bacteria less than 750 CFU/m^3 and fungal counts less than 150 UFC/m^3. Fungi are generally more dangerous than bacteria for documentary heritage. Fungi are not only potential biodeteriogens but they can also cause allergies (Gambale et al. 1993). It has been demonstrated that the environmental parameters temperature and relative humidity are critical for organic material preservation. The aerobiological monitoring evidenced that fungi exceeded the threshold values both in the main hall and the basement whereas bacteria were of concern only in the basement. In the morning, bacterial counts did not exceed the limit with the only exception of location 9. In contrast, in the afternoon, bacterial counts were always above the threshold. As concerns the basement, several locations were above the limit for bacteria.

Conservation literature reports that, to prevent biodeterioration, R.H. should be lower than 65% and the temperature should be lower than 20°C (MIBAC 1998). The air quality in the Historical Archive can be considered quite good in the main hall while in the basement a remediation action is needed especially to control R.H. (Laguardia et al. 2005). If contamination in the Capitolo d'Estate hall was due to external sources, windows and doors especially in the afternoon should not be opened by the Archive staff.

The *t* test evidenced no differences between the main hall in the morning and the basement likely because they are similar in that there is no external air circulating in the room and therefore there is a common nearly stagnant flow. This would explain also the ANOVA significant differences among the different locations of sampling. If the air is stagnant, it is easier that each sampling position is characterized by different conditions. In contrast, the opening of doors and windows favors air circulation and therefore more uniform environmental conditions. This fact might explain why the ANOVA test showed no statistically significant differences for the sampled locations in the afternoon.

4 Conclusions

Although some studies aiming at air quality monitoring have been carried out in museums, to the best of our knowledge, only few studies considering both physical–chemical and microbiological investigations have ever been performed in archives and libraries. In particular, at the Ca' Granda Archive in Milan, both in the main hall and in the basement, PM2.5 concentration and composition and criteria gaseous pollutants measurements as well as an aerobiological monitoring have been carried out. Our studies can therefore be the basis to propose sound conservation strategies and actions for a better preservation of the documents in these storage environments.

On the bases of the experimental results, we can conclude that the air quality in the Capitolo d'Estate hall is fairly good. On the contrary, the ambient conditions in the basement hall are quite worrying because of high relative humidity and PM concentration. Actually, in this hall, air stagnation favors pollutant accumulation. Our data evidenced that the microflora can potentially be the main cause of damage in the Ca' Granda Historical Archive and that the outdoor environment can be a source of contamination. The situation can be greatly improved by monitoring and controlling the ambient conditions.

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