

Indoor levels of volatile organic compounds at Florentine museum environments in Italy

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Abstract

Indoor Air Quality monitoring in cultural institutions is of particular concern to protect these places and the cultural heritage content. An indoor monitoring campaign was performed in three museums in Florence (Italy) to determine the occurrence and levels of volatile organic compounds (VOCs). VOCs of interest included BTEX (benzene, toluene, ethylbenzene, xylenes), terpenes, aldehydes, organic acids, and cyclic volatile methyl siloxanes (cVMS). The most abundant VOCs in all samples analyzed were BTEX, which were strictly related to the traffic source, followed by siloxanes and terpenes. Among BTEX, toluene was always the most abundant followed by xylenes, ethylbenzene, and benzene. cVMS in exhibition rooms with the presence of visitors showed higher values compared to samples collected when the museums were closed. Terpenes showed not only the influence of vegetation-biogenic sources surrounding a museum but could also be related to the wood used for the construction of showcases and furniture and the use of cleaning products. Data obtained also showed the presence of organic acids and aldehydes whose source can be traced back to exhibits themselves and wood-based furniture. Assessing the levels of organic acids in museums is important because, over time, it can cause deterioration of the artifacts.

KEYWORDS

BTEX, cultural heritage, indoor air quality, museum environments, volatile organic compounds

1 | INTRODUCTION

Considering that humans spend over 85% of their time indoor, in the last two decades various studies worldwide have focused their attention to monitoring the Indoor Air Quality (IAQ) of schools, offices, hospitals, shops, restaurants, gyms, etc, and the effects that it may have on materials and human health.¹⁻¹³

There are various sources responsible for releasing pollutants into the indoor atmosphere which are prevalently related to

building materials and equipment, products for cleaning, conserving and restoring, bio-contaminants, outdoor pollution, and combustion processes.¹⁴ The effects that air pollution and weathering conditions may have on buildings and artifacts of important artistic and historic value located outdoor have been extensively investigated, whereas the degradative effects that some pollutants could have on objects conserved indoor¹⁵ need further investigations. The common indoor conservation approach consisted of placing works of art/collection in special closed showcases according to the principle "a box in a box," considered able to inhibit the degradation action induced by exogenous agents. Unfortunately, the

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efficacy of this approach was disproved by the macroscopic evidence that buildings hosting museums have not been designed or specifically tailored to protect exposed objects from atmospheric pollution and that degradation phenomena occur even in museum showcases.^{1,16,17}

The synergic effect of heating, ventilation and air conditioning systems, as well as the impact of the visitors, the indoor/outdoor air exchange, and indoor pollutants from materials used in coating or the showcases construction, may act as discernable sources of indoor pollutants. There are few studies reporting the IAQ in Italian museums and historical buildings (a summary of the main studies is reported in Table S1). A survey of the indoor microclimatic conditions (ie, temperature and relative humidity) was carried out in sixteen libraries of the University of Modena.¹¹ Chianese et al (2012) focused the attention on SO₂, NO₂, O₃, and PM₁₀ in Capodimonte Museum in Naples, to evaluate whether they comply with limits regulated by national laws.

More recently, the distribution of VOCs (mainly formaldehyde) and total particulate matter was analyzed in the atmosphere of libraries and archives in Florence (Italy),¹² in order to evaluate the IAQ and define the best conservation conditions.

In this study, the same authors have investigated the occurrence and level of VOCs, in particular, BTEX, aldehydes, terpenes, and siloxanes in various Florentine museums and evaluated the influence of parameters, such as the number of visitors, vegetation-biogenic sources, and vehicular traffic on the VOC concentration levels. Florence is well known worldwide for its cultural heritage, part of which is conserved in confined environments such as museums, libraries, churches, and other institutions. Then, a qualitative and quantitative analysis of indoor VOC pollutants is mandatory to assess proper preservation strategies that allow to slow down the degradation processes induced by VOCs.^{4,18}

2 | MATERIALS AND METHODS

2.1 | Sampling site description

Indoor air measurements were conducted at Palatine Gallery, the National History Museum and the San Marco Museum, located in the city center of Florence between April and June 2017 (Figure 1). Samples were collected during the opening and the closing time of the structures investigated (details on opening and closing days and sampling dates are reported in Table S2).

The Palatine Gallery, including the Royal Apartments, is located on the first floor of Pitti Palace (PP), which was the former residence of the Grand Dukes of Tuscany (Medici and Lorraine) and of the Italian royal family (Savoy) between 1860 and 1919. The Gallery hosts over a thousand paintings from the 16th and 17th centuries, including the largest collection in the world of Raphael's paintings, as well as paintings by Botticelli, Filippo Lippi, Tiziano, Van Dyck, Caravaggio, and Rubens. Moreover, the rooms are furnished with objects coming from the Medici, Lorena, and Savoy collections (ie,

Practical Implications

- Indoor air monitoring represents a fundamental tool to protect cultural institutions, evaluate the exposure to indoor contaminants, and help stakeholders to develop monitoring protocols.
- The levels of VOCs, microclimate parameters, and the particulate matter should be regularly monitored,
- The monitoring of VOCs together with other chemical and microbiological will allow to evaluate potential changes in the Indoor Air Quality and to ensure the preservation of works of art.

tables made by semiprecious stones, precious objects, and furniture, silk tapestries on the walls).

The Natural History Museum (NHM) hosts ancient and important collections of extraordinary scientific and naturalistic value (ie, 16th-century herbaria, precious ancient waxworks, fossil skeletons of large mammals, collections of multicolored butterflies, large tourmaline crystals, ethnic jewels of native peoples, and stuffed mummies). The museum has six sections distributed in old buildings in the city center, and four of them were included in this study: in particular, the Anthropology and Ethnology Section (NHM_AS), hosting about 15 000 ethnological items and 6100 anthropological items, with a photographic collection containing almost 26 000 prints and 7000 negatives; the Mineralogy and Lithology Section (NHM_MS) hosts about 50 000 specimens; the Geology and Paleontology Section (NHM_PS) hosts about 200 000 objects coming from private collections of noted geologists and paleontologists, of particular concern the vertebrate fossil collection (26 000 specimens) with mammal fossils from the Pliocene and Pleistocene; and finally, the Zoology and Natural History Section, best known as "La Specola" (NHM_ZS), owns a collection of over three million zoological specimens, almost 5000 of which are exposed to general public. La Specola also hosts the largest and most famous wax anatomical collection anywhere in the world.

The San Marco Museum (SMM), located in the ancient Dominican convent of San Marco, was founded in 1436, enlarged in 1437 by the architect Michelozzo, and opened to the public in 1869. This building was the focal point of the 15th-century religion and culture of Florence, hosting personalities like S. Antonino Pierozzi, bishop of Florence, Cosimo il Vecchio de' Medici, and Fra Girolamo Savonarola. In particular, the Museum hosts the largest collection of sacred art in Florence, in particular, wall-paintings done by Beato Angelico, who lived there for several years and painted the cloisters, the Chapterhouse, the forty-four cells, and the corridors of the dormitory.

The museum environments were characterized by a difference in terms of artworks, number of visitors, and rooms' volume. All the sampling sites were characterized by the absence of forced ventilation, and a natural ventilation was favored by the opening of the windows on closing days. The sampling site description and meteorological parameters (ambient air pressure, humidity, and temperature



FIGURE 1 Sampling sites located in the city center of Florence (Italy)

mean values) are reported in Table 1; sampling site building plans are reported in Figure S1.

2.2 | Experimentals

VOC sampling and analysis were carried out according to the ISO 16000-29:2014 and following the procedures described in the literature.^{6,7,12,19,20} Briefly, sampling tubes containing Tenax GR (35/60 mesh) and Graphitized Carbon Black previously conditioned (320°C for 120 minutes, then at 335°C for 30 minutes with a 100 mL/min reverse flow of high purity (99.999%) Helium-EPA method TO-17, USEPA 1997), sealed, and stored at +4°C were used for the VOC air sampling. Acetic and formic acid were simultaneously sampled with specific tubes containing Tenax TA (35/60 mesh), Carboxen 1003 (40/60 mesh), and Carboxen 1003 (40/60 mesh) previously conditioned (100°C for 15 minutes, then at 200°C for 15 minutes, then at 300°C for 15 minutes, and finally at 350°C for other 15 minutes).

Air sampling was carried out at a height of about 1.5 m above the floor in the center of the room. Personal air samples were also included to collect air samples in the breathing zone continuously, while visitors/staff were moving around the exhibition room. The air sample was drawn using a GilAir3-operated air pump (Gilian–Sensydine) at a flow rate of about 120 mL/min for 40–50 min (to a

total of 3–5 L of air) and then through two sorbent tubes in series to evaluate the breakthrough effect. The accuracy of the air sampling volume was insured by the use of an airflow meter in series with a pump and a sorbent tube.

Three air samples were collected for each sampling site, and the average concentration values have been reported in Table 2. Samples collected were analyzed by GC-TD-MS technique using an Automatic Thermal Desorber UNITY2 (Markes International) coupled with a GC/MS-system (Agilent, GC6890N–MS 5973). Samples were desorbed at 320°C for 15 minutes, and the chromatographic separation was achieved on an Agilent DB624 capillary column (60 m × 250 μm × 1.40 μm). The column parameters were as follows: temperature program: 40°C for 2 min, followed by heating to 90°C at 5°C/min (hold 2 minutes), then increased to 120°C at a rate of 8°C/min (hold 4min), and then to 220°C at 10°C/min (hold 14 minutes). A helium flow of 1.5 mL/min was used as a carrier gas. An exemplum of chromatogram was reported in Supporting information file (Figure S2).

2.3 | Quality control

In order to evaluate blank emissions and artifact formations, a total of ten freshly conditioned sorbent tubes were analyzed. Field blanks

were also collected at each sampling site and analyzed as sampled tubes. To avoid contamination of sampling tubes, special precautions were taken from the team members consisting of handling and storing tubes in a clean laboratory and avoiding using personal care products during sampling and analysis procedures. External six-point calibration curves spiked on pre-cleaned tubes with the target compounds were used for quantification analysis. The reproducibility was also evaluated by spiking in triplicate sorbent tubes with a known concentration (5 ng/ μ L) of analytes and was expressed as the relative standard deviation (RSD) for each concentration level. The

linearity was determined in a range of linear response between 2.5 and 20 ng/ μ L. Analyses were performed within 48 hours from the sample collection to avoid losses. The limit of detection (LOD) for the target analytes was determined by applying a signal-to-noise ratio of three and defined as the average of all blank concentrations plus three times the standard deviation of the blanks. The limits of detection (LOD) were in the range: 0.002–0.08 μ g/m³ for benzene, toluene, ethylbenzene, xylenes (BTEX) (Fluka Buchs, Switzerland); 0.002–0.04 μ g/m³ for aldehydes (hexanal, furfural—Tetha Corporation, PA, USA; benzaldehyde—Fluka Buchs, Switzerland); 0.006–0.04 μ g/m³

TABLE 1 Sampling site description and meteorological parameters (ambient air pressure (P), humidity (RU), and temperature (T) mean values)

Museum	Section	Site Acronym	Site Description	T (°C)	RU (%)	P (mm Hg)
Natural History Museum (NHM)	Anthropology and Ethnology Section (AES)	NMH_AES1	Wood showcase containing mummies	19.8	51.2	747.0
		NMH_AES2	Wood showcase containing fabrics	20.2	47.7	747.6
		NMH_AES3	Personal air sample	19.0	52.1	748.0
	Geology and Paleontology Section (GPS)	NMH_GPS1	Wood showcase containing ancient furnishings	20.1	53.4	754.2
		NMH_GPS2	Wood showcase, recently repainted, that contains ancient horns	20.0	50.0	756.0
		NMH_GPS3	Personal air sample	22.0	55.0	757.0
	Zoology Section "La Specola" (ZSS)	NMH_ZSS1	Wood showcase containing stuffed birds from all around the world	20.2	45.2	748.6
		NMH_ZSS2	Wood showcases containing famous and ancient waxworks (XVIII sec.)	21.0	45.0	747.2
		NMH_ZSS3	Wood showcase containing a stuffed hippopotamus (XVIII sec.) belonged to the Grand Duke of Tuscany	20.5	50	750.0
		NMH_ZSS4	Personal air sample	21.0	56	757.9
Mineralogy and Lithology Section (MLS)	NMH_MLS1	Glass showcase containing minerals from Elba Island (Tuscany)	22.4	49	749.9	
	NMH_MLS2	Personal air sample	26.1	43	750.0	
San Marco Museum (SMM)	Ground Floor	SMM_1	The Hospice Hall, where pilgrims were received, is now a gallery where many of Beato Angelico's most important panel paintings have been gathered together. They include and features the Deposition of Christ, The Last Judgement (1431), the Madonna and Child, the Annalena Altarpiece, San Marco Altarpiece, the Tabernacle of the Linaioli	22.9	49	750.0
		SMM_2	The Cloister, created by Michelozzo, houses medieval frescoes on the walls decorated by Beato Angelico	24.6	52	748.3
		SMM_3	The small Refectory, housing a bookshop and "The last supper" frescoed by Ghirlandaio (XV Century)	20.3	49	750.1
		SMM_4	Chapter House, where Fra Angelico painted a complex and allegorical Crucifixion, finished in 1442.	21.2	46	748.8
	First Floor	SMM_5	Cell # 22: this cell faces the cloister side, on the wall, there is a fresco representing the "Crucifix adored by Saint Dominic"	22.7	48	749.2
		SMM_6	Girolamo Savonarola's cell, housing documents, books, and clothes belonged to the monk	21.5	51	751.0
		SMM_7	The northern corridor, housing a masterpiece of Renaissance, the "Annunciation" frescoed by Beato Angelico	22.6	48	749.9
		SMM_8	Personal air sample	23.7	50	749.3

(Continues)

TABLE 1 (Continued)

Museum	Section	Site Acronym	Site Description	T (°C)	RU (%)	P (mm Hg)
Pitti Palace (PP)	Royal Apartments	PP_1	Queen's Bedroom: ancient furnishing, silk wall hangings and curtains and carpets from Medici and Lorena Families	22.3	50	749.8
		PP_2	Green Room: it was frescoed by Giuseppe Castagnoli in the early 19th century. It exhibits an Intarsia Cabinet from the 17th century, a collection of gilded Bronzes. The throne room was decorated for King Vittorio Emanuele II of Savoy and is characterized by the red brocade on the walls and by the Japanese and Chinese Vases (17th-18th century). In the room hang a small Allegory of Peace between Florence and Fiesole by Luca Giordano and Caravaggio's 1610 Portrait of a Knight of Malta.	23	44	745.6
	Palatine Gallery	PP_3	Room of Saturn: contains the Madonna of the chair (1516) and Portrait of Cardinal Inghirami by Raphael; it also contains an Annunciation (1528) by Andrea del Sarto, and Jesus and the evangelist (1516) by Fra Bartolomeo.	24.3	47	749.1
		PP_4	Room of Apollo: contains two paintings by Titian, a Magdalen and Portrait of an English Nobleman (between 1530 and 1540) and "Cleopatra" painted by G. Reni	24	48	750.6
		PP_5	Room of Prometheus: contains a large collection of round-shaped paintings: among them is the Madonna with Child by Filippo Lippi (15th century), two portraits by Botticelli and paintings by Pontormo and Domenico Beccafumi.	24	42	746.2
		PP_6	Room of Flora: contains paintings by Tiziano, Perugino, Allori, etc In particular, this room host "Cleopatra" painted by Perugino	26	43	748.3
		PP_7	Room of Hercules: This is a part of the Volterrano quarter with paintings by minor artists, such as Borgognone and Colzi	23	51	747.5
		PP_8	Personal air sample	25	50	750.8

for acids (acetic acid, formic acid—Sigma-Aldrich), 0.03–0.11 $\mu\text{g}/\text{m}^3$ for terpenes (α -pinene and limonene) (Sigma-Aldrich); and 0.002–0.04 $\mu\text{g}/\text{m}^3$ for cyclic volatile methyl siloxanes (cVMS) (Sigma-Aldrich). The limit of quantification (LOQ) was three times the LOD.

3 | RESULTS AND DISCUSSION

3.1 | Total volatile organic compounds (TVOCs)

Total VOC (TVOC) concentrations in the indoor environments investigated varied from 79.9 $\mu\text{g}/\text{m}^3$ (NMH_GPS3) to 222.1 $\mu\text{g}/\text{m}^3$ (NMH_ZSS1) with an average value of $131.4 \pm 37.7 \mu\text{g}/\text{m}^3$ considering all exhibition rooms (Table 2). The high standard deviation values suggest that the sampling sites are differently influenced by various sources. To have an idea of the IAQ inside the museum environments, a comparison with TVOC values was done, as suggested by Pieri and coworkers.²⁰ TVOC concentrations of 200 $\mu\text{g}/\text{m}^3$, 300 $\mu\text{g}/\text{m}^3$ and 600 $\mu\text{g}/\text{m}^3$ have been indicated as indoor environment characterized by "very good IAQ," "good IAQ," or "satisfactory IAQ," respectively.^{20–22} In this study, TVOC concentrations were all below 200 $\mu\text{g}/\text{m}^3$ indicating a very good IAQ in all the museum environments. The VOCs of interest included BTEX,

terpenes (α -pinene and limonene), aldehydes (benzaldehyde and formaldehyde), organic acids (acetic and formic acids), and cVMS, in particular, hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6). Only in three exhibition rooms of the National History Museum, Zoology and Natural History Section, the presence of 1,4-dichlorobenzene was detected, at concentrations of 34.8 $\mu\text{g}/\text{m}^3$ (NMH_ZSS1), 36.5 $\mu\text{g}/\text{m}^3$ (NMH_ZSS3), and 7.3 $\mu\text{g}/\text{m}^3$ (NMH_AES1), respectively. The presence of this compound in only three rooms may be related to the presence of stuffed animals (NMH_ZSS1 and NMH_ZSS3) and old mummies (NMH_AES1) exhibited in the showcases located in the center of the rooms, where the air samplings were performed. In fact, 1,4-dichlorobenzene is one of the ingredients in disinfection products extensively used to prevent degradation processes by insects and mushrooms.^{6,23} However, later its use was discouraged because of demonstrated adverse effects to human health.²⁴ In fact, as reported by Dawson,²⁵ its concentration level in indoor museum environments should be monitored because it may have potential effects on exhibited materials (ie, clearing of the inks, yellowing of paper materials, damaging leather materials) in years.

The most abundant VOCs were BTEX, strictly related to the traffic source, followed by siloxanes. The calculus of percentage of BTEX

comparing to the other total organic compounds constituted about 36% on average of the sum of all VOCs quantified, as also found by Cincinelli and coworkers in the indoor environments of libraries and archives in Florence.¹² The highest values were determined in the San Marco museum, located in a city center area, affected by continuous and intensive vehicular traffic.

3.1.1 | Benzene, toluene, ethylbenzene, xylenes (BTEX)

BTEX compounds have been determined in all indoor air samples analyzed, with values ranging from 25.3 $\mu\text{g}/\text{m}^3$ (NMH-AES3) to 59.1 $\mu\text{g}/\text{m}^3$ (SMM_2) for the exhibition rooms without visitors, and from 25.2 $\mu\text{g}/\text{m}^3$ (NMH_MLS1) to 74.7 $\mu\text{g}/\text{m}^3$ (SMM_6) for the exhibition rooms open to public. As expected, among BTEX, toluene was always the most abundant compound followed by xylenes, ethylbenzene, and benzene. Even if BTEX has no known to affect cultural heritage,¹⁰ they could give an indication of the urban traffic on IAQ. Following the European Directive 2002/69/EC on limit emissions of benzene (5 $\mu\text{g}/\text{m}^3$ as the annual average value in outdoor air), BTEX monitoring programs have been introduced to most of the air quality networks in Europe. In urban air, outdoor concentrations of benzene are mainly related to traffic sources and affected by seasonal and meteorological conditions, while its indoor concentrations are usually higher than the outdoor environment, because of the potential influence of outdoor sources and limited forced and natural ventilation.

According to the American Conference of Governmental Industrial Hygienists (ACGIH) which suggested Indoor Air Quality parameters of 1.6 and 8 mg/m^3 for benzene expressed as TLV-TWA and TLV-STEL, respectively, data of this study showed no relevant toxicological issues for visitors and museum employers exposed to this compound. This is confirmed by the WHO guidelines for Indoor Air Quality that report concentration values of airborne benzene associated with an excess lifetime risk of 1/10 000, 1/100 000, and 1/1000 000 of 17, 1.7, and 0.17 $\mu\text{g}/\text{m}^3$, respectively. Pearson's correlations of the BTEX concentrations showed correlations greater than $r^2 = 0.53$ with highly statistically significant at $P < .01$, suggesting that all investigated compounds had a similar primary source and dispersion pattern. The higher correlations were found between toluene and xylenes ($r^2 = 0.85$) and between ethylbenzene and xylenes ($r^2 = 0.84$), which suggested their potential origin from gasoline²⁶ (see Table 3).

The toluene/benzene (T/B) ratio, which has been extensively used as an indicator of traffic emission (T/B > 3), showed values ranging between 4.5 and 19.0, reflecting relatively fresh vehicular emission sources as supported by Cincinelli et al¹² and Caselli et al²⁷ in the urban air of Florence and Bari, respectively. The traffic source was also supported by the xylenes/ethylbenzene (X/E) ratio that exhibited relatively constant values (3.1 ± 0.4), according to vehicular traffic sources (mean value 3.5).^{25,27-29} The influence of outdoor sources to the BTEX concentrations was also evaluated by the calculation of the ratio of the indoor (I) to the outdoor

(O) air concentration of BTEX. The estimation of parameter permits to have an idea about the impact of outdoor pollution and the relative contribution of indoor sources. An I/O < 1 indicates a high contribution of outdoor sources^{12,21}; however, this ratio becomes more useful if it is applied simultaneously in several compounds with similar environmental behavior, like in this case BTEX. The average I/O was below the unity in all cases (PP: open day 0.90 ± 0.097 , closing day 0.72 ± 0.15 ; SMM: open day 0.93 ± 0.14 , closing day 0.90 ± 0.10 ; NMH: open day 0.80 ± 0.13 , closing day 0.62 ± 0.11). This result seems to confirm the presence of strong outdoor sources for BTEX.

The higher toluene concentration values with respect to the other BTEX may be related to additional sources for this VOC. In fact, its presence may be due not only to air pollution from motor vehicle exhausts, but also to the release from a variety of products used in paints and other finishes, adhesives, and personal care products, which could be present in the indoor environments.

3.1.2 | Terpenes

Terpenes, unsaturated VOCs, can be constituent of wood-based materials and essential oils derived,⁷ produced by plants biogenic activity,¹⁰ and being fundamental ingredients in cleaning formulations. α -pinene and limonene concentrations varied from 2.3 to 15.1 $\mu\text{g}/\text{m}^3$ and from 5.8 to 28.1 $\mu\text{g}/\text{m}^3$, respectively. Limonene levels were similar to those found in indoor air samples at the Museum of Capodimonte in Naples,¹⁰ but lower than those found in various European indoor environments.³⁰

The presence of terpenes in the Florentine museum environments may be due to the use of coniferous wood for the showcases or resin-rich softwoods, such as pine and spruce.^{6,7} However, wood, wood products, and coatings cannot be the principal emission sources for mono-terpenes in indoor environments where wood exhibition boxes are missing and/or the number of wood furniture is limited, as in the Palatine Gallery. In this location, air samples presented the highest terpenes concentrations probably related to the biogenic activity from the plants in the surrounding Boboli Garden, which extends from the hill behind the Pitti Palace. This hypothesis seems to be supported by the high terpene values found in the outdoor samples contemporary collected nearby Boboli Garden and Botanical Garden ($24.47 \pm 3.47 \mu\text{g}/\text{m}^3$ and $19.48 \pm 3.32 \mu\text{g}/\text{m}^3$, respectively). The similar concentration levels between indoor and outdoor samples seem to confirm the contribution of the free exchange of the air masses in these naturally ventilated environments.

3.1.3 | Cyclic volatile methyl siloxanes (cVMSs)

Cyclic volatile methyl siloxanes (cVMSs), such as D3, D4, D5, and D6, are high production volume chemicals that are used in a wide

TABLE 2 Concentrations ($\mu\text{g}/\text{m}^3$) of BTEX, cVMS, aldehydes, terpenes, organic acids, and 1,4-dichlorobenzene in the indoor air samples (O = museum open to the public; C = museum closed to the public)

	PP_1 O		PP_2 O		PP_5 O		PP_6 O		PP_8 O	
	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
Benzene	2.05	0.52	1.57	0.35	1.43	0.14	2.18	0.20	2.11	0.20
Toluene	35.69	8.88	26.22	5.99	26.93	2.49	29.25	2.71	32.23	3.03
Ethylbenzene	4.12	1.03	5.27	1.20	4.15	0.38	4.03	0.37	5.07	0.48
Xylenes	15.97	3.97	13.27	3.03	13.52	1.25	12.33	1.14	12.93	1.21
Σ BTEX	57.83	14.40	46.33	10.58	46.03	4.26	47.79	4.43	52.34	4.92
D3	2.21	0.55	1.22	0.27	2.13	0.20	2.24	0.21	4.34	0.41
D4	6.46	1.61	4.13	1.03	4.98	0.46	7.14	0.66	9.21	0.87
D5	28.96	7.21	16.47	4.10	29.67	2.75	26.70	2.47	31.34	2.94
D6	10.24	2.55	9.45	2.35	7.56	0.70	14.41	1.33	15.41	1.45
Σ Siloxanes	47.87	11.91	31.27	7.57	44.34	4.11	50.49	4.68	60.30	5.67
Pinene	15.12	3.76	13.16	3.01	9.45	0.88	13.78	1.28	14.64	1.38
Limonene	19.15	4.76	27.86	6.37	21.23	1.97	17.43	1.61	28.13	2.64
Σ Terpenes	34.27	8.53	41.02	9.37	30.68	2.84	31.21	2.89	42.77	4.02
<i>1,4 dichlorobenzene</i>										
Hexanal	0.55	0.14	0.66	0.15	0.23	0.02	0.36	0.03	0.26	0.02
Furfural	16.97	4.22	13.18	3.01	14.27	1.32	15.57	1.44	13.56	1.27
Benzaldehyde	19.44	4.84	22.15	5.06	23.80	2.20	19.62	1.82	15.77	1.48
Σ Aldehydes	36.96	9.20	35.99	8.22	38.30	3.55	35.55	3.29	29.59	2.78
Acetic Acid	2.78	0.69	4.83	1.10	3.13	0.29	1.37	0.13	0.82	0.08
Formic Acid	0.40	0.10	0.80	0.18	0.78	0.07	0.35	0.03	0.36	0.03
Σ Organic Acids	3.18	0.79	5.63	1.29	3.91	0.36	1.73	0.16	1.18	0.11
TVOCs	180.11	44.82	160.25	32.92	163.26	15.12	166.77	15.45	186.17	17.49
	SMM_7 O		NMH_AES1_O		NMH_AES2_O		NMH_GPS1_O			
	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev		
Benzene	2.01	0.19	1.48	0.33	1.46	0.14	1.69	0.39		
Toluene	34.14	3.26	24.63	5.62	25.73	2.38	25.81	5.89		
Ethylbenzene	4.09	0.39	4.25	0.97	4.29	0.40	3.35	0.76		
Xylenes	12.70	1.21	11.92	2.72	11.74	1.09	10.40	2.37		
Σ BTEX	52.94	5.05	42.27	9.64	43.22	9.86	41.25	9.42		
D3	4.28	0.41	3.01	0.69	3.54	0.33	2.98	0.68		
D4	10.34	0.99	4.58	1.05	5.18	0.48	4.75	1.08		
D5	21.37	2.04	16.14	3.68	17.19	1.59	17.60	4.02		
D6	11.18	1.07	9.03	2.06	8.41	0.78	8.53	1.95		
Σ Siloxanes	47.17	4.50	32.76	7.48	34.32	3.18	33.86	7.73		
Pinene	7.11	0.68	8.13	1.86	8.59	0.80	7.04	1.61		
Limonene	10.98	1.05	11.12	2.54	13.43	1.24	16.68	3.81		
Σ Terpenes	18.09	1.73	19.25	4.39	22.02	2.04	23.72	5.41		
<i>1,4 dichlorobenzene</i>			7.26	1.66						
Hexanal	0.43	0.04	0.45	0.10	0.24	0.02	0.55	0.12		
Furfural	10.81	1.03	12.88	2.94	20.21	1.87	10.79	2.46		
Benzaldehyde	13.42	1.28	18.78	4.29	12.45	1.15	16.78	3.83		
Σ Aldehydes	24.66	2.35	32.11	7.33	32.90	3.05	28.12	6.42		
Acetic Acid	5.40	0.52	5.45	1.24	3.90	0.36	2.73	0.62		

SMM_1 O		SMM_2 O		SMM_3 O		SMM_5 O		SMM_6 O	
Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
2.53	0.24	2.18	0.50	2.42	0.23	2.16	0.20	2.79	0.26
33.85	3.21	41.45	9.47	44.25	4.19	38.50	3.66	46.69	4.36
3.39	0.32	6.17	1.41	5.19	0.49	5.31	0.50	6.78	0.64
12.35	1.17	16.02	3.66	17.13	1.62	15.41	1.48	18.39	1.75
52.11	4.95	65.83	15.04	69.00	6.54	61.38	5.84	74.65	7.02
3.24	0.31	4.32	0.99	5.26	0.50	5.34	0.51	5.19	0.48
5.13	0.48	7.18	1.64	7.79	0.74	8.81	0.84	8.74	0.82
24.53	2.31	21.92	5.01	19.55	1.85	29.18	2.79	24.53	2.29
12.05	1.14	8.20	1.87	8.98	0.85	10.97	1.05	9.76	0.91
44.94	4.24	41.62	9.51	41.59	3.95	54.30	5.20	48.22	4.50
9.87	0.92	9.03	2.06	8.35	0.79	7.87	0.75	6.52	0.61
15.56	1.46	12.34	2.82	9.89	0.94	12.13	1.16	14.62	1.37
25.43	2.39	21.37	4.88	18.25	1.73	20.00	1.92	21.14	1.97
0.31	0.03	0.70	0.16	0.28	0.03	0.56	0.05	0.21	0.02
7.91	0.75	9.47	2.16	9.13	0.87	11.86	1.14	12.32	1.15
14.05	1.33	10.20	2.33	10.38	0.99	12.76	1.22	14.23	1.33
22.26	2.10	20.37	4.65	19.80	1.88	25.18	2.41	26.76	2.50
1.81	0.17	2.45	0.56	4.75	1.09	5.85	0.56	5.03	0.47
0.38	0.04			0.35	0.08	0.37	0.04	0.70	0.07
2.19	0.21	2.45	0.56	5.11	1.17	6.22	0.60	5.73	0.54
146.94	13.88	151.65	34.64	153.73	13.39	167.09	15.97	176.51	16.54
NMH_GPS2_O		NMH_ZSS1_O		NMH_ZSS2_O		NMH_ZSS3_O		NMSH_MLS1_O	
Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
1.57	0.15	1.82	0.42	1.89	0.18	1.51	0.34	1.34	0.13
24.60	2.35	30.97	7.07	27.40	2.63	26.41	6.03	13.67	1.30
4.79	0.46	4.38	1.00	3.15	0.30	4.68	1.07	3.07	0.29
10.34	0.99	12.53	2.86	10.06	0.96	13.82	3.15	7.09	0.68
41.33	9.43	49.70	11.34	42.58	9.72	46.42	10.60	25.17	5.74
3.40	0.32	2.81	0.64	3.42	0.78	2.58	0.59	2.78	0.63
4.84	0.46	5.64	1.29	4.68	1.07	5.01	1.14	5.23	1.19
14.24	1.36	19.83	4.53	17.53	4.00	18.43	4.21	18.16	4.14
8.15	0.78	9.76	2.23	11.14	2.54	13.24	3.02	12.47	2.85
30.62	2.92	38.04	8.68	36.77	8.39	39.26	8.96	38.64	8.82
6.15	0.59	4.23	0.97	5.15	1.18	8.24	1.88	7.51	1.71
14.50	1.38	10.90	2.49	9.17	2.09	12.53	2.86	11.80	2.69
20.65	1.97	15.13	3.45	14.32	3.27	20.77	4.74	19.31	4.41
		34.76	7.93			36.50	8.33		
0.59	0.06	0.54	0.12	0.32	0.07	0.45	0.10	0.34	0.08
12.31	1.17	18.90	4.31	16.78	3.83	13.67	3.12	14.75	3.37
21.32	2.03	24.67	5.63	23.56	5.38	19.80	4.52	22.41	5.12
34.22	3.26	44.11	10.07	40.66	9.28	33.92	7.74	37.50	8.56
2.64	0.25	4.55	1.04	4.60	1.06	5.55	1.27	1.46	0.33

(Continues)

TABLE 2 (Continued)

	SMM_7_O		NMH_AES1_O		NMH_AES2_O		NMH_GPS1_O			
	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
Formic Acid	0.42	0.04	8.16	1.86	2.20	0.20	0.63	0.14		
Σ Organic Acids	5.82	0.56	13.61	3.11	6.11	1.39	3.36	0.77		
TVOCs	148.68	14.18	147.26	33.61	138.57	12.84	130.30	29.74		
	PP_1_C		PP_2_C		PP_3_C		PP_4_C		PP_5_C	
	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
Benzene	2.23	0.21	1.56	0.15	2.10	0.20	1.54	0.15	1.79	0.17
Toluene	28.39	2.71	27.52	2.63	25.42	2.42	22.56	2.15	18.96	1.81
Ethylbenzene	4.26	0.41	4.49	0.43	3.87	0.37	3.35	0.32	3.95	0.38
Xylenes	12.39	1.18	13.62	1.30	10.11	0.96	9.34	0.89	10.52	1.00
Σ BTEX	47.27	4.51	47.19	4.50	41.50	3.96	36.79	3.51	35.22	3.36
D3	1.12	0.11	1.14	0.11	1.21	0.12	2.20	0.21	2.14	0.20
D4	3.25	0.31	3.26	0.31	3.81	0.36	3.43	0.33	2.51	0.24
D5	7.01	0.67	9.60	0.92	7.27	0.69	8.42	0.80	7.96	0.76
D6	4.28	0.41	2.85	0.27	5.67	0.54	4.83	0.46	3.72	0.35
Σ Siloxanes	15.66	1.49	16.85	1.61	17.95	1.71	18.87	1.80	16.33	1.56
Pinene	9.03	0.86	8.91	0.85	8.67	0.83	6.74	0.64	5.78	0.55
Limonene	16.43	1.57	14.65	1.40	17.85	1.70	13.89	1.32	13.64	1.30
Σ Terpenes	25.46	2.43	23.56	2.25	26.52	2.53	20.63	1.97	19.42	1.85
<i>1,4 dichlorobenzene</i>										
Hexanal	0.16	0.02	0.39	0.04	0.45	0.04	0.41	0.04	0.18	0.02
Furfural	14.96	1.43	5.67	0.54	7.81	0.74	8.54	0.81	9.56	0.91
Benzaldehyde	11.87	1.13	8.71	0.83	10.34	0.99	12.32	1.18	10.44	1.00
Σ Aldehydes	26.83	2.56	14.38	1.37	18.15	1.73	20.86	1.99	20.00	1.91
Acetic Acid	2.41	0.23	1.81	0.17	0.91	0.09	1.05	0.10	2.04	0.19
Formic Acid	0.40	0.04	0.53	0.05	0.51	0.05	0.75	0.07	0.68	0.06
Σ Organic Acids	2.82	0.27	2.34	0.22	1.42	0.14	1.79	0.17	2.72	0.26
TVOCs	118.20	11.27	104.70	9.99	106.00	10.11	99.35	9.48	93.87	8.95
	SMM_3_C		SMM_4_C		SMM_5_C		SMM_6_C		SMM_7_C	
	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
Benzene	1.53	0.35	1.87	0.43	1.68	0.38	1.75	0.40	1.56	0.36
Toluene	34.49	7.87	32.30	3.08	25.29	5.77	32.45	7.41	26.01	5.94
Ethylbenzene	5.63	1.29	4.93	1.13	4.77	1.09	4.89	1.12	3.06	0.70
Xylenes	17.27	3.94	14.68	3.35	15.08	3.44	16.67	3.80	9.81	2.24
Σ BTEX	58.92	13.45	53.78	7.98	46.82	10.69	55.76	12.73	40.44	9.23
D3	1.31	0.30	2.01	0.19	2.17	0.50	1.78	0.41	1.19	0.27
D4	4.32	0.99	5.44	1.24	3.21	0.73	3.36	0.77	2.41	0.55
D5	10.74	2.45	9.72	2.22	6.57	1.50	8.03	1.83	5.76	1.31
D6	4.06	0.93	6.98	1.59	4.89	1.12	5.97	1.36	3.19	0.73
Σ Siloxanes	20.43	4.66	24.15	5.24	16.84	3.84	19.14	4.37	12.55	2.86
Pinene	3.89	0.89	4.12	0.94	5.61	1.28	5.80	1.32	4.62	1.05
Limonene	8.11	1.85	8.41	1.92	6.43	1.47	7.24	1.65	5.89	1.34
Σ Terpenes	12.00	2.74	12.53	2.86	12.04	2.75	13.04	2.98	10.51	2.40

NMH_GPS2_O		NMH_ZSS1_O		NMH_ZSS2_O		NMH_ZSS3_O		NMSH_MLS1_O	
Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
0.50	0.05	7.33	1.67	2.49	0.57	8.43	1.92		
3.14	0.72	11.88	2.71	7.09	1.62	13.97	3.19	1.46	0.33
129.91	12.39	193.61	44.20	141.34	25.54	190.84	43.56	122.07	20.69
PP_6_C		PP_7_C		PP_8_C		SMM_1_C		SMM_2_C	
Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
1.32	0.33	1.69	0.16	1.43	0.36	1.16	0.26	1.97	0.45
16.72	4.16	19.62	4.88	17.54	4.00	26.02	5.94	35.68	8.14
2.46	0.61	3.63	0.83	3.44	0.79	3.47	0.79	4.67	1.07
7.96	1.98	9.27	2.31	11.87	2.71	12.40	2.83	16.78	3.83
28.46	7.08	34.21	7.57	34.28	7.62	43.05	9.83	59.10	13.49
1.89	0.47	2.13	0.49	1.89	0.43	1.22	0.28	1.16	0.26
2.98	0.74	3.68	0.84	2.19	0.50	2.42	0.55	2.45	0.56
8.11	2.02	7.81	1.78	5.08	1.16	8.61	1.97	9.92	2.26
2.58	0.64	4.62	1.05	3.58	0.82	2.95	0.67	6.18	1.41
15.56	3.87	18.24	4.16	12.74	2.91	15.20	3.47	19.71	4.50
9.02	2.24	5.49	1.25	7.40	1.69	4.45	1.02	3.31	0.76
12.80	3.18	17.68	1.69	18.11	4.13	9.18	2.10	7.58	1.73
21.82	5.43	23.17	1.33	25.51	5.82	13.63	3.11	10.89	2.49
0.24	0.06	0.38	0.09	0.14	0.03	0.23	0.05	0.19	0.04
9.23	2.30	6.80	1.55	9.89	2.26	7.68	1.75	9.80	2.24
11.62	2.89	9.56	2.18	12.32	2.81	13.41	3.06	15.54	3.55
20.85	5.19	16.36	3.73	22.21	5.07	21.09	4.81	25.34	5.78
1.72	0.43	1.43	0.33	0.60	0.14	0.95	0.22	1.81	0.42
0.20	0.02	0.18	0.04	0.46	0.11	0.47	0.12	0.32	0.07
1.92	0.44	1.61	0.37	1.06	0.24	1.42	0.33	2.13	0.49
88.85	22.07	93.96	14.23	95.94	21.69	94.62	21.53	117.36	26.79
NMH_AES3_C		NMH_GPS3_C		NMH_ZSS4_C		NMH_ZSS6_C		NMH_ZSS6_C	
Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
1.40	0.13	1.24	0.28	1.60	0.37	1.40	0.32	1.57	0.36
13.59	1.30	16.58	3.78	17.57	4.01	19.23	4.39	20.19	4.61
2.47	0.24	2.97	0.68	3.31	0.76	3.60	0.82	5.17	1.18
7.87	0.75	9.33	2.13	8.29	1.89	10.89	2.49	12.95	2.96
25.33	2.42	30.12	6.87	30.77	7.02	35.12	8.02	39.88	9.10
2.13	0.49	2.12	0.48	1.45	0.33	1.32	0.30	1.12	0.26
3.23	0.74	3.20	0.73	2.38	0.54	4.51	1.03	4.21	0.96
7.39	1.69	10.31	2.35	7.48	1.71	12.11	2.76	10.38	2.37
4.78	1.09	4.67	1.07	3.87	0.88	5.32	1.21	3.81	0.87
17.53	4.00	20.30	4.63	15.18	3.46	23.26	5.31	19.52	4.46
5.90	1.35	3.24	0.74	2.45	0.56	5.12	1.17	2.31	0.53
7.09	1.62	6.79	1.55	5.81	1.33	7.89	1.80	5.78	1.32
12.99	2.96	10.03	2.29	8.26	1.89	13.01	2.97	8.09	1.85

(Continues)

TABLE 2 (Continued)

	SMM_3_C		SMM_4_C		SMM_5_C		SMM_6_C		SMM_7_C	
	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
<i>1.4 dichlorobenzene</i>										
Hexanal	0.40	0.09	0.24	0.05	0.11	0.02	0.14	0.03	0.17	0.04
Furfural	7.67	1.75	7.89	1.80	8.90	2.03	5.70	1.30	3.45	0.79
Benzaldehyde	14.59	3.33	12.76	2.91	8.67	1.98	9.53	2.18	10.11	2.31
Σ Aldehydes	22.26	5.08	20.65	4.71	17.57	4.01	15.23	3.48	13.56	3.10
Acetic Acid	5.88	1.34	5.88	0.56	7.40	1.69	4.78	1.09	5.55	1.27
Formic Acid	0.15	0.03	0.77	0.18	0.21	0.05	0.25	0.06	0.70	0.16
Σ Organic Acids	6.03	1.38	6.66	1.52	7.61	1.74	5.03	1.15	6.25	1.43
TVOCs	120.03	27.40	117.99	15.55	100.99	23.05	108.34	24.73	83.48	19.05

range of applications including coating and sealing, antifoaming agents, and household and personal care products.^{19,20,31} To date, literature data on their indoor air concentrations are lacking, and increased monitoring is needed to more accurately assess their effect on human health and the environment, cultural heritage included. cVMSs were determined in all exhibition rooms with concentrations ranging from 12.6 to 60.3 $\mu\text{g}/\text{m}^3$, with an average value of $29.4 \pm 13.7 \mu\text{g}/\text{m}^3$. D5 was the dominant cVMSs ($15.1 \pm 8.1 \mu\text{g}/\text{m}^3$) followed by D6 ($7.5 \pm 3.7 \mu\text{g}/\text{m}^3$), D4 ($4.9 \pm 2.2 \mu\text{g}/\text{m}^3$), and D3 ($2.5 \pm 1.3 \mu\text{g}/\text{m}^3$), in line with the siloxane profiles reported from other authors and the known composition of personal care and cleaning products.^{12,19,20,32}

A mean value through the sample collected at each sampling site was calculated in order to evidence, in the same museum, differences between closing and opening days.

cVMS concentrations in exhibition rooms with the presence of visitors showed higher values with respect to the samples collected in the same rooms when the museums were closed to the public (see Figure 2).

This trend seems to support the hypothesis that personal care products are the principal source of cyclic siloxanes in the investigated indoor environments. In particular, concentrations of D4 and D5 have also been shown to be reflective of occupant density.³³ Moreover, the D5/D4 ratio has been recently used to determine sources of cyclic siloxanes in the environment,^{34,35} with high D5/D4 ratios suggesting point sources. The D5/D4 ratios ranged from 1.8 to 6, with an average value of 3, similar to the range 2.6-4 for indoor air samples found by Shields and coworkers.³³

3.1.4 | Aldehydes

Total aldehyde concentrations (mean value of $25.7 \pm 8.43 \mu\text{g}/\text{m}^3$) ranged from 13.7 to 38.1 $\mu\text{g}/\text{m}^3$ at art galleries and from 14.0 to 43.6 $\mu\text{g}/\text{m}^3$ at Museum of Natural History. These values were in good agreement with those found by Schieweck et al⁶ (range 20-110 $\mu\text{g}/\text{m}^3$) and Orecchio et al³⁶ (median 32 $\mu\text{g}/\text{m}^3$) in air samples collected

in storage rooms of Lower Saxony State Museum Hanover and in public environments (including the Chemistry and the Zoological Museum of Palermo), respectively.

The highest concentrations were measured at NMH_AES and NMH_ZS sections where zoological exhibits and old mummies were present (mean concentration values: $26.02 \pm 10.7 \mu\text{g}/\text{m}^3$ and $29.4 \pm 13.8 \mu\text{g}/\text{m}^3$, respectively). Moreover, the old lignocellulosic cabinets could give a further contribution to the presence of aldehydes in the atmosphere.⁶ The high levels of aldehydes in particular at NMH_ZS could be related not only to the presence of old stuffed animals placed in old and not sealed cabinets but also to the absence of air conditioning systems or artificial ventilation as observed by Orecchio et al,³⁶ at similar sampling sites in Sicily. A higher presence of visitors at NH_LMS with respect to the other NMH sections could represent an additional source of this class of compounds in the ambient air. Even Art Galleries showed a higher contribution of aldehydes in the presence of visitors (presence of visitors: PG $30.8 \pm 18.0 \mu\text{g}/\text{m}^3$ —SMM $25.6 \pm 7.3 \mu\text{g}/\text{m}^3$ —empty museum: PG $14.9 \pm 6.30 \mu\text{g}/\text{m}^3$ —SMM $18.2 \pm 6.40 \mu\text{g}/\text{m}^3$). Aldehydes, in particular benzaldehyde that is often present in personal care products (ie, flavoring and denaturant agents) or household products,^{36,37} as previously observed, represent a source of these pollutants in the indoor air.

The presence of aldehydes in indoor environments could represent, in some cases, a health concern, and international safety regulation suggested air quality guidelines especially for Furfural in indoor air.^{3,7,12,13,36,38} Actually, there are no limit values for benzaldehyde but prolonged exposure to the vapors of this compound should be avoided. The furfural values determined in this study do

TABLE 3 Correlation coefficients among BTEX at all exhibition rooms

	Benzene	Toluene	Ethylbenzene	Xylenes
Benzene	1			
Toluene	0.766	1		
Ethylbenzene	0.512	0.747	1	
Xylenes	0.527	0.852	0.841	1

NMH_AES3_C		NMH_GPS3_C		NMH_ZSS4_C		NMH_ZSS6_C		NMH_ZSS6_C	
Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev	Mean	St. Dev
0.11	0.02	0.23	0.05	0.21	0.03	0.19	0.04	0.16	0.04
5.78	1.32	7.11	1.62	7.23	1.65	4.76	1.09	5.56	1.27
9.80	2.24	6.78	1.55	8.18	1.87	9.03	2.06	8.98	2.05
15.58	3.56	14.12	3.22	15.62	3.54	13.98	3.19	14.70	3.35
3.48	0.79	3.61	0.82	4.93	1.12	2.81	0.64	3.04	0.69
2.19	0.50	0.32	0.07	5.74	1.31	1.52	0.35		
5.67	1.29	3.94	0.90	10.67	2.43	4.34	0.99	3.04	0.69
77.21	10.49	78.50	17.92	80.50	18.34	89.70	20.47	85.23	19.45

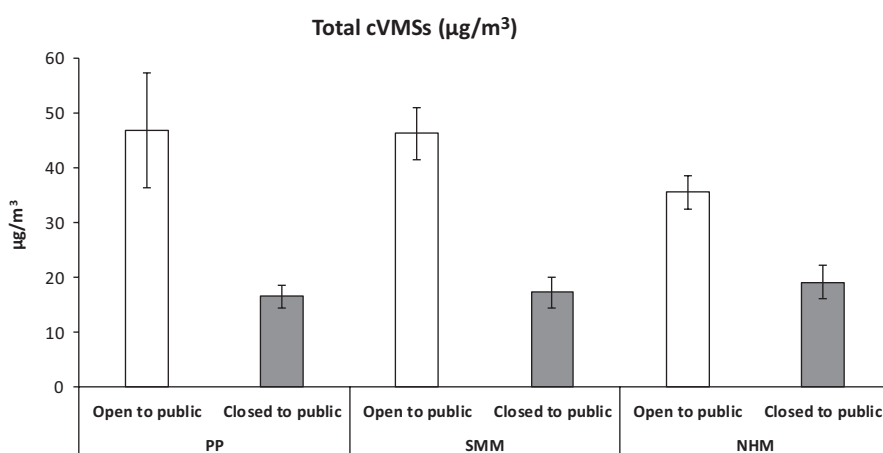


FIGURE 2 Mean cVMS (cyclic volatile methyl siloxanes) concentrations in exhibition rooms in the presence of visitors (open to public) and when the museums were closed to the public. The acronym PP (Pitti Palace), SMM (San Marco Museum), and NHM (Natural history museum) represent the main museum environment as reported in Table 2

not represent a health risk for visitors and personnel both for short- and long-term exposure (TWA suggested is 7.9 µg/m³), but the presence of these compounds should be monitored.³⁹

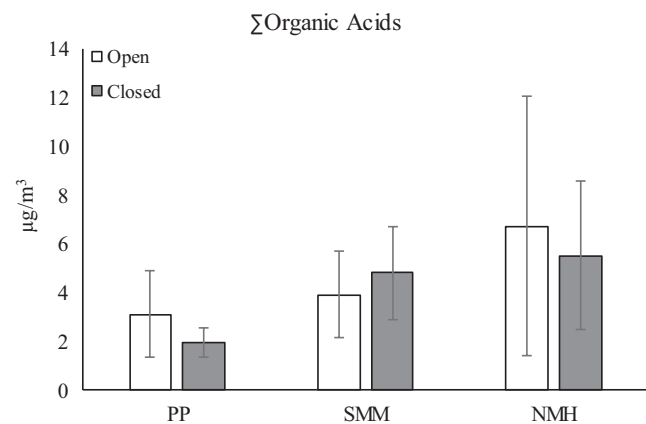


FIGURE 3 Mean organic acid concentrations (in particular acetic and formic acid) in exhibition rooms when the museum environments were open and closed to the public. The acronym PP (Pitti Palace), SMM (San Marco Museum), and NHM (Natural history museum) represent the main museum environment as reported in Table 2

3.1.5 | Organic acids

Acetic and formic acids are naturally released by wood-based materials⁴⁰ but can also be emitted from adhesives, sealants, and/or derived from degradation of cellulose acetate. Several studies identify storage in wood and wood products as the main source of acetic and formic acids; the release can increase together with the temperature.^{16,41} Moreover, the acetate and formate, that are responsible for potential corrosion effects on bronze, are contained, in some cases, in sodium-based chemicals used in conservation treatments or sodium from burial⁶; in particular, a study conducted by Schieweck et al⁶ identified a relationship between the museum air composition and the museum typology. Organic acids were determined in all samples with concentrations ranging from 1.06 to 14.0 µg/m³ with a prevalence of acetic acid; lower values were determined at NMH_MLS (modern glass showcases). In accordance with the studies conducted by Schieweck et al⁶, the highest values were detected in storage rooms of NHM museum, in particular at AES and ZSS sections where stuffed animals and old mummies are stored. In Table 2, organic acid concentration values are reported. Moreover, a higher percentage of formic acid, comparable to acetic acid values, was observed. In particular, the highest concentration of formic acid was observed at NMH_ZS3

(8.43 $\mu\text{g}/\text{m}^3$) where, periodically, some products for the conservation of the dermis of animals are used. The concentrations were quite similar in all the museum environments except for MLS section. This observation seems to indicate a potential contribution of wooden-based materials that characterize the main furniture of all the sites analyzed, to the ambient air concentration. The hypothesis of indoor sources is strengthened by the fact that there are no marked variations, unlike as observed in the case of siloxanes, among the samples collected on the opening and closing days of the museums (Figure 3). The presence of acetic and formic acids in the indoor air can represent a health concern for visitors and/or the personnel. The guidance values suggested for these compounds³⁹ are higher respect to those found in our samples (TLV-TWA: 25 and 9.4 $\mu\text{g}/\text{m}^3$ and TLV-STEL:37 and 19 $\mu\text{g}/\text{m}^3$ for acetic and formic acid, respectively) to indicate that the Indoor Air Quality is safe. However, the presence of compounds with a relevant toxicological profile should be routinely determined to preserve not only the safety of the personnel but also visitors.

4 | CONCLUSIONS

This work aimed to evaluate the occurrence and levels of VOCs in cultural heritage institutions in Florence (Italy), during hours that the museums were both open and closed to the public. BTEXs were the most abundant class of chemicals, followed by cVMSs and terpenes. The results showed that the investigated indoor environments were strongly influenced by the outdoor sources, in particular BTEX, which are related to traffic vehicles, and terpenes, which seemed to be related to biogenic sources. Even if BTEX has no known effects on cultural heritage, their monitoring is fundamental because being principally emitted by road traffic, they may offer an indication of the contribution of that source on air quality inside the museums and the air masses exchanges. Data also evidenced indoor sources that can contribute to the air concentrations of organic acids and aldehydes that can derive from exhibits themselves and wood-based furniture. It is of concern the monitoring of organic acids that, over time, can cause damage to the stored items, such as corrosion, discoloration, or deterioration. Moreover, results showed that the flow of visitors influenced the high concentrations of cVMSs determined, considering that these compounds are mainly used in personal care products and household products, such as detergents and deodorants. To date, there are not specific guidelines on the Indoor Air Quality of VOCs to preserve cultural heritage. However, the level of VOCs should be regularly monitored, together with other chemical and microbiological analyses to evaluate potential changes in the Indoor Air Quality and to ensure the preservation of works of art exposed.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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