

# Evaluation of the concentration of harmful air pollutants in a cultural heritage site by passive sampling

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**Abstract** – The monitoring of the concentration of harmful air pollutants is mandatory to prevent the deterioration of cultural heritage and, at the same time, safeguard the health of visitors and workers. The present study is focused on the determination of the concentration of specific air pollutants (nitrogen dioxide and aromatic hydrocarbons, precisely benzene, toluene, ethylbenzene and xylene) in the Sanctuary of the Beata Vergine dei Miracoli (Saronno, Italy) by passive air sampling. The results of this monitoring suggest that indoor concentration of NO<sub>2</sub> and benzene are always higher than outdoor ones. Further investigations should be performed to assess the effective concentrations to which, not only the works of art, but also people are exposed.

## I. INTRODUCTION

The degradation of cultural heritage caused by exposure to airborne and aqueous pollutants is increasingly becoming a serious problem for cultural heritage preservation [1–5]. In fact, several pollutants such as carbon dioxide (CO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), and sulfur dioxide (SO<sub>2</sub>) [6] have negative effects on buildings, artworks, sculptures [7], frescoes [8], paintings and so on. Not the least, the high concentration of certain pollutants in indoor environments, including sanctuaries, monument complexes and museum areas, can pose risks to human health [9–13].

Consequently, monitoring the concentration of pollutants that are hazardous to both human health and cultural heritage is essential. In particular, some pollutants

can be linked to vehicular traffic such as NO<sub>2</sub>, aromatic hydrocarbons (e.g. benzene, toluene, ethylbenzene, xylenes, namely BTEX), whereas others (e.g. CO<sub>2</sub> [14] and NH<sub>3</sub> [15]) are due to the presence of visitors.

Moreover, the indoor air quality was recently evaluated through the measurement of the carbon stable isotope ratio ( $\delta^{13}\text{C}$ ), a parameter employed in several fields of environmental science [16–18]. Since the isotopic carbon composition varied with the concentration of pollutants, this innovative approach allowed to easily monitor the air quality in the archeological and museum sites [14,15].

Obviously, monuments located in the historic center of large cities are the main historical buildings exposed to such degrading anthropogenic emissions. As a result, the concentration of hazardous pollutants should be periodically monitored in these locations in order to safeguard the artworks contained therein and at the same time the health of workers and/or visitors.

Atmospheric monitoring can be carried out through active or passive sampling or the use of continuous monitoring stations [19,20]. Active sampling involves the use of air aspiration systems and is carried out over short periods of time, so it is not preferable for long-term monitoring activities. On the other hand, passive sampling returns time-weighted average concentrations that are useful in air quality assessment and makes it easy to carry out monitoring over long times. Passive sampling is governed by diffusive processes [21], so it relies on the principles of Fick's first law which can be expressed as:

$$J_i = -D_i \frac{C_0 - C}{l} \quad (1)$$

where  $J_i$  is the diffusive flux,  $D_i$  is the diffusion coefficient of the considered analyte,  $l$  is length diffusive path,  $C$  is the concentration of the given analyte at the end of the diffusion layer and  $C_0$  is concentration of the analyte at the beginning of the diffusion layer [22].

Several passive sampling devices are commercially available, that differ in their geometric characteristics (diffusive path and diffusive surface) and consequently on the sampling flow rate ( $\phi_i$ ). This quantity is defined as the amount of pollutant the device samples in the unit of time, expressed in function of geometrical parameters as:

$$\phi_i = D_i \frac{S}{l} \quad (2)$$

where  $D_i$  is the diffusion coefficient of the considered analyte,  $l$  is length diffusive path, and  $S$  the diffusive surface.

The present work is focused on the determination of the concentration of different harmful air pollutants ( $\text{NO}_2$ , aromatic hydrocarbons, i.e. BTEX) in the Sanctuary of the Beata Vergine dei Miracoli di Saronno (VA) by passive sampling. Monitoring the concentration of these pollutants is critical to determine whether they can cause harm to the various artworks present in the Sanctuary, and the effect of the visitor's presence on their values.

#### A. Case study: The sanctuary of the Beata Vergine dei Miracoli (Saronno (VA) - Italy)

The sanctuary of the Beata Vergine dei Miracoli is located in the small town of Saronno, Varese, Italy (Figure 1).



Fig. 1. Front view of the sanctuary of the Beata Vergine dei Miracoli.

This marian sanctuary was erected in 1498 to give

hospitality to the simulacrum of the “Madonna dei Miracoli”, believed to be the dispenser of miraculous healings. Its construction was completed in 1525 [23]. Among the various works of art in it, the frescoes by Bernardino Luini and two large wooden sculpsures (“Cenacolo” and “Compianto sul Cristo morto”) by Andrea da Corbetta and Alberto da Lodi are most noteworthy (Figure 2).

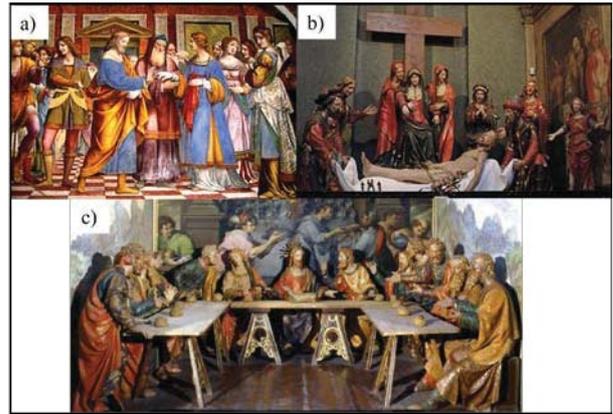


Fig. 2. a) Fresco by Bernardino Luini, “Sposalizio della Vergine”; wooden sculpsures by Andrea da Corbetta and Alberto da Lodi: b) “Compianto sul Cristo morto”, c) “Cenacolo”.

Given the artistic richness of the Sanctuary, environmental monitoring is fundamental for the preservation of artworks to limit the degradation phenomena related to poor air quality.

## II. MATERIALS AND METHODS

#### A. Air pollutants considered in this study

Pollutants monitored in this study are BTEX and  $\text{NO}_2$  according to the National Institute for Occupational Safety and Health (NIOSH) methodologies, the United States federal agency for research and prevention of work-related injury and illness. The NIOSH methodologies employed for these pollutants are the following:

- N° 1500 for BTEX;
- N° 6014 for Nitrogen Dioxide.

#### B. Passive air sampling

The air monitoring in the Sanctuary of the Beata Vergine dei Miracoli was developed using passive samplers from April to May 2022. Radial diffusive samplers were employed. In particular, RING® devices (purchased from Aquaria S.r.l., Milan, Italy) [24,25] were used as radial diffusive samplers. Depending on the considered pollutant, different sorbent materials were employed: activated carbon for BTEX, triethanolamine for  $\text{NO}_2$ .

Five sampling points were monitored by passive

sampling: three inside the Sanctuary and close to the works of art (indoor environments) and two outside it (outdoor environments). The choice of proper positions of the air quality measuring devices allows for more correct characterization of pollutant concentration [26]. For each sampling point, two diffusive samplers for each pollutant were exposed for a sampling time of 2 weeks: one from April 27 to May 11 and the other from May 11 to May 25.

### C. Analytical determinations

A spectroscopic assay on water extracts (Griess-Saltzman reaction) was employed for the detection of NO<sub>2</sub> using a Varian Cary® 50 UV-VIS spectrophotometer [27–29]. Calibration standard solutions in the concentration range 0.05-0.1 mg/mL of NO<sub>2</sub><sup>-</sup> were prepared by successive dilution of a stock solution 1 g/L made starting from NaNO<sub>2</sub>.

Chemical desorption with carbon disulfide (CS<sub>2</sub>) was used for BTEX extraction from activated carbon. Chromatographic analysis on the obtained extracts was used for BTEX determination (Agilent Technologies gas chromatography with flame ionization detector [30,31]). Calibration curves for each aromatic hydrocarbon was recorded using standard solutions in CS<sub>2</sub> prepared by dilution of a standard mix in dimethyl sulfoxide (1 g/L of each BTEX).

### D. Determination of air concentration

The air concentration in µg/m<sup>3</sup> of NO<sub>2</sub> was calculated using the following equation (3):

$$C \left( \frac{\mu\text{g}}{\text{m}^3} \right) = \frac{m_{\text{NO}_2}}{t_{\text{NO}_2}} * K \quad (3)$$

where m<sub>NO<sub>2</sub></sub> is the mass of NO<sub>2</sub> in µg, t<sub>NO<sub>2</sub></sub> is the exposure time in hours and K is a constant supplied by the passive devices' vendors, with a value of 157.82 h/m<sup>3</sup>.

For each BTEX, the air concentration (µg/m<sup>3</sup>) was determined from the equation (4):

$$C \left( \frac{\mu\text{g}}{\text{m}^3} \right) = \frac{m_{\text{BTEX}} * 10^6}{t_{\text{BTEX}} * F} \quad (4)$$

where m<sub>BTEX</sub> is the mass of each BTEX in µg, t<sub>BTEX</sub> is the exposure time in minutes and F is sampling flow rate provided by the passive devices' vendors, with values of 73, 66, 60 and 64 mL/min for benzene, toluene, ethylbenzene and xylene respectively.

## III. DISCUSSION

The air concentration of certain air pollutants such as nitrogen oxides and aromatic hydrocarbons is a critical parameter for air quality and must be monitored both in indoor and outdoor environments. In this context, it is of great interest to evaluate the concentrations of these pollutants near places of artistic and cultural interest such

as museums, art galleries, archaeological sites, national parks, temples, churches and sanctuaries. In fact, high concentrations of them can cause deterioration of the works of art, and, at the same time, have harmful effects on the health of workers and visitors. It should also be considered that the attendance of visitors can also affect the concentration of pollutants in indoor environments such as the Sanctuary of the Beata Vergine dei Miracoli.

Figures 3 and 4 show the average concentration of the considered air pollutants, expressed as µg/m<sup>3</sup>, recorded by passive air sampling in the five sampling points (both indoor and outdoor) during the sampling period of 4 weeks. The values of NO<sub>2</sub> concentration were in the range 7-22 µg/m<sup>3</sup>, with outdoor concentrations always lower than indoor ones (see Figure 3). This result is in line with the principle of accumulation of pollutants indoors due to poor aeration of these types of environments [32]. It also indicates that there are indoor sources of this pollutant, such as candle burning during religious rites.

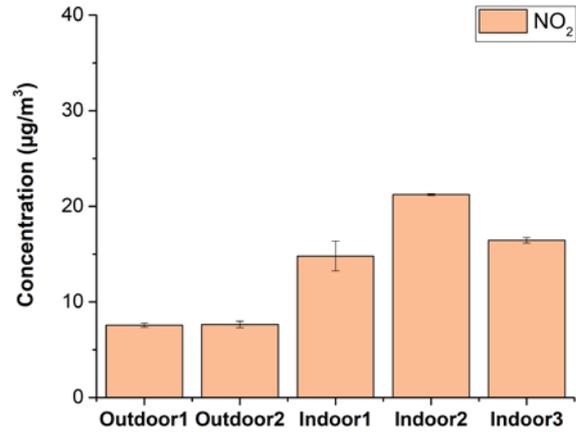


Fig.3. Air concentration of NO<sub>2</sub> (µg/m<sup>3</sup>) recorded with radial passive samplers.

The recorded values are always higher than the recommended limit values for NO<sub>2</sub> concentration in museum environments (5 µg/m<sup>3</sup>) to achieve proper conservation of artifacts [33], suggesting the need of proper strategy to improve indoor air quality. On the other hand, no concern for human health is posed since these values are lower than annual average regulatory limit (40 µg/m<sup>3</sup>) of Italian law [34]. Further data will be analysed to make a fully comparison of these results with data from the ARPA (Agenzia regionale per la protezione ambientale) Lombardy control unit. Moreover, it should be noted that it is not possible to have information on any concentration spikes during the sampling period, since passive sampling returns time-weighted average concentrations of air pollutant.

Concerning BTEX (see Figure 4), concentrations of toluene, ethylbenzene, and xylenes are similar between outdoor and indoor environments, with values in the ranges 0.2-2 µg/m<sup>3</sup>. Indeed, benzene concentrations in

indoor environments are much higher than those recorded in the outdoor ones, becoming close to the annual average regulatory limit ( $5 \mu\text{g}/\text{m}^3$ ) of Italian law [34].

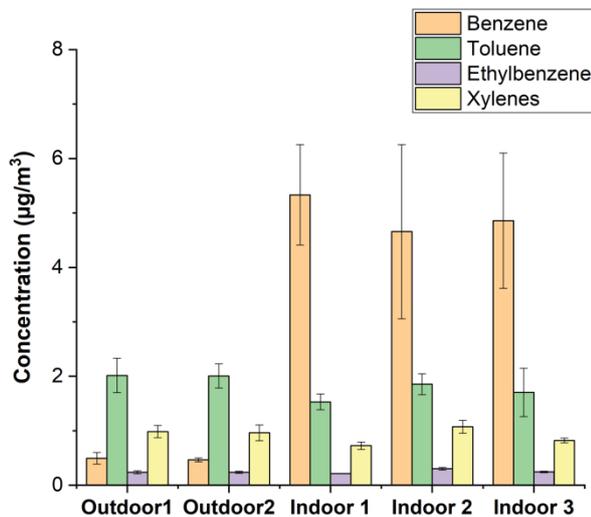


Fig. 4. Air concentration of BTEX ( $\mu\text{g}/\text{m}^3$ ) recorded with radial passive samplers.

It is worth noting that on the base of benzene/toluene (B/T) ratio it is possible to make some hypotheses on possible sources for these pollutants [35]. In outdoor environments this ratio is lower than 1, indicating that sources of BTEX are industrial activities and vehicular traffic. Whereas, in indoor environments B/T ratio is greater than 1, suggesting incense and candle burning as main sources [36–38].

As reported in literature, the indoor concentrations of certain pollutants can be higher than outdoor ones, posing a risk for human health [35,39]. In fact, exposure to high concentrations of air pollutants is linked to the onset of disease in humans [40]. These results can be considered serious problems for the health of visitors and workers, and for the preservation of works of art, so further studies need to be conducted to evaluate its sources to prevent these high concentrations.

#### IV. CONCLUSION

In view of the artistic richness of the Sanctuary of the Beata Vergine dei Miracoli, air pollution monitoring is essential for the preventive conservation of the works of art and assess the exposure risk for workers and visitors. The air concentrations of nitrogen dioxide and benzene, toluene, ethylbenzene and xylene (BTEX) were measured by passive air sampling. Indoor concentrations of  $\text{NO}_2$  and benzene are always higher than outdoor ones, whereas those of toluene, ethylbenzene and xylene in the two types of environments are similar. This is only a preliminary study and other parameters should be taken into account to fully assess the air quality in this sanctuary.

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