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Article

Preliminary air quality and microclimatic conditions study in the *Santuario della Beata Vergine dei Miracoli* in Saronno (VA)

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Abstract: In the present work, microclimatic conditions (temperature (T), relative humidity (RH) and illuminance (I)) together with air quality (both aerosol particulate matter (PM) and gaseous pollutants) have been monitored to evaluate environmental conditions inside the *Santuario della Beata Vergine dei Miracoli* in Saronno (VA), a masterpiece of Italian Renaissance. For this purpose, dataloggers were used to carry out T, RH, and I measurements, whereas an optical particle counter (OPC) was employed to perform the particle count and determine the concentration of aerosol PM. Finally, diffusive passive samplers were used to determine the concentration of nitrogen dioxide (NO_2) and BTEX (benzene, toluene, ethylbenzene, and xylenes). To identify possible spatial variations, the studies were conducted at different sites and different heights in the Sanctuary. Particular focus was given to the Easter week during which liturgical services attracting large numbers of people were carried out. Also, a comparison with outdoor values was performed to highlight accumulation phenomena and other variations in the concentrations of the species. Despite indoor concentrations of pollutants and variations of the thermohygrometric parameters were generally lower compared to outdoors (for example, 5.2-15.0 μg m^{-3} versus 17.7-45.3 μg m^{-3} for NO_2), microclimatic conditions were often not in line with Italian legislation and technical standards.

Keywords: air quality, microclimate, cultural heritage, preventive conservation

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1. Introduction

In the last years, the conservation of cultural heritage has become a topic of increasing concern among the scientific community to guarantee optimal indoor conditions for safeguarding a wide range of works of art stored in museum environments, as well as historical archives [1–4].

The *Santuario della Beata Vergine dei Miracoli* was built between the XV and XVII centuries following a miraculous event and is located in Saronno, a small town in the Lombardy region of Northern Italy. Once the architecture of the sanctuary was completed at the start of the XVI century, some of the most renowned and influential artists of the time were summoned to work on the interior decorations[5]. The most famous Lombard painter of that time, Bernardino Luini, decorated the apse and presbytery of the church with some masterpieces, such as the *Marriage of the Virgin*. Instead, the dome was entirely frescoed by Gaudenzio Ferrari, another outstanding Lombard painter of the 16th century. In addition, two marvelous wooden sculptural groups, the *Deposition* (1528-1529) and the

Last Supper (1531-1532) were carved by the sculptor Andrea da Corbetta and decorated and gilded by Alberto da Lodi [5].

Poor indoor air quality and microclimatic conditions are two factors that contribute significantly to the degradation of works of art such as the ones previously mentioned [4,6,7]. For this reason, museums have imposed concentration limits on the major air pollutants, along with temperature, relative humidity and illuminance ranges that need to be respected [8,9]. However, the same regulations do not apply directly to sanctuaries and other indoor sites which attract large numbers of people acting as vehicles for the penetration of pollutants from outdoors [4,6]. Hence, a proper and thorough air quality characterization is of the utmost importance for safeguarding the works of art in such places.

Pollutants can directly damage artworks by originating yellowing or blackening phenomena and, because of their high reactivity, they can accelerate degradation processes such as corrosion and oxidation [10]. It is important to consider that the damage caused by indoor air pollutants on museum objects is not always so evident and obvious. Furthermore, we should remember that pollutants act in a synergic way together with other factors (humidity, temperature, illuminance), and often the overall effect could be even worse than that caused by any individual one [2].

While in outdoor environments the pollutants are emitted by both natural and anthropogenic sources (for example, in urban environments by fossil fuel combustion, biomass burning, industrial emissions, etc.) [11,12], in indoor environments, together with a contribution from outdoors (due to air penetration), the works of art themselves can be responsible for pollutant emissions [13] (for example, fossil finds can release some toxic compounds used in conservative treatments) [14]. Often, levels of internal air pollution, especially in urban environments, can easily reach external pollution levels, particularly when appropriate air filtering systems are not used [15,16]. Furthermore, there is a wide range of pollutants that arise from specific indoor activities [17], building materials emissions [14] or are due to the presence of visitors [3] who are responsible for particle transportation. In this regard, indoor-outdoor ratios are a useful tool for establishing the likely sources of air pollutants within buildings [18].

The most harmful gaseous pollutants to cultural heritage are NO_X, SO_2, and O_3 and volatile organic compounds (VOCs) [10,19]. These pollutants mainly originate from outdoor sources even if some indoor sources are often present [7,12]. These species are responsible for numerous negative effects on the objects stored in museum environments including, but not limited to, chromatic alterations, superficial deposits, and erosion [4,10]. NO_X and SO_2 are primary pollutants and originate mainly from traffic emissions and combustion processes [12]. Differently, ozone is a secondary pollutant that is formed predominantly in polluted areas following the reaction between molecular oxygen (O_2) and atomic oxygen (O), which in turn is generated by the photolysis of nitrogen dioxide [20]. Instead, volatile organic compounds represent an extremely diverse class of compounds, both of primary and secondary origin, with numerous outdoor and indoor sources [21]. Amongst VOCs, BTEX (benzene, toluene, ethylbenzene, and xylenes) are the compounds that are usually found in greater concentrations, especially in highly polluted areas [22]. They typically share common sources, the most important being combustion processes and industrial emissions [23].

An additional risk factor for the goods preserved in museums is represented by aerosol PM [6]. Particles dispersed in the atmosphere can be of variable size in an interval that can range from a few nanometers to tens of microns [17]. The more common fractions that are normally measured outdoors are PM10 and PM2.5 (particles with an aerodynamic diameter of less than 10 and 2.5 microns, respectively). The ultrafine fraction, on the other hand, is that consisting of particles with a diameter of less than 100 nm. The hazard linked to the particles is dependent not only on their concentration (expressed as $\mu g\ m^{-3}$) but also on their chemical composition and their size [24,25]. Normally air quality monitoring takes place outdoors (cities, background and rural sites, remote sites, etc.); nevertheless, more recently it turned out to be clear that pollutant monitoring should be carried out also in museum environments. Worrying sources of pollution can be present inside the museum and can be exacerbated by outdated air circulation systems, penetration, and accumulation from the outdoors [2,3].

Internationally, many museum institutions have established internal protocols that, although representing an important reference, are not necessarily accepted and implemented in all contexts. Following numerous studies on air pollution, threshold limits or maximum exposure levels to harmful pollutants have been assigned for outdoor environments. Indeed, pollutant concentration limits are regulated for ambient air because of the negative effects of air pollution on human health. The European Union has developed an extensive body of legislation that establishes standards and objectives for several pollutants in the air. In particular, the EU's air quality directives (2008/50/EC Directive on Ambient Air Quality and Cleaner Air for Europe and 2004/107/EC Directive on heavy metals and polycyclic aromatic hydrocarbons in ambient air) set pollutant concentrations thresholds that must not be exceeded in a given period of time. On the contrary, there are no limits regarding indoor air quality that must not be exceeded and a unique internationally-accepted protocol does not yet exist. In general, guidelines and recommendations establish basic criteria giving indications and suggestions on the levels for some of the main parameters (for example T, RH, I, gaseous pollutants, and particulate matter) [13,26], but none of these must be enforced by law.

To define a standard regarding the methods of analysis and assessment of environmental conditions suitable for the preservation of artifacts in their specific environment, the Italian Ministry of Cultural Heritage (MIBAC) has developed the D.M. 10/05/2001 "Guidance document on technical-scientific criteria and museum functioning and development standards". This document is based on several scientific studies carried out from the first half of the 1980s and illustrates the recommended levels of the main pollutants (NO_2, SO_2, PM10, O_3) and thermohygrometric parameters (T, RH, I) for the safeguard of the artifacts (Table 1). These values vary depending on the type and origin of collections; nevertheless, the guidance document recommends avoiding abrupt daily variations and cyclical day-night variations.

Table 1. Recommended microclimatic conditions in museum environments according to the D.M. 10/05/2001.

Parameter	Limit Values or Ranges
SO_2	<0.4 ppb (vol)
NO_2	<2.5 ppb (vol)
O_3	1 ppb (vol)
PM10	20-30 μg m^{-3}
Temperature	19-24 °C (painted wood) 6-25 °C (mural paintings)
Relative Humidity	45-65 % (painted wood) 45-60 % (mural paintings)
Illuminance	<150 lux (moderately light-sensitive exhibits and artifacts)

Moreover, in 1999 the Italian National Institution for Standardization published a document as part of the UNI 10829 rule "Goods of historical and artistic interest. Environmental conservation conditions. Measurement and analysis", which is aimed at the conservation of artworks located in buildings specifically designed for this purpose. Once again, this technical standard indicates recommended ranges for the main microclimatic variables (T, RH), focusing on average values and temporal gradients (Table 2).

Table 2. Recommended microclimatic conditions in museum environments according to the UNI 10829:1999 technical standard.

Parameter	Limit Values or Ranges
Temperature	19-24 °C (painted wood) 10-24 °C (mural paintings)
Maximum daily temperature variation	1.5 °C (painted wood)
Relative Humidity	50-60 % (painted wood) 45-55 % (mural paintings)
Maximum daily relative humidity variation	4 % (painted wood)

Both documents focus on the idea of preventive conservation as a way to minimize restoration work and preserve the integrity of the artifact. Along these lines, the main goal of this study was to carry out a preliminary evaluation of the potential degradation risks within the Sanctuary. This was achieved by monitoring the concentrations of the main air pollutants (NO_2, BTEX and PM) and environmental parameters (T, RH, I) using appropriate instrumentation. By performing an annual monitoring campaign, a complete picture of the Sanctuary's microclimate was achieved, highlighting possible risk factors for the works of art and the importance of carrying out similar studies in all indoor sites hosting important artifacts, not only museums.

2. Material and methods

All the sampling sites in which the campaign was conducted were chosen due to their proximity to the most important works of art of the Sanctuary. Special attention was focused on the two main lateral chapels hosting the wooden sculptural groups of the *Deposition* and *Last Supper*, since these locations are potentially the most affected by different sources of pollutants. Firstly, they are adjacent to the main altar where, during religious ceremonies, candles are lit and incense is burnt. Secondly, they are often the main attraction of weekly guided tours with numerous visitors and worshippers. Moreover, sampling at different heights was performed to evaluate the homogeneity of the conditions within the church. The specific monitoring periods for all the different parameters were determined in accordance with the Sanctuary officials and the availability of the desired sites.

2.1 Thermohygrometric parameters

Dataloggers were employed to monitor temperature, relative humidity, and illuminance during the following period: 23/02/21 – 28/08/21. Specifically, USB Mini TH dataloggers (XS Instruments, Carpi, Italy) were used to measure temperature and relative humidity. Measurement ranges were: -40/+80°C for temperature (± 0.5 °C (-40/-10)°C; ± 0.3 °C (-10/+ 80)°C) and 0/100% for relative humidity (± 3%). The resolution was 0.01°C for temperature and 0.01% for relative humidity. Instead, HOBO U12-012 dataloggers (Onset Computer Corporation, Bourne, MA, USA) were used to measure illuminance. The measurement range was 0-32300 lumens m^{-2} (± 2.5%), with a resolution of the external input channels of 0.6 mV.

A total of 7 dataloggers were used in this study (DL1-7), five measuring temperature and relative humidity (DL1-5), and two measuring illuminances (DL6-7). The instruments were placed in five different sampling sites, at three different heights in the Sanctuary (Figure 1). On the ground floor, dataloggers were placed nearby the two main lateral chapels hosting the wooden sculptural groups of the *Last Supper* and the *Deposition*. On the first floor, instruments were positioned on the two ledges directly above the chapels and, on the second floor, one datalogger was placed on the side of the dome. Table 3 summarizes the locations and parameters monitored by each one of the dataloggers.

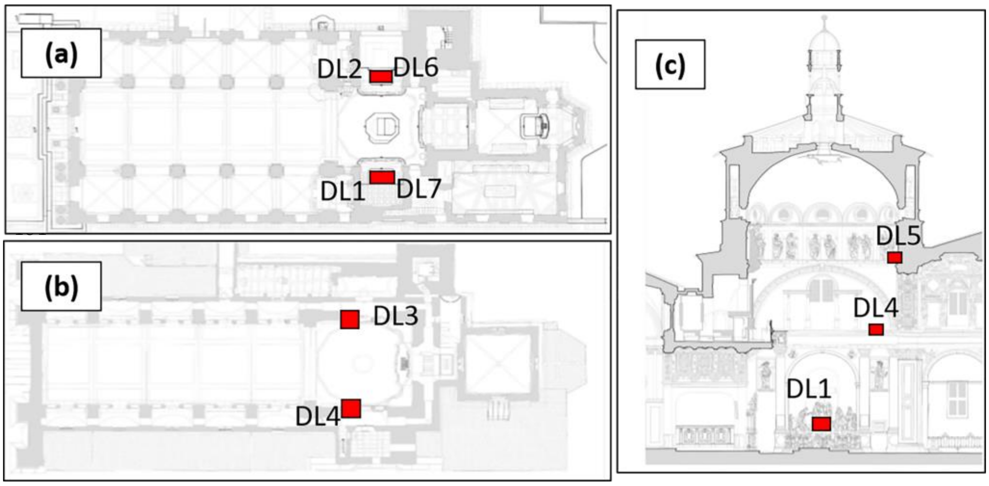

Figure 1. Floor plans and sections of the sanctuary showing the placement of data loggers: (a) ground floor plan, (b) first floor plan, (c) right-side section (*Deposition*).

Table 3. Locations and monitored parameters of the dataloggers.

Datalogger	Location	Parameters monitored
DL1	Ground floor, main lateral chapel, *Deposition*	Temperature, Relative Humidity
DL2	Ground floor, main lateral chapel, *Last Supper*	Temperature, Relative Humidity
DL3	First floor, ledge above main lateral chapel, *Last Supper*	Temperature, Relative Humidity
DL4	First floor, ledge above main lateral chapel, *Deposition*	Temperature, Relative Humidity
DL5	Second floor, dome	Temperature, Relative Humidity
DL6	Ground floor, main lateral chapel, *Last Supper*	Illuminance
DL7	Ground floor, main lateral chapel, *Deposition*	Illuminance

The choice of the parameters in relation to the sampling site was based on specific conservation issues of the locations. Temperature and relative humidity are parameters which can vary with height and therefore these parameters were monitored on three different floors of the Sanctuary. Instead, the presence of an LED lighting system at the two main lateral chapels (*Deposition* and *Last Supper*) required the monitoring of illuminance specifically in these sites.

2.2 Particulate Matter

An optical particle counter (P-Dust Monit, conTec Engineering Srl, Milano, Italy) was employed to monitor particulate matter concentrations (Figure 2).

Figure 2. P-Dust Monit positioned in one of the main chapels, nearby the sculptural group of the *Deposition*.

The aerosol particles were aspirated with a constant-flow pump, which sucks in air through a radially symmetrical probe and conveys it into a chamber where they are individually hit by a laser light beam. The energy reflected by each particle, which is proportional to its size, is measured by a high-speed photodiode that outputs both counting and dimensional characterization signals. The measurement sampling range is between 0 and 1000 μg m^{-3}, with a sensitivity of 0.1 μg m^{-3}. Measurements were performed in real-time with a detection every 60 seconds.

The particles were classified into eight different dimensional classes (0.3-0.5 μm; 0.5-0.7 μm; 0.7-1.0 μm; 1.0-2.0 μm; 2.0-3.0 μm; 3.0-5.0 μm; 5.0-10 μm; >10 μm) and PM concentrations were expressed as PM10, PM2.5 and PM1. The campaign was carried out between 02/03/2021 and 12/12/2021, in which the P-Dust Monit was placed alternatively in three different sampling sites: the two main lateral chapels (*Deposition* and *Last Supper*) and the *Choir* on the first floor (Figure 3).

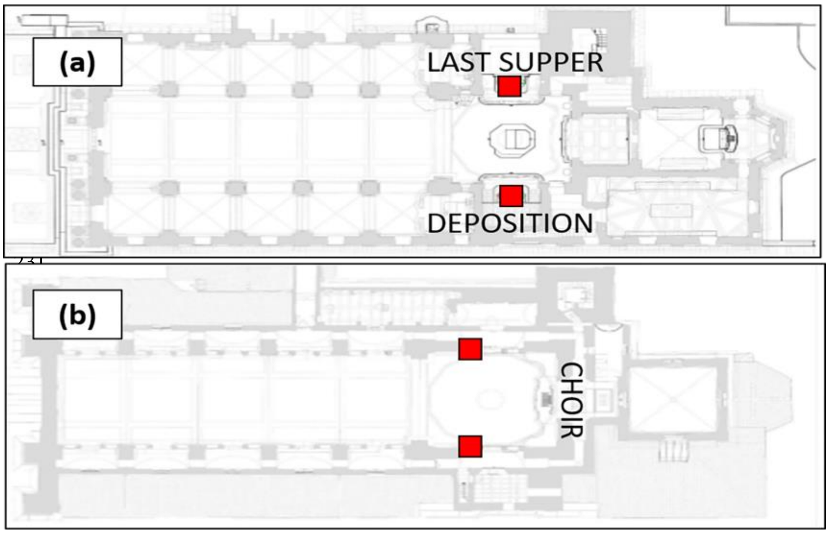

Figure 3. Planimetry of (a) the ground floor and (b) the first floor with the indication of the three sampling sites.

For all the sites, monitoring was conducted during weekdays, weekends, and other public holidays. A longer period was monitored for the *Last Supper* site in order to evaluate the impact of the Holy Week (28/03/2021 – 03/04/2021) on the pollutant concentrations. One of the two main lateral chapels was chosen to carry out sampling during these festivities for the same reasons outlined in the opening paragraph of this section.

2.3 Gaseous Pollutants (NO_2 and BTEX)

Passive samplers, RING® radial diffusive devices purchased from Aquaria (Aquaria Srl, Milan, Italy), were used for pollutant sampling (Figure 4) according to NIOSH methodologies n°1500 for BTEX and n°6014 for NO_2. The devices were positioned in the same sampling sites chosen for the monitoring of PM (Figure 3). Nitrogen dioxide was sampled from 23/03/2021 to 02/04/2021 (*Deposition* and *Last Supper*) and from 14/12/2021 to 28/12/2021 (*Deposition*, *Last Supper*, and *Choir*). Instead, BTEX were sampled from 23/03/2021 to 02/04/2021 (*Deposition*).

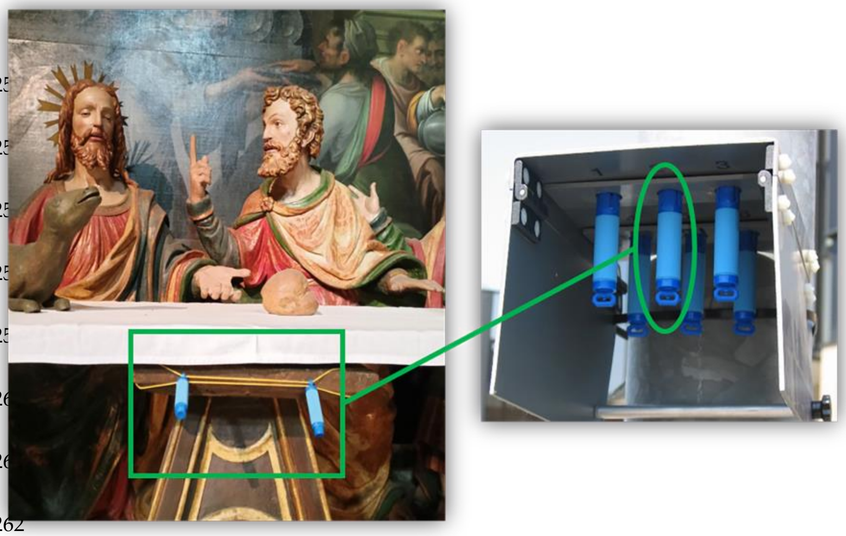

Figure 4. Diffusive passive samplers positioned in one of the main chapels, nearby the sculptural group of the *Last Supper*.

2.4 Preliminary assessment of the state of conservation of the wooden sculptures

In order to further evaluate the microclimatic conditions within the Sanctuary, a preliminary assessment of the state of conservation of the wooden sculptures was performed through a series of non-invasive analyses. X-Ray Fluorescence (XRF) was performed directly on the artifacts with the aim to identify the constituent materials of the sculptures. Differently, Scanning Electron Microscopy coupled to Energy-Dispersive X-ray spectroscopy (SEM-EDX) was used to perform morphological investigations and determine the elemental composition of the powder deposited on the works of art. The combined use of these techniques was employed to understand the possible interaction between the materials and the particulate deposit. Indeed, the evaluation of the chemical-physical interactions can reveal important information regarding the conservation status of the wooden sculptures.

XRF analysis was carried out using a Spectro xSORT portable XRF spectrometer. Acquisition parameters were the following: current intensity: 50 μA; voltage: 40 kV; acquisition time: 60 s; spot diameter: 9 mm. Measurements were carried out by referring to the UNINormal 10705 "X-ray fluorescence analysis with portable instrumentation" and 10945 "Cultural heritage: characterization of pictorial layers. Generalities on analytical techniques used" technical standards.

Instead, the particulate material deposited on the sculptures was retrieved with the use of a brush. SEM-EDX analysis was performed with a TM4000PlusII Scanning Electron Microscope (Hitachi, Tokyo, Japan) coupled with an EDX microprobe. The images were obtained using back-scattered electron (BSE) mode in low vacuum conditions, and analyses of selected point locations were also performed in the same conditions.

3. Results

3.1. Thermohygrometric parameters

In Figure 5, the average daily temperature and relative humidity values are reported for DL3, along with a comparison with outdoor values (ARPA Sensing Station, Saronno Santuario). Similar trends were observed for the other sampling sites and no significant differences in terms of absolute values were found (Figure S1, Figure S2), indicating the presence of homogenous conditions within the Sanctuary.

The trends observed in Figure 5 show a lower indoor temperature and relative humidity variability than outdoors. On the one hand, with a view to avoiding abrupt variations, the fact of not being significantly affected by external events is positive for the conservation of cultural heritage. However, compared to the recommended ranges and maximum values indicated in the UNI 10829:1999 technical standard, there were significant days in which these limits were overrun (Table 4).

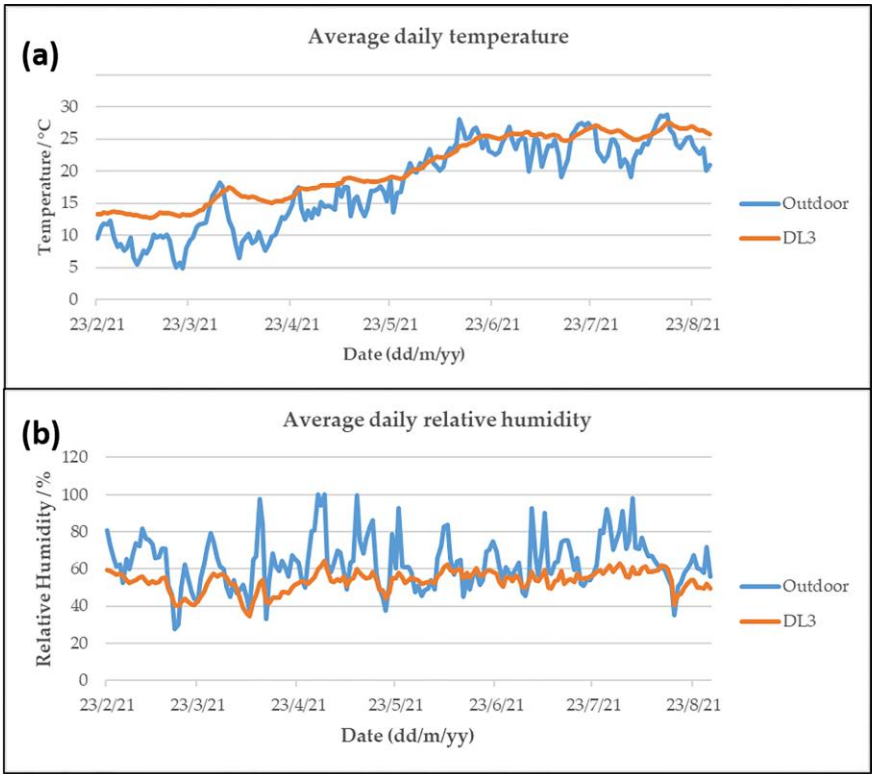

Figure 5. (a) Average daily temperature and (b) average daily relative humidity values reported for DL3 compared to outdoor trends.

Table 4. Percentage of overrun days of the limits indicated in the UNI 10829:1999 technical standard.

Parameter	Datalogger	Overrun days (painted wood) / %	Overrun days (wall paintings) / %
Average daily temperature	DL 1	88	36
	DL 2	97	39
	DL 3	89	35
	DL 4	90	47
	DL 5	88	30
Average daily relative humidity	DL 1	51	76
	DL 2	50	79
	DL 3	29	53
	DL 4	61	67
	DL 5	36	61
Maximum daily relative humidity variation	DL 1	52	-
	DL 2	57	-
	DL 3	57	-
	DL 4	55	-
	DL 5	64	-
Maximum daily temperature variation	DL 1	3	-
	DL 2	1	-
	DL 3	9	-
	DL 4	4	-
	DL 5	15	-

These results highlight stable daily temperatures and greater daily relative humidity variations within the Sanctuary. Moreover, for both parameters DL5 was associated with a greater number of days in which the respective limits were exceeded. This suggests an effect of the sampling height on temperature and relative humidity variations, indicating more stable conditions on the ground and first floor of the church. On the one hand, considering that the limits only apply to painted wood, these conditions may represent only a partial problem for the church. On the other hand, the D.M. 10/05/2001 recommends avoiding abrupt variations of all thermohygrometric parameters, independently of the type of artifact under consideration, suggesting that these values may represent an issue also for the frescoes present in the Sanctuary.

Many overrun days were also observed for absolute average temperature and relative humidity values. In these cases, the recommended ranges differed depending on the type of artifact under consideration. The temperature was highly dependent on the outdoor values (Figure 5) and therefore overruns were observed during the colder and the hotter months of the year. The window in which the temperatures complied with the values reported in the technical standard was very limited for painted wood, and greater for wall paintings, as evidenced by the percentage days of overrun; respectively, more than 87% and less than 48%. Moving on to relative humidity, once again the ranges were different for the two types of artifacts considered and, in this case, a higher number of overrun days was observed for wall paintings as opposed to painted wood. Trends were not correlated with seasonality, as was the case for temperature, and overruns were observed randomly across all the months of sampling.

The D.M. 10/05/2001 suggests similar ranges for absolute temperature and wider ones for relative humidity compared to the UNI 10829:1999 technical standard (Table 1). With regards to temperature, the same percentage of overrun days would have been observed if the results were compared to the ranges of the Ministerial Decree. Instead, this percentage would have been lower for relative humidity by making the same comparison. However, the average values observed in the monitored period frequently fell also outside the ministerial recommendations (Figure S2) confirming the fact that thermohygrometric parameters are not controlled in the ideal way for the preservation of cultural heritage within the Sanctuary.

With regards to illuminance, the Italian legislation places both wooden materials and frescoes under the same photosensitivity category (II, medium) and specifies a maximum illuminance of 150 lux. The results obtained for DL6 (*Last Supper)* and DL7 (*Deposition*) are displayed in Table 5.

Table 5. Illuminance values inside the Sanctuary.

Data Logger	Maximum illuminance / lux	Minimum illuminance / lux	Average illuminance / lux
6	32.28	11.84	19.37
7	19.37	11.84	12.84

Both maximum and average values do not exceed the indicated threshold and remain below 50 lux which is the recommended limit for highly photosensitive materials, such as silks and inks. Hence, the lighting levels within the Sanctuary are appropriate and do not represent a threat to the works of art.

3.2. Particulate Matter

Despite numerous sources stating that the fine fraction of PM is the most dangerous for the conservation of cultural heritage [25], the D.M. 10/05/2001 only states limits for the concentration of the coarser particles (PM10). Figure 6 shows the average daily concentration of PM10 detected in the three sampling sites, compared to the limit (20-30 μg m^{-3}) recommended by the ministerial decree.

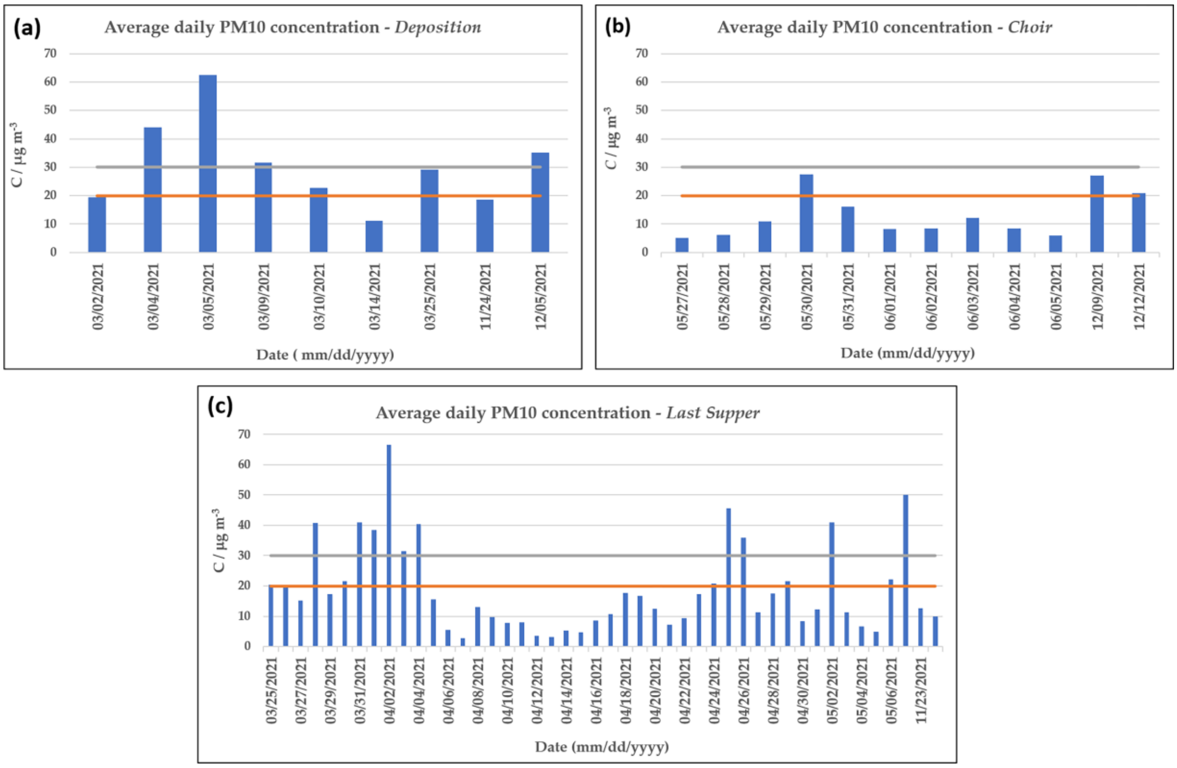

Figure 6. Average daily PM10 concentrations in the three sampling sites: a)*Deposition*, b) *Choir*, and c) *Last Supper*. The orange and grey horizontal lines indicate the two maximum concentration limits indicated in the D.M. 10/05/2001.

For most of the monitored days, PM10 concentration levels were below or within the specified range. However, occasional days of overrun were observed for the sampling sites in the two main later chapels, *Deposition* and *Last Supper*. Despite not performing the monitoring campaigns in parallel for the three sites, these preliminary results seem to suggest that particulate matter is mostly concentrated on the ground floor of the Sanctuary and is not transported quantitatively at greater heights.

Thanks to the use of an optical particle counter, more detailed information regarding the dimensional speciation of the particles was obtained. As an example, the results relating to the *Last Supper* sampling site are reported in Figure 7, but similar values were obtained also for the other two sites (Figure S3, Figure S4).

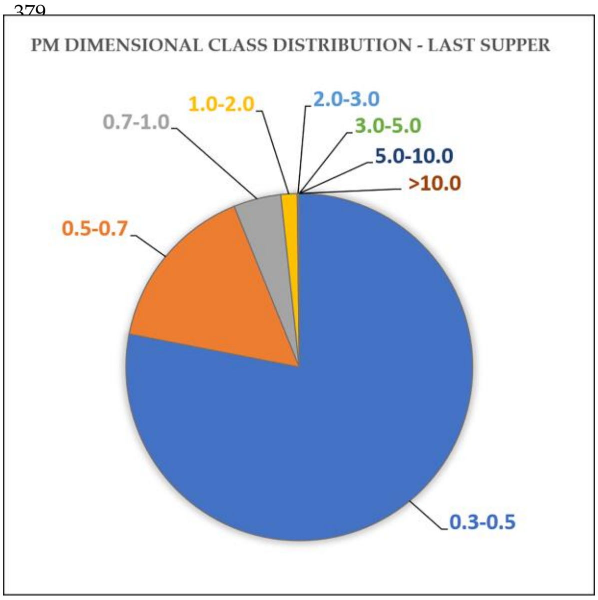

Figure 7. Particulate matter dimensional class distribution for the sampling site *Last Supper*. The ranges of the dimensional class are expressed in μm.

The results show the predominance of the smaller particles (0.3-0.5 μm) and an overall decreasing contribution to the total number of particles with increasing size. This is reflected also in the mass concentration values since PM1 (particles with an aerodynamic diameter of less than 1 μm) almost always accounts for more than 50% of the mass of PM10 (Table 6).

Table 6. PM10, PM2.5, and PM1 average daily concentrations for the sampling site *Deposition*.

Date	PM10 concentration / μg m^{-3}	PM2.5 concentration / μg m^{-3}	PM1 concentration / μg m^{-3}
03/02/2021	19.4	15.4	14.0
03/04/2021	44.1	37.6	29.7
03/05/2021	62.6	35.9	28.6
03/09/2021	31.7	30.1	29.0
03/10/2021	22.7	20.6	19.5
03/14/2021	11.0	7.2	6.5
03/25/2021	29.2	24.7	22.9

Similar ratios between the concentrations of the three fractions were also observed in the other two sampling sites (Table S1, Table S2). Considering that, even if sporadic, daily average PM10 concentrations exceeding the 30 μg m^{-3} limit have been observed for both sites on the ground floor, the fact that the fine fraction accounts for most of these particles represents a potential threat to the works of art.

In order to evaluate the origin and causes behind the presence of PM within the Sanctuary, indoor concentrations have been compared with outdoor values (Figure 8).

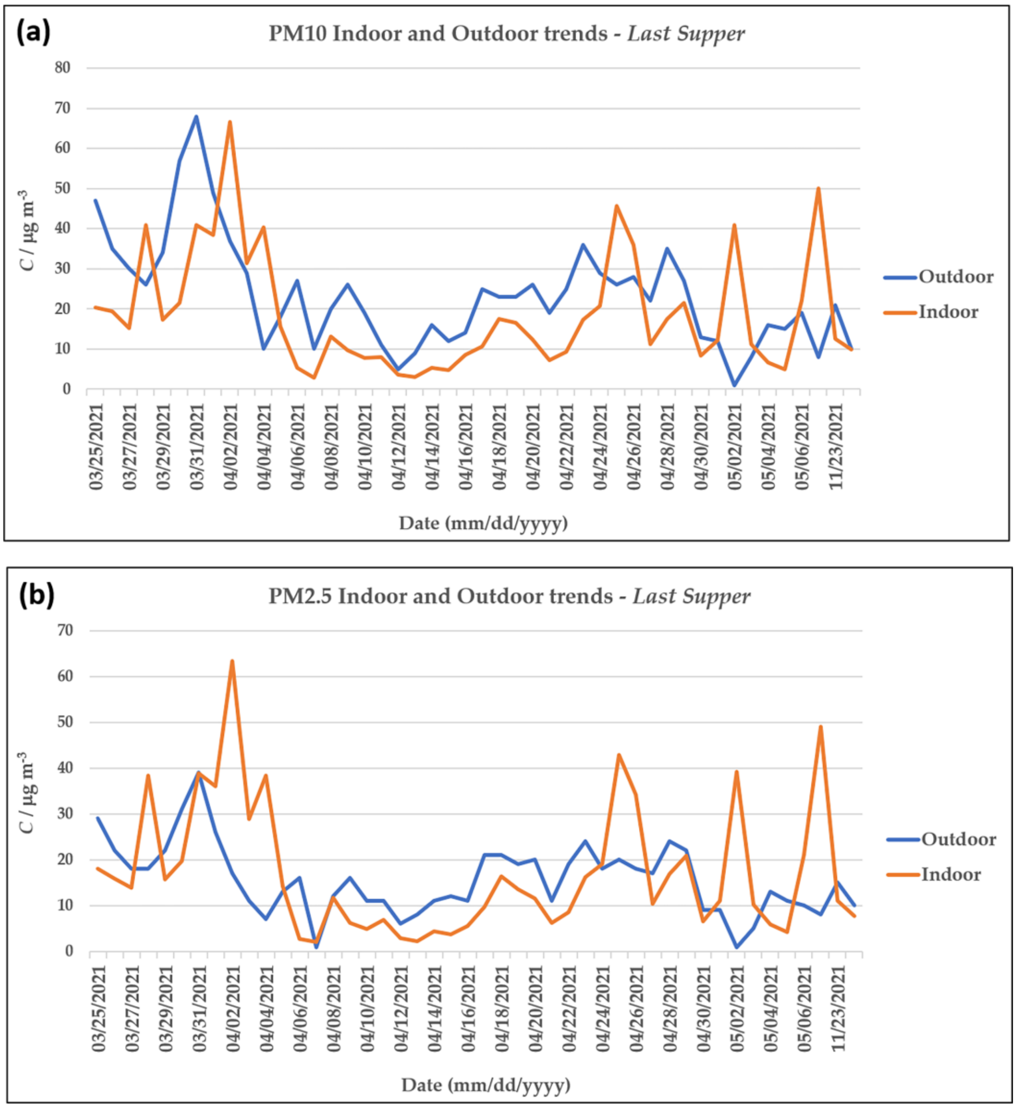

Figure 8. (a) PM10 and (b) PM2.5 indoor and outdoor trends for the sampling site *Last Supper*.

For most of the sampling periods, indoor values followed outdoor trends whilst remaining at lower concentrations, highlighting a shielding effect of the Sanctuary which prevents the penetration of a fraction of the particles. However, occasional days in which the indoor values were higher than outdoor ones were observed. Almost all these cases coincided with weekends or other public holidays, which are known to attract a greater number of visitors and worshippers. Indeed, sampling conducted during the Holy Week (28/03/2021 – 03/04/2021) highlighted numerous days in which the outdoor concentrations were overrun, for both PM10 and PM2.5.

Moreover, indoor/outdoor (I/O) ratios were calculated for weekdays and for public holidays (Figure 9). For the sampling sites *Last Supper* and *Choir,* a clear difference could be observed between the two different periods. Average I/O ratios are lower than 1 during weekdays, confirming a partial shielding effect of the Sanctuary, whereas they are higher than 1 during public holidays, indicating the presence of specific sources to the days in question such as a higher influx of people, the use of candles and incense burning. The effect is less pronounced for the sampling site *Deposition*; probably due to a minor impact of the sources in the days in which sampling was carried out for this site. Indeed, the monitoring campaigns were not carried out in parallel and the number of visitors and the use of candles and incense may vary from day to day.

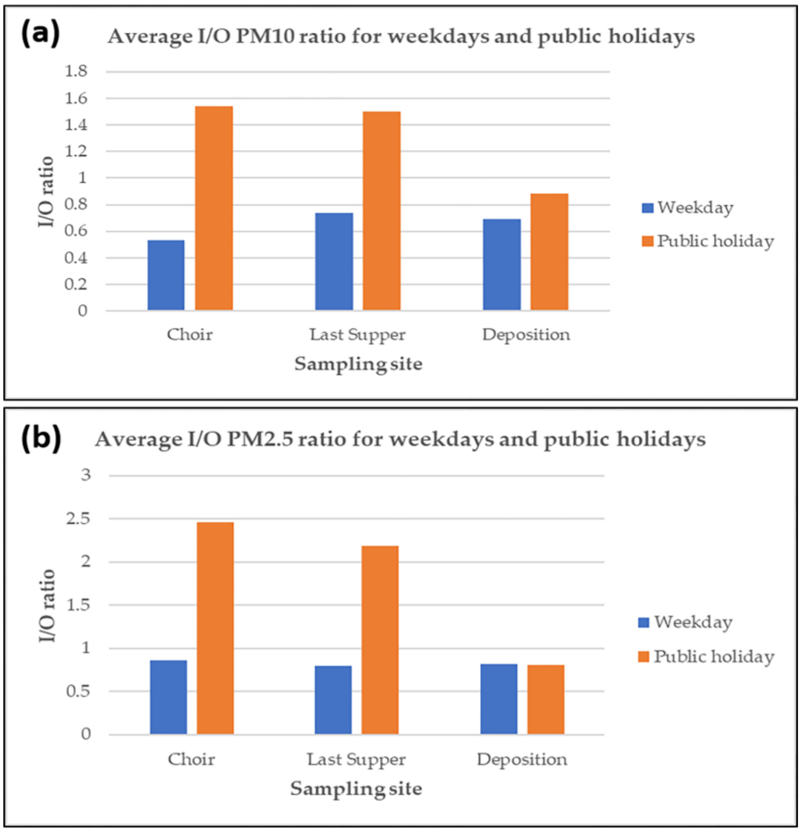

Figure 9. Average I/O ratio for a) PM10 and b) PM2.5 during weekdays and public holidays for the three sampling sites.

More in-depth analysis of the PM10 and PM2.5 values enabled also to conclude that the smaller particles are the ones that tend to accumulate indoors during public holidays and other festivities. Indeed, PM10/PM2.5 ratios calculated for both indoor and outdoor environments show that these values are comparable during weekdays, whereas during public holidays the outdoor PM10/PM2.5 ratios are often higher than indoors (Figure 10).

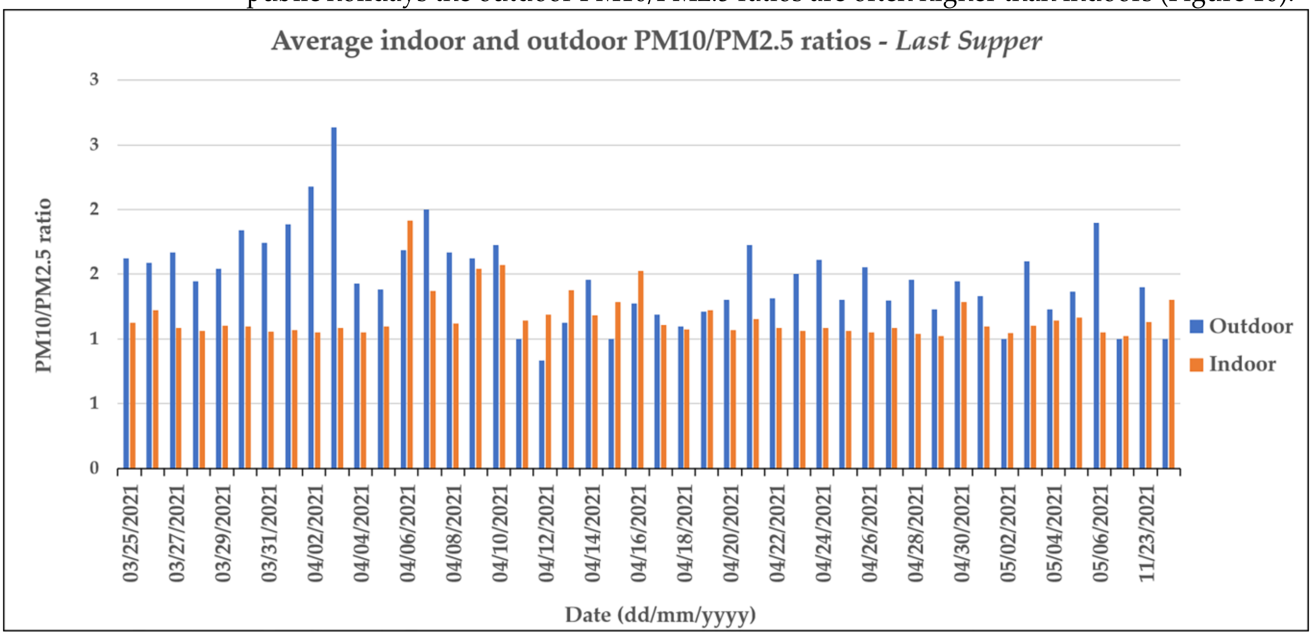

Figure 10. Average indoor and outdoor PM10/PM2.5 ratios for the sampling site *Last Supper*.

These differences were particularly evident in the *Last Supper* sampling site because the monitoring campaign was carried out partly during the Holy Week, in which numerous festivities and religious ceremonies are concentrated. Indeed, the results show that on the same days in which the indoor concentrations are higher than outdoors, the difference between the PM10/PM2.5 ratio increases in favor of the outdoors. This suggests that the transport of larger particles from outdoors to indoors is limited compared to the smaller ones, which tend to accumulate in closed spaces leading to higher average indoor daily concentrations of particulate matter.

3.3. Gaseous pollutants (NO_2 and BTEX)

The use of passive diffusive samplers allowed for the determination of average NO_2 and BTEX pollutant concentrations over the entire exposure period. Table 7 shows the results obtained for NO_2 in the two studied time frames, the recommended values indicated in the D.M. 10/05/2001, and the average outdoor concentrations.

Table 7. Nitrogen dioxide concentrations inside the Sanctuary compared with outdoor values and recommended limits.

Sampling site	Sampling period	NO_2 indoor concentration / μg m^{-3}	NO_2 outdoor concentration / μg m^{-3}	NO_2 limit (D.M. 10/05/2001) / μg m^{-3}
Last Supper	02/03/2021 – 23/03/2021	5.2	18.3	4.99
Deposition	23/03/2021 – 02/04/2021	6.7	17.7	4.89
Last Supper	14/12/2021 – 28/12/2021	15.0	45.3	5.08
Deposition	14/12/2021 – 28/12/2021	14.0	45.3	5.08
Choir	14/12/2021 – 28/12/2021	13.0	45.3	5.08

As was the case for particulate matter, also NO_2 concentrations are lower indoors compared to outdoors, once again highlighting a partial shielding effect of the Sanctuary. Despite this, the indoor concentrations registered are always higher than the limits of the Italian legislation suggesting a problematic situation for the works of art.

As opposed to nitrogen oxides, BTEX is a class of compounds that has not been extensively studied. The amount of data regarding the possible effects on cultural heritage, both in literature and in legislative documents, is lacking. However, volatile organic compounds (VOCs), including BTEX, are known to have multiple outdoor and indoor sources [22] and diagnostic ratios between the different species are useful to establish the most probable sources of pollution [21]. The preliminary results of this campaign show similar concentrations of benzene and toluene (1.6 and 1.7 μg m^{-3}, respectively), while measurable amounts of ethylbenzene and xylenes were not observed. Similar concentrations of toluene and benzene are an indication of vehicular traffic as the main source of pollution [21]. This is not surprising considering the location of the Sanctuary, which is found near the A9 highway (Figure 11)**Figure 11.** Location of the Sanctuary with respect to the A9 Highway.

3.4 Preliminary assessment of the state of conservation of the wooden sculptures

Preliminary analyses on the conditions of some wooden sculptures present in the two main chapels of the Sanctuary were carried out using X-Ray Fluorescence (XRF) directly on the works of art and Scanning Electron Microscopy coupled with Energy-Dispersive X-ray spectroscopy (SEM-EDX) on the dust deposited on the sculptures. This enabled to establish the presence of degradation phenomena originating from poor indoor air quality and microclimatic conditions. Indeed, the X-ray fluorescence spectra highlighted the presence of cinnabar (HgS) as the main pigment used to decorate the sculptures (Figure 12) and the same elements (Hg and S) were identified in the EDX spectra of the retrieved dust (Figure 13).

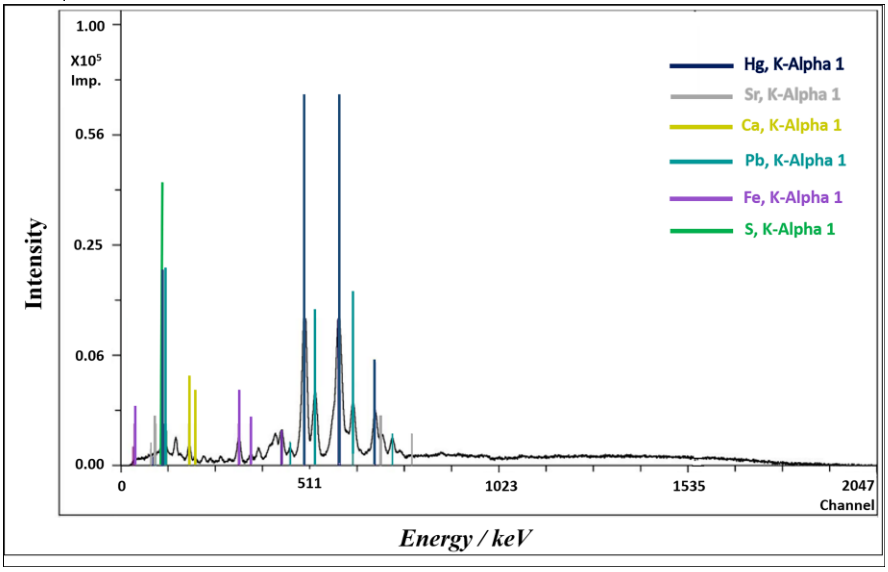

Figure 12. X-Ray Fluorescence spectrum of the wooden sculptural group.

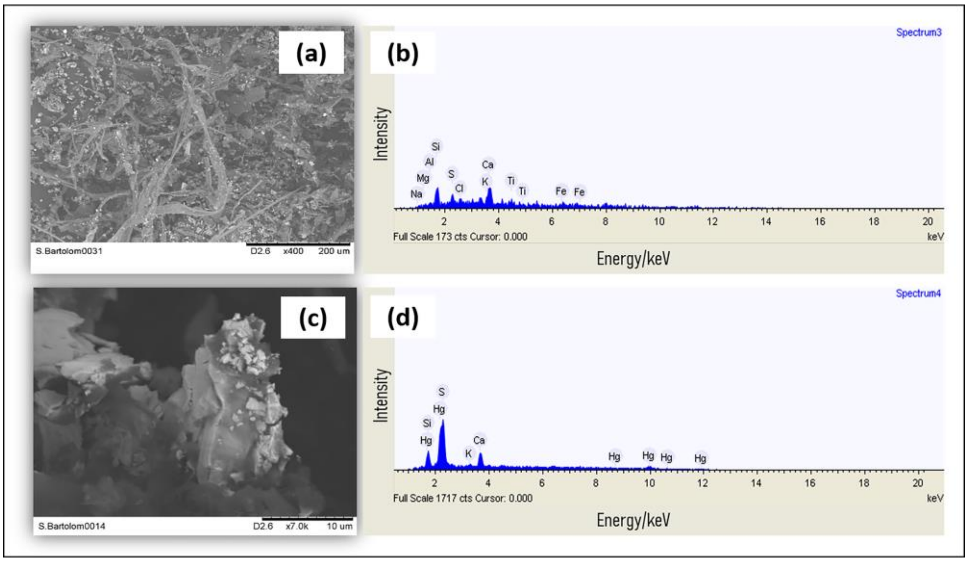

Figure 13. (a) SEM image of the dust deposited on the wooden sculptures (Area = 0.80 mm x 0.60 mm, 400x magnification). (b) EDX spectrum of the image presented in (a). (c) Point image of the dust deposited on the wooden sculptures (Area = 0.04 mm x 0.03 mm, 7000x magnification). (d) EDX spectrum of the image presented in (c). Experimental parameters: accelerating voltage = 15kV; working distance = 6500 μm; emission current = 65 mA; acquisition time = 150 s.

SEM analysis of the dust deposited on the wooden sculptures highlighted the presence of all the main constituents of atmospheric dust [27] including magnesium, sodium calcium, chlorine, silicon, potassium, and iron. However, point analyses at greater magnifications enabled the detection of mercury, which is an element that is hardly ever found in concentrations above the instrumental SEM-EDX detection limits in atmospheric dust. The presence of this element most certainly derives from the underlying substrate which is represented by the wooden statue, highlighting the partial detachment of the pictorial film.

The combined results of the two techniques indicate a poor state of conservation of the wooden sculptures. Considering that the powder was retrieved with the simple use of a brush, the fact that the same elements composing the substrate (identified thanks to the use of XRF) were also found in the deposited powder highlights the fragility of the artifact. The partial detachment of the pigment which was observed could be due to the chemical-physical interaction between the substrate and the deposited particulate matter, the degradation induced by the poor microclimatic conditions and air quality highlighted in the study, or a combination of the two.

4. Discussion

Museum objects should last for centuries or even millennia. Granted that degradation is an inevitable natural and progressive process, it can be accelerated by poor microclimatic conditions. Indeed, exposure to harmful pollutants and non-ideal thermohygrometric parameters, even if only slightly outside the recommended values, may cause substantial deterioration effects in the long run. Therefore, being able to conduct monitoring campaigns, such as the one in this study, is crucial in order to understand the conditions to which the works of art are exposed, evaluate the possible risks, and eventually act accordingly to prevent possible damage. This is often a challenging task considering the complexity and diversity of the artifacts that can be found on the same site, which renders particularly difficult the definitions of absolute optimal ranges and/or critical values for the proper conservation of cultural heritage.

Indeed, in this study, it was not uncommon to observe days of sampling in which microclimatic conditions in the Sanctuary were within the recommended values for painted wood but not for wall paintings, and vice versa. This was true for temperature and relative humidity values, highlighting the difficulty of finding a balance between proper conditions for one type of artifact and the other. However, the number of overrun days was above 29% for both parameters in terms of average daily values, reaching values up to 97% (DL2, average daily temperature, painted wood). This suggests the presence of non-ideal microclimatic conditions inside the Sanctuary, regardless of the type of artifact under consideration.

With regards to particulate matter, the overall conditions in the church were less concerning, at least in terms of the number of days in which the limits were overrun. However, indoor PM concentration values increased significantly during weekends and other public holidays. One of the reasons behind this increase may be related to a larger influx of people, which often is associated with the festivities. In fact, several other studies highlighted the role of visitors as vehicles for the transport of particles from the outdoors [4,6,7]. However, the same studies indicate that visitors tend to favor the transport of larger particles (>1 μm) [6], whereas the results of this study seem to indicate the opposite. Other possible sources of particulate matter include the burning of candles and incense, which are regularly practiced during religious ceremonies. Indeed, other studies have shown that concentrations inside churches can reach up to ten times the outdoor concentrations values, and this is particularly true for the finer fractions [28]. The indoor-outdoor differences observed in our study are less pronounced, probably due to a less extensive use of candles and incense; however, the impact on the overall indoor concentrations is still appreciable.

Museums have already started to act on the issue of visitors acting as vehicles for the penetration of pollutants by putting in place safety measures such as restricted entries and ionization chambers [29]. These measures would certainly be more difficult to implement in a Sanctuary. As long as organized tours and visits are concerned, the possibility of limiting access and separating people into smaller groups could still be a viable option.

However, the same cannot be applied to religious ceremonies such as the typical Sunday Mass, and alternatives for protecting the works of art must be found.

The direct impact of visitors on the concentration of gaseous pollutants could not be observed in this study given the type of sampling system employed; however, an overview of the concentration of gaseous pollutants (NO_2 and BTEX) was achieved. The average levels of nitrogen oxides fell within the range of values observed in literature (3-28.5 μg m^{-3}) [7,30] but were always higher than the recommended values of the Italian legislation. This is certainly a potential risk for the works of art since nitrogen oxides are known precursors of aggressive species such as nitric and nitrous acids [7]. A partial shielding effect of the Sanctuary was observed also for nitrogen oxides since the outdoor concentrations were always higher than indoor ones. Despite this, a clear dependence on outdoor pollutant levels was observed, since indoor NO_2 concentrations were higher during the winter campaign compared to the one carried out in spring. Moreover, no significant differences in terms of the ability to penetrate from outdoors was observed for the different seasons. This may be because, unlike what occurs in museums which tend to have greater pollutant penetrations during the summer [6], the air exchange rate in churches does not vary significantly between the different seasons.

With regards to BTEX, the results of this study confirm limited penetration of pollutants from outdoors, since the concentrations observed within the Sanctuary are lower than typical outdoor values of similarly polluted areas [31]. On the one hand, concentrations of benzene (1.6 μg m^{-3}) and toluene (1.7 μg m^{-3}) are lower than those found in some museum areas in Florence (1.4-2.8 μg m^{-3} for benzene and 13-35 μg m^{-3} for toluene) [19] and Naples (4.3-6.8 μg m^{-3} for benzene and 7-19 μg m^{-3} for toluene) [7]. On the other hand, these values are close to those observed in a small museum of Salerno (0.8-3.2 μg m^{-3} for benzene and 0.7-3.2 μg m^{-3} for toluene) [30]. Moreover, diagnostic ratios (toluene/benzene ratios) point to vehicular traffic as being one of the main sources of air pollution inside the Sanctuary. Therefore, despite previous results highlighting a limited penetration of pollutants, there still is a noticeable impact of outdoor sources on the air quality within the Sanctuary.

Taking into consideration the results of the entire campaign, it is possible to conclude that overall microclimatic conditions inside the Sanctuary represent a potential threat to the works of art. The use of appropriate sampling techniques and diagnostic methodologies was crucial in formulating this assessment. Indeed, the use of dataloggers enabled the continuous monitoring of the thermohygrometric parameters, which was essential in order to establish daily variations which were then compared to the normative references. Indeed, except for illuminance, all of the monitored parameters were outside the specified ranges for the proper conservation of cultural heritage. The use of an optical particle counter also allowed the continuous monitoring of particulate matter which enabled the determination of concentration peaks which were then related to specific events occurring within the Sanctuary and therefore the identification of indoor sources of pollution was possible. Moreover, the use of diffusive passive samplers enabled to complete the evaluation of air quality by sampling NO_2, which is one of the most aggressive and dangerous species for cultural heritage, and BTEX, which in turn enabled the identification of the main outdoor sources of pollution which impacted air quality also within the church. Finally, the combined used of XRF and SEM-EDX was crucial in order to identify degradation phenomena of the wooden sculptures, such as the partial detachment of the pictorial film. Moving forward the issue will be to find a way to control these parameters in an environment such as a Sanctuary. In recent years, museums have equipped themselves with HVAC (Heating, Ventilation, and Air Conditioning) systems in order to control thermohygrometric parameters within the desired ranges to ensure optimal microclimatic conditions for the works of art [32]. However, several limitations to these systems have been highlighted [33] and alternatives are currently being studied [34]. The application to a place such as this Sanctuary, considering the dimensions of the building, would be a very difficult task; without considering the cost of setting up these systems. Careful considerations will have to made in accordance with local authorities in order to find the optimal solution for the protection of the works of art. The next stages of the work will include a second, more extensive, monitoring campaign. One of the future perspectives will entail the development and testing of new temperature, relative humidity, and illuminance sensors enabling the remote and real-time visualization of the parameters. This will allow to avoid time-consuming operations such as the download and subsequent elaboration of data, and the immediate detection of values outside the recommended ranges. This could enable a quicker and more targeted identification of the events responsible for any overrun. Tests will also be conducted on new optical particle counters, designed specifically for applications in the cultural heritage field. These devices monitor the same parameters, but are silent and smaller in size, therefore of low visual impact. These characteristics make them easily adaptable in numerous settings without having to conceal parts of the work of art or disturb the visitors in any way. Moreover, continuous monitoring of the gaseous pollutants employing advanced monitoring stations will be performed in order to evaluate temporal concentration differences, which was not possible with the passive samplers employed in this study. Hopefully, once validated, all of these systems will enable a complete spatial coverage of the Sanctuary aiding the enactment of targeted measures aimed at the conservation of cultural heritage.

5. Conclusions

Numerous studies during the last thirty years have highlighted the relation between poor microclimatic conditions and the deterioration of the works of art. Consequently, extensive monitoring campaigns were conducted in environments hosting important artifacts, especially museums, and mitigations strategies are slowly being implemented. However, the research regarding alternative sites, such as churches and sanctuaries, which in many cases contain works of art of historic and artistic interest, is lacking.

With the aim to start filling this void, the current study focused on the determination of the microclimatic conditions and air quality within the *Santuario della Beata Vergine dei Miracoli*. An annual monitoring campaign was carried out measuring temperature, relative humidity, and illuminance values, along with particulate matter and gaseous pollutants concentrations. The results of this study highlighted poor microclimatic conditions with the Sanctuary, representing a potential threat for the conservation of the works of art. Aside from the specific implications for the studied site, hopefully this work will represent a watershed for the more extensive study of churches, sanctuaries and other alternative sites hosting important works of art. This may certainly represent the most important contribution of this paper to the field of cultural heritage conservation.

Further developments of this work will include the completion of the monitoring campaign. Diffusive passive samplers will be employed to study a wider range of gaseous pollutants (NO_x, SO_2, H_2S, NH_3, etc.) in order to gain a complete picture of air quality within the Sanctuary. Moreover, continuous analyzers for the study of the same pollutants will be employed in order to evaluate daily trends and variations. Finally, particulate matter gravimetric sampling will be performed in order to determine the chemical composition of the particles, which is extremely important in establishing the sources and the hazard linked to this pollutant.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: Average daily temperature trends in the Sanctuary; Figure S2: Average daily relative humidity trends in the Sanctuary; Figure S3: Particulate matter dimensional class distribution for the sampling site *Deposition*. The ranges of the dimensional class are expressed in μm; Figure S4: Particulate matter dimensional class distribution for the sampling site *Choir*. The ranges of the dimensional class are expressed in μm Table S1: PM10, PM2.5 and PM1 average daily concentrations for the sampling site *Last Supper*; Table S2: PM10, PM2.5 and PM1 average daily concentrations for the sampling site *Choir*.

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