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Assessment of some air pollutants in the Sanctuary of the Beata Vergine dei Miracoli (Saronno, Italy) and first evaluation of a new axial passive sampler for nitrogen dioxide

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ABSTRACT

In the present study the concentration of some air pollutants (nitrogen dioxide, sulphur dioxide, hydrogen sulphide, ammonia and BTEX, i.e. benzene, toluene, ethylbenzene and xylene) was monitored inside and outside the Sanctuary of the Beata Vergine dei Miracoli (Saronno, Italy) by passive air sampling (using radial samplers), during two sampling periods in 2022 (April 27-May 11 and May 11-May 25). Concurrently, particulate matter (PM10 and PM2.5) concentration was determined by using sensors based on laser scattering technology. Moreover, we took advantage of the location of this sanctuary (proximity to an air monitoring central unit) to evaluate the performance of a new axial-type sampler for nitrogen dioxide. Sulphur dioxide concentration was in the range 0.8–3.1 $\mu g/m^3$, with outdoor values higher than indoor ones, whereas no detectable concentrations of hydrogen sulphide were found (<0.1 $\mu g/m^3$). A different trend was observed for ammonia, where indoor concentrations were higher than outdoor ones (3.6–5.5 vs 2.7–3.1 $\mu g/m^3$). Among BTEX, only for benzene statistical differences (*p-value* < 0.05) between the indoor and outdoor concentrations were found, suggesting additional indoor sources for this hydrocarbon. Toluene results as the most abundant among these hydrocarbons (1.7–2.3 $\mu g/m^3$) in outdoor environments, whereas, in indoor environments, benzene has the higher concentration (6–9 $\mu g/m^3$). The indoor concentrations of NO_2 (15.4–22.2 $\mu g/m^3$ for radial samplers and 48–60 $\mu g/m^3$ for axial samplers) are not only much higher than the recommended limit values to guarantee proper conservation of artefacts (5 $\mu g/m^3$), but also close to the values for human health preservation (40 $\mu g/m^3$), suggesting the need of proper strategy to improve indoor air quality inside the Sanctuary. The preliminary results obtained for the new axial-type sampler for nitrogen dioxide are very encouraging, given the closeness of the obtained concentration data to those measured by monitoring central unit, even though further experiments will have to be carried out to validate this sampler.

1. Introduction

To determine air quality in a specific environment and assess the sources of pollutants (such as gaseous inorganic or organic compounds), it is necessary to measure their concentration in order to take precautions based on pollution levels.

Air pollution is one of the greatest threats to the prevention of cultural heritage deterioration [1]. There are indeed several pollutants that, due to their acidic or oxidating characteristics, can cause damage to cultural heritage after exposure to certain concentrations for long periods [2–4]. Among the acids, sulphur dioxide (SO_2) [5] and nitrogen dioxide (NO_2), typical pollutants in urban and industrial areas, are the most prominent, although organic acids such as acetic and formic acid are relevant in the degradation of metal artefacts [6]. Sulphur and nitrogen oxides in the air can easily dissolve in water to generate the corresponding sulphuric and nitric acids, with significant corrosive

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effects on various materials of cultural monuments (stones, metals, and wood products) [7]. In addition, sulphur dioxide, in combination with other pollutants such as atmospheric particulate matter, generates the degradation of calcite surfaces, i.e. the formation of black crusts [8–10].

Based on this evidence, Italian guidelines for museum environments suggest stringent limits for concentrations of these pollutants to safeguard works of art (1.0 μg/m^3 and 5.0 μg/m^3 for sulphur dioxide and nitrogen dioxide respectively) [11]. However, there are still no legal limits internationally for this type of environment. For such harmful air pollutants, it is also very important to assess emission sources in order to identify suitable strategies for reducing their indoor concentrations.

In this context, it is of great importance to choose methods that are simple, inexpensive, easily applicable, reliable, and allow simultaneous sampling of air pollutants at multiple sites even without the need for electricity. The use of diffusive or passive air samplers is precious to easily perform long-term monitoring activities without the need for expensive equipment, which are typically employed in active air sampling. Their small size, easy handling, and low cost make these systems ideal for monitoring air quality in cultural heritage sites [12–14], such as museums churches and archaeological sites, where bulkier systems can detract from the beauty of the artwork they contain. Moreover, comparison of passive samplers with the automatic analysers for gaseous pollutants (e.g. NOx) shows that these systems are reasonably reliable, providing a suitable and cheap alternative to the former [15].

Passive sampling is based on the diffusive processes of gases and is therefore governed by Fick's first law [16–18]. In recent years, more and more efforts are being made to develop systems that are easy to use, can be reused several times and are made of inexpensive materials [19–21], so different passive sampling devices are commercially available. They differ in flow direction (axial or radial) and geometric features (diffusive path length and cross-sectional area of the diffusive surface) that affect the sampling rate, defined as the amount of pollutant the device samples in the unit of time [22]. In the case of axial geometry, although the sampling rate is lower than radial one, the high ratio between the diffusive path length and the cross-sectional area offers the advantage of minimizing the influence of external factors and obtained the concentration directly from Fick's law [18].

The aim of this study is the air quality assessment inside the Sanctuary of the Beata Vergine dei Miracoli, in Saronno (Varese, Italy). Several pollutants were considered: NO_2, SO_2, hydrogen sulphide (H_2S), ammonia (NH_3), BTEX, i.e. benzene, toluene, ethylbenzene and xylene, and particulate matter (PM10 and PM2.5). Moreover, we took advantage of the location of this sanctuary (near a regional monitoring station) to evaluate the performance of a new axial-type sampler for NO_2.

2. Materials and methods

2.1. Passive air sampling

The air monitoring was conducted using passive samplers. Pollutants considered in this study were BTEX, NO_2, SO_2, NH_3 and H_2S. Axial and radial diffusive samplers were employed (Fig. 1). RING® devices (purchased from Aquaria S.r.l., Milan, Italy) were used as radial diffusive samplers for all analytes. Axial samplers, developed in collaboration with Sense Square S.r.l. (Salerno, Italy), were employed for nitrogen dioxide (CitiSense).

Depending on the considered pollutants, different sorbent materials were employed: activated carbon for BTEX, triethanolamine solution (30 %) for NO_2 and SO_2, phosphoric acid solution (5 %) for NH_3 and zinc acetate solution (10 %) for H_2S. Details of analytical determinations are reported in the supporting materials. Briefly, UV–VIS spectroscopic assays [23] were employed for NO_2 (Griess-Saltzman), H_2S (Methylene Blue method) and NH_3 (Salicylic methods), whereas chromatographic analyses were used for SO_2 (ion chromatography as sulphate) and BTEX (gas chromatography with flame ionization detector [24,25]).

2.2. Particulate matter (PM10 and PM2.5) monitoring

To monitor the levels of dispersed air pollutants two Sensy sensors have been installed. The Sensy sensor, developed by Sense Square S.r.l. (Salerno, Italy), is based on laser scattering technology that allows the continuous measurement of PM10 and PM2.5 particles with high temporal resolution and microclimatic parameters such as temperature, atmospheric pressure and relative humidity. The sensor characteristics

Table 1
Characteristics of Sensy sensor.

Parameter	Accuracy	Technology
Temperature	±0.3 °C	Band-Gap
Humidity	±3 %	Capacitive
PM10	±5 μg/m^3	Laser Scattering
PM2.5	±5 μg/m^3	Laser Scattering

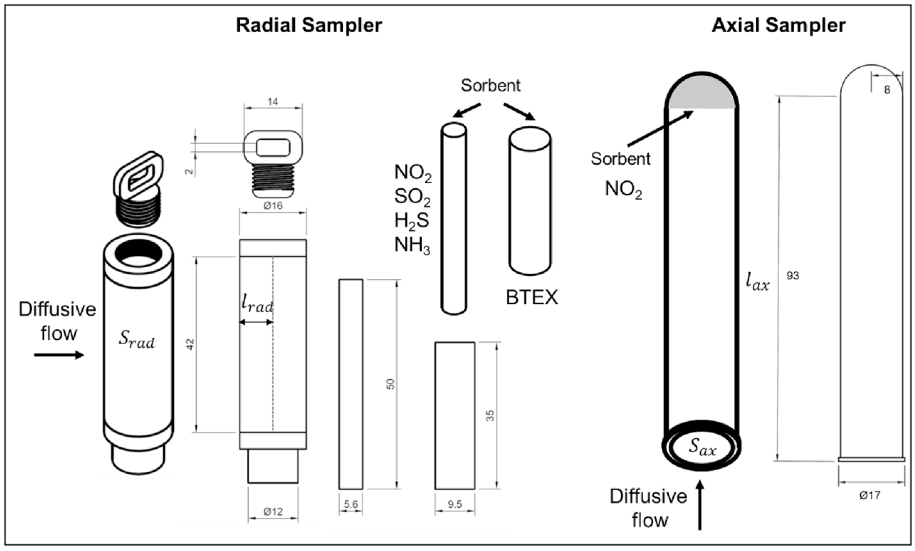

Fig. 1. Schematic representation of the two types of samplers (radial and axial) used in this study; S is the cross-sectional area of the diffusive surface and l is the distance between the sampler inlet and the sorbent material. Dimensions are given in millimetres.

are shown in Table 1.

2.3. Sampling points

The sanctuary of the Beata Vergine dei Miracoli is located in the small town of Saronno (Varese, Italy) [12]. One Sensy sensor has been installed inside the sanctuary (near the wooden statues representing the *Last Supper*) and the other outside it, at first floor plan (*Outdoor_FF*). Five sampling points were monitored by passive sampling: three inside the Sanctuary and close to the works of art (indoor environments) and two outside (outdoor environments). Two sampling periods were considered for a sampling time of 2 weeks in the spring of 2022: one from April 27 to May 11 and the other from May 11 to May 25. A detailed description of all samples is reported in the supporting materials. The location of the selected sampling points for the indoor environment is shown in Fig. 2: two are on the ground floor, near the wooden sculptural groups of the *Deposition* and *Last Supper (*by Andrea da Corbetta and Alberto da Lodi), which, thanks to their artistic interest, are places often crowded by tourists and religious; one is on the first floor near the *Choir*, having a large influx of worshippers during religious rites.

For outdoor environment, two sampling points were considered, one at ground floor plan (*Outdoor_GF*) and the other at first floor plan (*Outdoor_FF*).

2.4. Statistical analysis

Statistical analysis, one-way ANOVA (analysis of variance), was performed using R studio software (version 4.1.1). In particular, were evaluated:

- the statistical differences between the indoor and outdoor concentrations of the considered pollutants (different sampling points);
- the statistical differences between the concentrations recorded in different sampling periods;
- the statistical differences between the concentrations of NO_2 recorded with axial and radial samplers. The null hypotheses for the ANOVA analysis were that there are no differences between: indoor and outdoor concentration values detected for the same pollutant during the same sampling period; concentration recorded in different sampling period; concentrations of NO_2 recorded with axial and radial samplers. Hence, the independent variables were the "type of environment" (indoor and outdoor), the "sampling period" (27/04/22–11/05/22 and 11/05/22–25/05/22), and the "type of sampler" (axial and radial), whereas the dependent variable was the air concentration of the considered pollutants. The significance level was $\alpha = 0.05$. Non-metric multidimensional scaling (NMDS) was also performed to confirm the presence of significative differences between the sampling periods and the two samplers. NMDS was conducted with the Bray-Curtis dissimilarity matrix and three ordination axes were generated for each analysis. The analyses to retain three ordination axes, after some trials with two and four axes, as this appeared to generally capture a large amount of the variation in the data while minimizing NMDS stress. NMDS analyses were performed and visualized in R, through the vegan package, and 95 % confidence intervals around each group of datapoints were drawn.

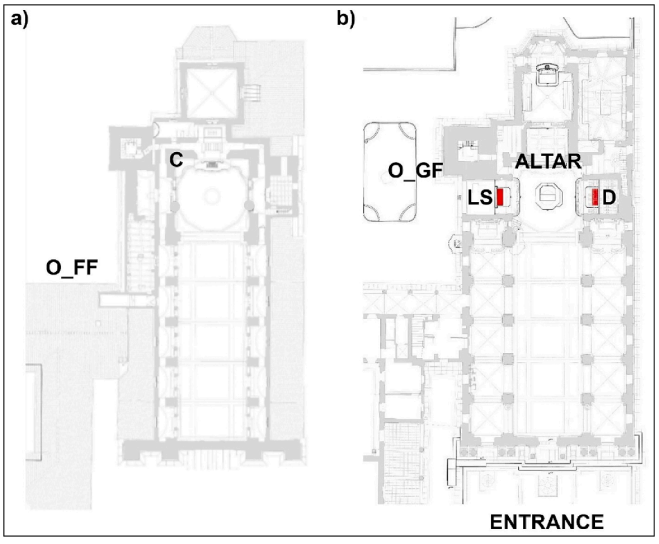

Fig. 2. Floor plans and sections of the sanctuary showing the placement of air samplers: (a) first floor plan, (b) ground floor plan. C: *Choir*; D: *Deposition*; LS: *Last Supper*; O_FF: *Outdoor first floor*; O_GF: *Outdoor ground floor*.

3. Results and discussion

3.1. Air concentration of sulphur dioxide and ammonia

The air concentration of sulphur dioxide and ammonia was monitored for the first time in the Sanctuary of the Beata Vergine dei Miracoli, by using radial passive air samplers, during two sampling periods (April 27-May 11 and May 11-May 25). Sulphur dioxide is produced from industrial activities (petroleum refining, non-ferrous metal smelting and burning of coal for energy production), as well as the combustion of solid fossil fuels, and is considered the most relevant pollutant for degradation of material (corrosion of metals and stone) [5]. Monitoring its indoor concentration is very important, as exposure to this pollutant can result in an increased risk of lung cancer and heart and respiratory diseases [26–28]. Not least, it is one of the most dangerous pollutants to cultural heritage precisely because of its corrosive properties. In fact, a concentration lower than 1.0 $\mu g/m^3$ is recommended in museum environments to avoid deterioration of the works of art [11].

SO_2 concentrations (Fig. 3) were in the range 0.8–3.1 $\mu g/m^3$ in line with the concentration observed in other places of cultural interest located in historic centres [29].

The outdoor concentrations found on the ground floor (2.7 ± 0.4 $\mu g/m^3$ and 3.1 ± 0.5 $\mu g/m^3$) are statistically higher than those detected on the first floor (1.7 ± 0.3 $\mu g/m^3$ and 2.1 ± 0.3 $\mu g/m^3$), following the principle of dilution of pollutants with the height of the sampling point. Regarding the indoor sampling points, the highest concentrations are observed at the *Last Supper* (2.5 ± 0.4 $\mu g/m^3$ and 2.6 ± 0.3 $\mu g/m^3$), and the lowest at the *Deposition* (0.8 ± 0.1 $\mu g/m^3$). No statistical differences (*p-value* > 0.05) for SO_2 concentrations measured at the same point in the different sampling periods were observed except for *Choir*, for which the concentration in the second sampling period is much greater than the first one (2.4 ± 0.4 $\mu g/m^3$ vs 1.0 ± 0.1 $\mu g/m^3$). Regarding the other sulphur pollutant sampled, i.e. H_2S, air concentrations below the limit of detection (LOD) of the technique used were found (<0.1 $\mu g/m^3$), indicating how the presence of this pollutant is negligible at the location examined.

The ratio of the indoor (I) to the outdoor (O) air concentrations was calculated to evaluate the contribution of outdoor pollution to indoor one. The observed I/O ratios for SO_2 were lower than 1, indicating transport of this pollutant from outside to inside the Sanctuary. Moreover, it should be considered that most of these concentrations are above the recommended limit values for SO_2 concentration (about 1.0 $\mu g/m^3$) in museum environments to achieve proper conservation of works of art.

As opposed to sulphur dioxide, even basic-type pollutants such as ammonia should be monitored in indoor environments containing works of art, as they can cause its degradation as well. In our case, ammonia concentrations (Fig. 4) are in the range 1.5–5.5 $\mu g/m^3$ in line with the concentration observed in the "Refectory of Santa Maria delle Grazie" (Milan, Italy), which houses one of the most important paintings of Leonardo da Vinci (the Last Supper) [30], and other indoor environments [31].

Statistically higher concentrations (*p-value* < 0.05) were observed in

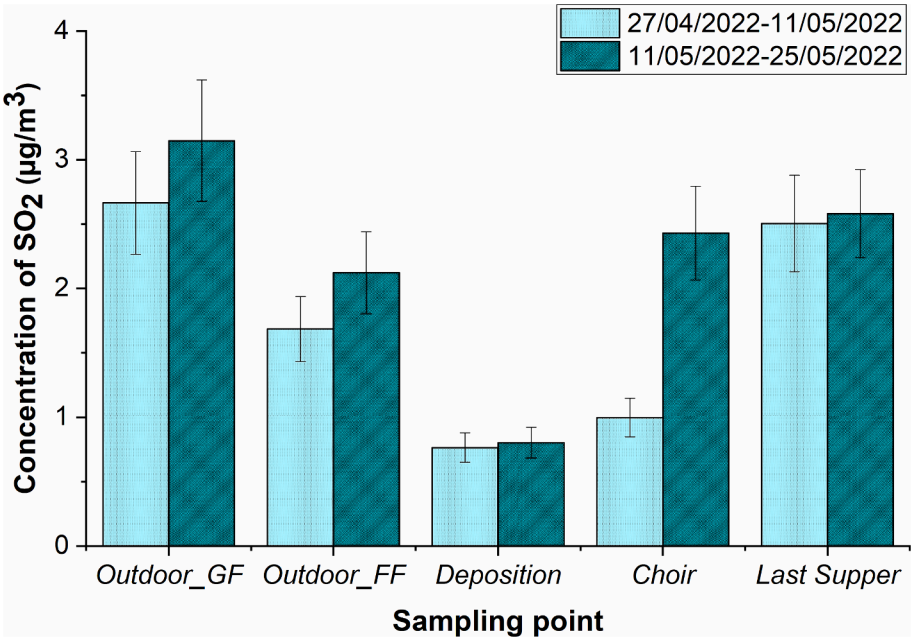

Fig. 3. Air concentration of sulphur dioxide, with standard deviation, during the two sampling periods.

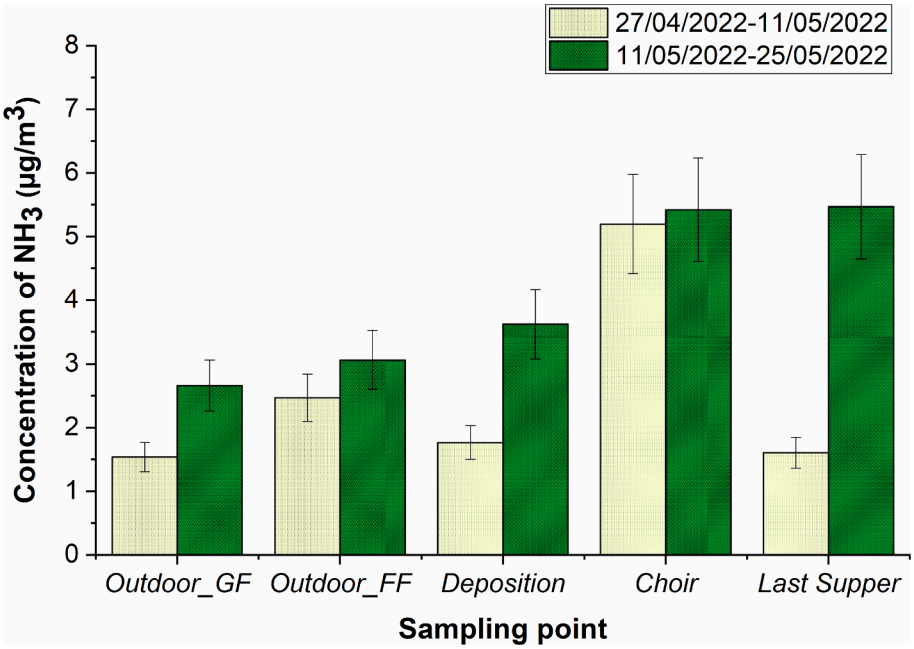

Fig. 4. Air concentration of ammonia, with standard deviation, during the two sampling periods.

the second sampling period than in the first one for all sampling points except for *Choir*. Moreover, from the concentration data of the second sampling period, it is easily observed that the ammonia concentration in indoor environments (3.6–5.5 μg/m^3) is higher than that in outdoor environments (2.7–3.1 μg/m^3), with I/O ratios between 1.3 and 2.0. This can be explained by considering that ammonia is a pollutant often linked to the presence of humans in indoor environments. Thus, it can be assumed that the increase in concentration at the *Last Supper* and *Deposition* sites in the second sampling period is due to an increase in both external concentrations (given that the Sanctuary is located in an area of the Po Valley where manure is spread in May), but more importantly, the influx of visitors to these two sites inside the Sanctuary. Indeed, in May, the worshippers flock to this Marian Sanctuary because of the Marian celebrations that take place at this time of year. In the case of the *Choir*, no difference is observed in the two sampling periods given that it is a place of maximum attendance during religious rites, for which, in fact, the highest ammonia concentrations were detected (5.2 $\pm$ 0.8 μg/m^3 and 5.5 $\pm$ 0.8 μg/m^3). Although there are no guidelines for ammonia concentrations in museum areas, the concentrations observed near the works of art contained in the Sanctuary are not negligible and should be reduced for their safeguard.

3.2. Air concentration of BTEX and diagnostic ratios

Although the degradative effects of BTEX on cultural heritage are not yet known, their monitoring in indoor environments such as museums,

and religious places, is gaining momentum in recent years. Indeed, concentration levels of these pollutants can give an indication of the influence of urban traffic on indoor air quality in this type of environments. Among BTEXs, benzene has a limit in outdoor air of 5 μg/m^3 as the annual average value (European Directive 2008/50/CE) [32], so its air concentration is constantly monitored in Europe [33].

In a preliminary study, BTEX concentration in the Sanctuary of the Beata Vergine dei Miracoli was monitored during a period of lower afflux of visitors (from 23 March to 2 April 2021) in only one indoor sampling point (*Deposition*) [34]. Lower concentration of BTEX was observed, with similar values for benzene and toluene (1.6 and 1.7 μg/m^3, respectively).

In this study, a complete characterization of the concentration of these compounds was performed during April−May 2022 (a period of the year with a high afflux of visitors at the Sanctuary), for both indoor and outdoor environment to evaluate the influence of visitors in the distribution of BTEX concentrations. BTEX concentrations during the two sampling periods are reported in Fig. 5. No statistical differences (*p-value* > 0.05) for concentrations measured at the same point in different sampling periods were observed. Considering the type of environment, only for benzene, statistical differences (*p-value* < 0.05) between the indoor and outdoor concentrations were found.

As expected, in outdoor environments, toluene results as the most abundant among the monitored hydrocarbons (1.7–2.3 μg/m^3), followed by xylenes (0.8–1.1 μg/m^3), benzene (0.39–0.6 μg/m^3) and ethylbenzene (0.21–0.27 μg/m^3). In indoor environments, benzene concentration (6–9 μg/m^3) is much higher than that of outdoor environments. Consequently, for this type of environment, benzene is the most abundant, followed by toluene (1.2–2.1 μg/m^3), xylenes (0.6–1.2 μg/m^3), and ethylbenzene (0.21–0.33 μg/m^3). The correlation analysis among BTEX concentrations in indoor and outdoor environments is shown in Table 2. No correlation is observed between the concentration of benzene and that of the other BTEX, both indoors and outdoors, suggesting a different source for this type of pollutant. On the contrary, significant positive correlation coefficients (at the 0.05 level) are found between toluene-ethylbenzene, toluene-xylenes and ethylbenzene-xylenes. This evidence suggested that these BTEX have a common source [35].

The higher correlations were found between ethylbenzene-xylenes, for both indoor (Pearson's r of 0.99) and outdoor (Pearson's r of 0.98) environments, and between toluene-ethylbenzene (Pearson's r of 0.99) and toluene-xylenes (Pearson's r of 0.98) for outdoor environments, indicating their possible origin from gasoline [36]. Lower correlation coefficients were observed between toluene-ethylbenzene (Pearson's r of 0.80) and toluene-xylenes (Pearson's r of 0.73) for indoor environments, suggesting an additional source of toluene in this type of environment.

Table 2
Correlation coefficients (Pearson's r) among BTEX concentrations in indoor and outdoor environments.

Indoor	Benzene	Toluene	Ethylbenzene	Xylenes
Benzene	1.00	0.12*	0.28*	0.30*
Toluene		1.00	0.80	0.73
Ethylbenzene			1.00	0.99
Xylenes				1.00
Outdoor	Benzene	Toluene	Ethylbenzene	Xylenes
Benzene	1.00	0.35*	0.42*	0.40*
Toluene		1.00	0.99	0.98
Ethylbenzene			1.00	0.98
Xylenes				1.00

* Not statistically significant at the 0.05 level.

In order to identify possible sources of BTEX, diagnostic ratios [37–40], such as toluene/benzene (T/B) and (m-p)xylene/ethylbenzene (X/E) were calculated for all sampling points (Fig. 6).

Regarding the T/B ratio, opposite trends are observed between outdoor and indoor environments, as reflected by the higher concentrations of benzene in indoor environments. In particular, T/B ratios in the range 2.8–3.5 and 4.3–5.4 were obtained for outdoor environments during the two sampling periods respectively, indicating vehicular traffic emission as sources (T/B > 3) [36,41]. This evidence is confirmed by the X/E mixing ratio (mean of 2.8 ± 0.4 and 3.9 ± 0.5, for the two sampling periods respectively), as reported in literature [35,42,43]. For indoor environment, the X/E mixing ratios (mean of 2.4 ± 0.3 and 2.6 ± 0.3, for the two sampling periods respectively) were close to those calculated for outdoor environment, whereas T/B ratios are very low (range 0.27–0.35 and 0.16–0.33, for the two sampling periods respectively). Different studies reported a T/B ratio lower than 1 as indicator of biomass combustion as BTEX main source [44,45], however this source is not present within the sanctuary so we can exclude it as a possible indoor source of benzene in our case study.

The average I/O ratios for toluene, ethylbenzene and xylenes were close to 1 (0.9 ± 0.2, 1.1 ± 0.1, 1.0 ± 0.2 respectively), confirming the presence of strong outdoor sources of these compounds. In the case of benzene, on the contrary, an average value of 14 ± 5 is observed, indicating additional specific indoor sources for this pollutant such as incense, candle burning and cigarettes [46–48], as already suggested by diagnostic reports. Indeed, the first two may explain the higher concentrations of benzene in the sanctuary, given that incense and candle burning are performed during all religious ceremonies. As reported in the literature, indoor benzene concentrations are often higher than outdoor concentrations due to limited forced and natural ventilation. Moreover, benzene concentrations in indoor environments are higher

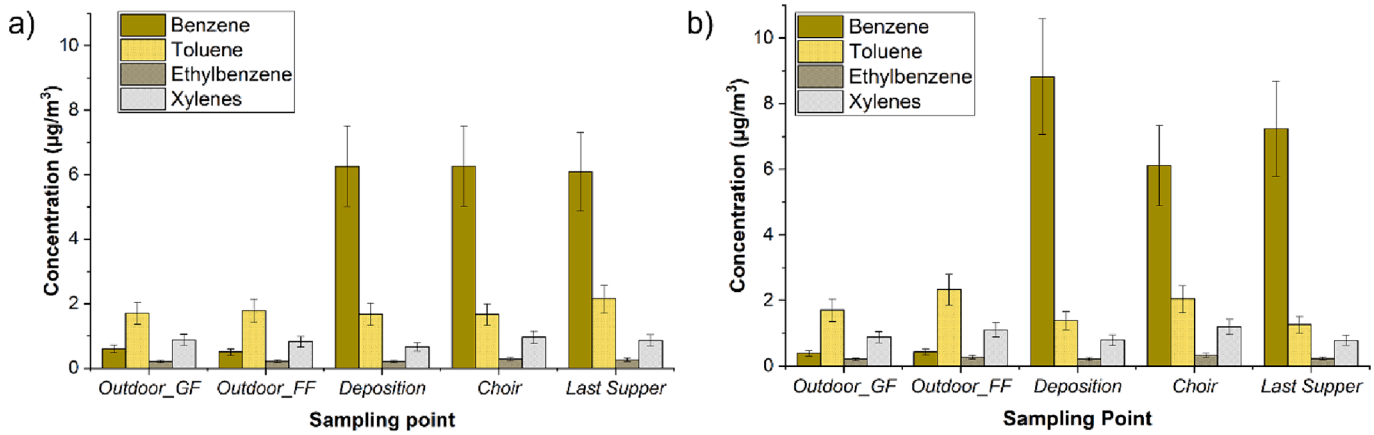

Fig. 5. Comparison of air concentration of BTEX, with standard deviation, during the two sampling periods: a) from 27/04/2022 to 11/05/2022; b) from 11/05/2022 to 25/05/2022.

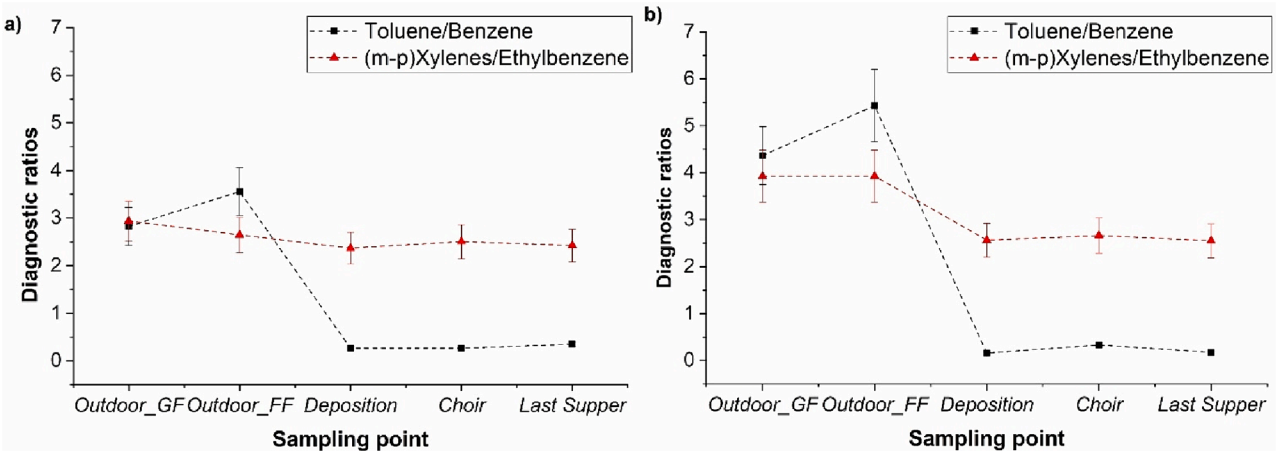

Fig. 6. Comparison of diagnostic ratios, toluene/benzene (black) and (m-p)xylenes/ethylbenzene (red), with their standard deviation, during the two sampling periods: a) from 27/04/2022 to 11/05/2022; b) from 11/05/2022 to 25/05/2022. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

than the annual average regulatory limit (5 μg/m^3) in Europe, posing a risk for human health [49]. These findings highlight possible problems for the health of visitors and workers, and for the preservation of the works of art, so better strategies are needed for reducing these high concentrations that occur during periods of high visitor influx.

3.3. Air concentration of particulate matter (PM10 and PM2.5)

The results of particulate matter monitoring at the Sanctuary of the Beata Vergine dei Miracoli during the sampling period 27 April – 25 May 2022, for indoor (*Last Supper*) and outdoor (*Outdoor_FF*) environments, are reported in Fig. 7. The system used allows for the continuous monitoring of particulate matter by constantly returning observed concentration values, making it possible to check how the concentration varies daily over the sampling period.

Observing the recorded data of fine particles indoors and outdoors, it is possible to identify a trend of higher concentration during the first two weeks of May 2022: PM10 and PM2.5 concentrations reached value close to 50 μg/m^3 and 45 μg/m^3 respectively. Furthermore, only during this period (May 1–15), the average daily concentration of PM10 at the *Last Supper* exceeded the limit recommended by the ministerial decree in numerous occasions (20–30 μg/m^3). Concentrations above the aforementioned limit were observed only indoors, highlighting accumulation of particulate matter within the sanctuary. This finding is in agreement with the results obtained in a previous campaign conducted with a different optical particle counter [34].

To assess the differences in particulate concentrations over the two sampling periods, the average PM10 and PM2.5 concentrations at the two sampled points were calculated (Fig. 8).

No significant differences were observed between the two sampling periods. Indoor concentrations of both PM10 and PM2.5 were comparable, whereas average outdoor values were higher during the first period but always below levels of concern. Average indoor concentration of PM10 and PM2.5 were higher than outdoor ones, influenced by the indoor peaks in concentration observed during the first two weeks of May (Fig. 7). Several could be causes responsible for this difference, such as the afflux of visitors and worshippers during religious ceremonies and guided tours, incense and candle burning, and all cleaning activities which resuspend part of the deposited particles. When comparing indoor PM10 and PM2.5 values for the same period, it is evident that the entirety of PM10 is composed of PM2.5, meaning that the particles which

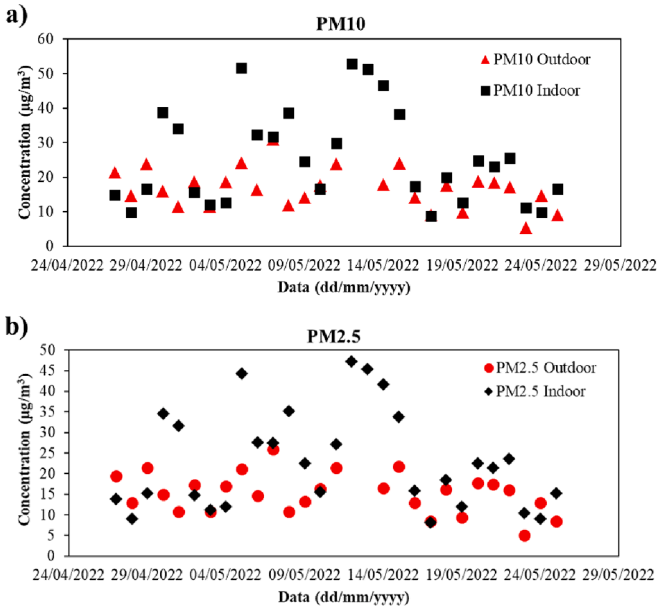

Fig. 7. Comparison between outdoor (red) and indoor (black) concentration of particulate matter during the total sampling period, from 27/04/2022 to 25/05/2022: a) PM10 and b) PM2.5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

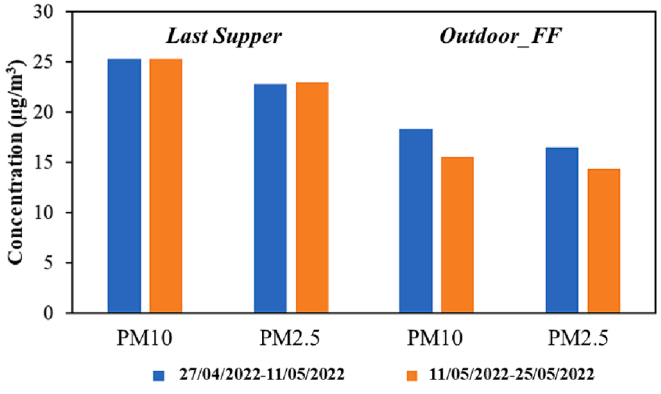

Fig. 8. Average concentrations of PM10 and PM2.5 in both indoor and outdoor environment during the two sampling periods, from 27/04/2022 to 11/05/2022 (blue) and from 11/05/2022 to 25/05/2022 (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

are present in the sanctuary are the smaller-sized ones, which are more dangerous both for human health and for the works of art.

3.4. Air concentration of nitrogen dioxide and evaluation of the performance of a new axial sampler

Nitrogen dioxide is among the most monitored pollutants in both outdoor and indoor environments [50,51]. The human health effects of this pollutant have long been known to regard mainly the respiratory system (coughing, wheezing or difficulty breathing, asthma and respiratory infections) [52], while due to its acidic character it has a strong corrosive effect on various materials of cultural monuments [1]. Consequently, European directives impose stringent concentration limit values for outdoor emission to protect human health (40 μg/m^3), while lower concentrations (below 5 μg/m^3) are recommended in museum environments to avoid deterioration of works of art [11].

In a previous study [34], NO_2 concentration inside the Sanctuary of the Beata Vergine dei Miracoli was determined by radial passive air samplers in 2021, during spring (March-April for *Deposition* and *Last Supper*) and winter (December for *Deposition*, *Last Supper* and *Choir*). As expected, higher concentrations were detected in December (13–15 μg/m^3) respect to the spring period (5.2–6.7 μg/m^3). These concentrations were above the limits reported, indicating a problematic situation for the works of art inside the sanctuary.

Based on these assumptions, in this work, NO_2 concentrations were evaluated for the same indoor environments (*Deposition*, *Last Supper* and *Choir*) and for two outdoor points (*Outdoor_GF* and *Outdoor_FF*) in correspondence with the monitored indoor points, during the peak visitor period throughout the year at the sanctuary (April 27–May 25, 2022), by using both radial and axial passive air samplers. The purpose of this monitoring was twofold: first, to determine the variation of NO_2 concentrations near the works of art compared to the outdoor values in a spring period that at the same time had a high influx of visitors and religious people, and second, to take advantage of the location of this sanctuary to evaluate the performance of a new axial-type sampler for NO_2. In fact, the outdoor sampling points were chosen for their proximity to an ARPA (Agenzia Regionale per la Protezione Ambientale) Lombardy monitoring station. The values reported by this type of control unit are a reference for nitrogen dioxide as they use the analytic technique provided for by the regulations UNI EN 14211:2012, i.e. the chemiluminescence analyser. Fig. 9 shows the concentrations measured by the ARPA station during the two sampling periods: NO_2 air concentration ranges from 9.8 to 25.7 μg/m^3, with an average value of 18.2 ± 1.0 μg/m^3, in the first sampling period (from 27/04/2022 to 11/05/2022), and from 10.9 to 24.3 μg/m^3, with an average value of 16.3 ± 1.3 μg/m^3, in the second sampling period (from 11/05/2022 to 25/05/2022).

The reported values are in line with the location of the sanctuary (near the A9 Highway) [34] and the sampling season. The concentration values obtained during sampling with both radial and axial samplers are shown in Fig. 10, where the average concentrations reported by the ARPA monitoring unit are also shown for outdoor sampling points.

No statistical differences (*p-value* > 0.05) for NO_2 concentrations measured at the same point in different sampling periods were observed, while statistical differences (*p-value* < 0.05) between the indoor and outdoor concentrations, were observed for both types of samplers. In fact, the indoor NO_2 concentrations were in the range 15.4–22.2 μg/m^3 for radial samplers and 48–60 μg/m^3 for axial samplers, values always higher than outdoor ones (range 6.6–8.1 μg/m^3 and 18–20 μg/m^3, respectively).

ANOVA tables are showed in supporting material file. The NMDS analysis (Fig. 11) confirmed the results obtained by ANOVA. The ordination plots clearly showed that no statistical differences were revealed between sampling periods, in fact, the confidence ellipses for each sampler in each period are completely superimposed (Fig. 11a). Instead, the ordination plot showing the differences between the two samplers (namely axial and radial) show a clear distance between the respective confidence ellipses (Fig. 11b).

These results are in line with the principle of accumulation of pollutants in indoor environments [53], but in contrast with the results of a previous campaign [34]. In this case, it is possible that the sampling period played a significant role. Moreover, I/O ratios from 1.9 to 3.3 were observed, indicating that there are also indoor sources of NO_2 inside the sanctuary, and plausible source can be the candle burning during religious rites, practice that increase during period of high afflux of visitors.

Outdoor concentrations of NO_2 recorded with axial samplers were 19 ± 5 μg/m^3 (*Outdoor_GF*) and 20 ± 2 μg/m^3 (*Outdoor_FF*) during the first sampling period, and 20 ± 5 μg/m^3 (*Outdoor_GF*) and 18 ± 3 μg/m^3 (*Outdoor_FF*) during the second sampling period. Statistical differences (p-value < 0.05) were observed between NO_2 concentrations obtained by radial versus axial samplers for each sampling point. Radial samplers, in fact, return NO_2 concentrations 2.5–3 times lower than axial ones: 8.1 ± 0.8 μg/m^3 (*Outdoor_GF*) and 6.6 ± 0.6 μg/m^3 (*Outdoor_FF*), and 7.8 ± 0.4 μg/m^3 (*Outdoor_GF*) and 7.1 ± 0.8 μg/m^3 (*Outdoor_FF*) for the first and second sampling period respectively (Fig. 10). Based on these preliminary data, a strong correlation (Pearson's r of 0.90, R^2 of 0.81 and *p-value* < 0.05) is observed between the data obtained with the two types

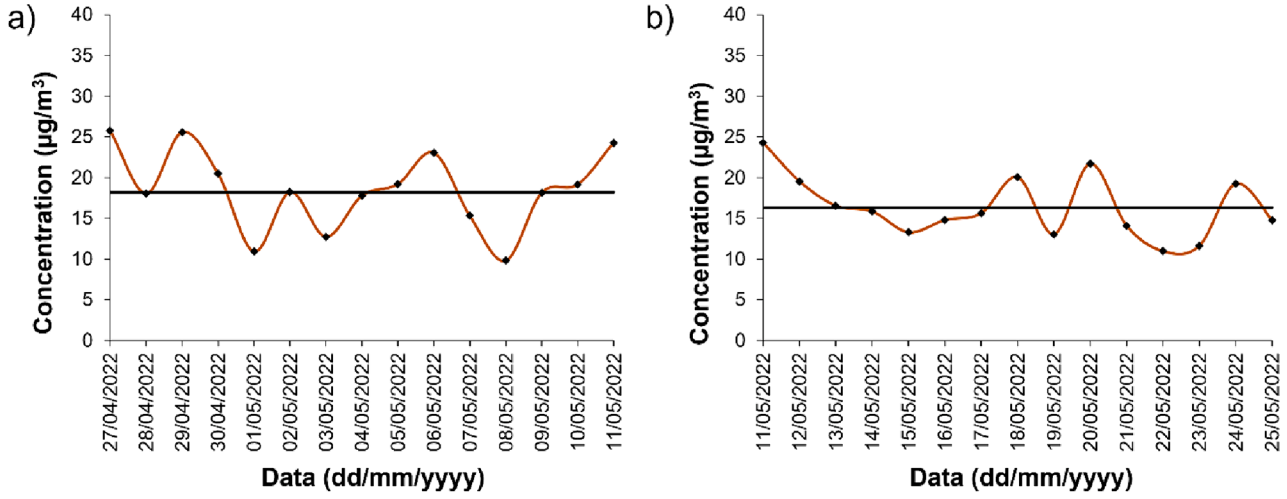

Fig. 9. Air concentration of nitrogen dioxide from ARPA Lombardy monitoring station during the two sampling periods: a) from 27/04/2022 to 11/05/2022; b) from 11/05/2022 to 25/05/2022. Black lines indicate the average concentration value.

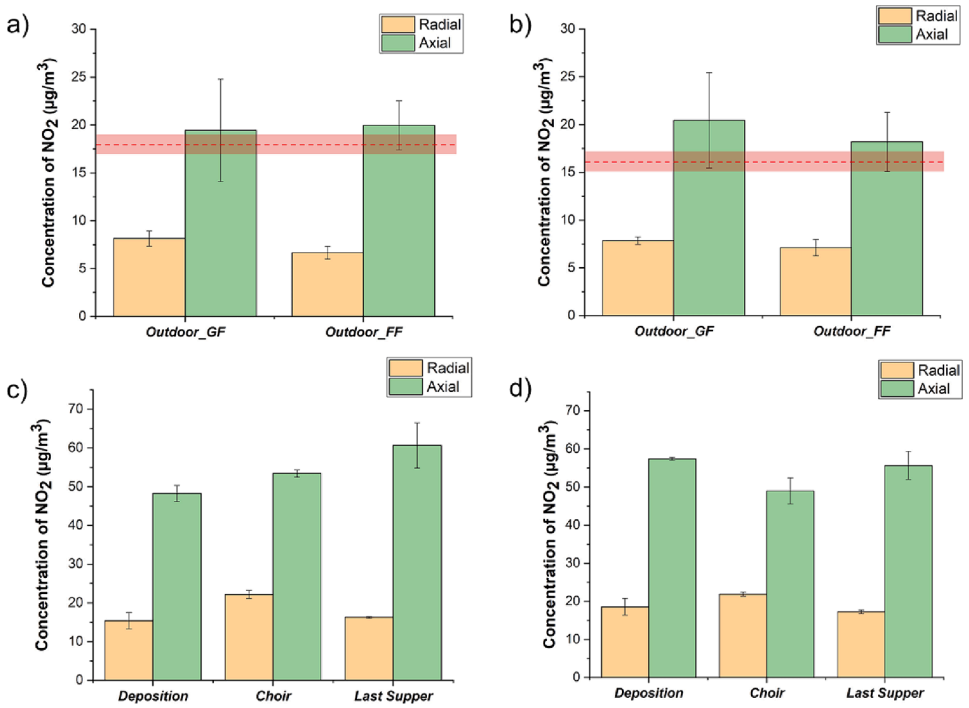

Fig. 10. Comparison of air concentration of nitrogen dioxide, with standard deviation, from axial (green) and radial (orange) samplers during the two sampling periods: a) and c) from 27/04/2022 to 11/05/2022; b) and d) from 11/05/2022 to 25/05/2022. The dashed red line represents the average concentration measured by the ARPA station over the specified sampling period. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of samplers for both outdoor and indoor environments (see supporting material).

It is interesting to note that the values obtained with axial samplers are closer to those of the control unit than the concentrations found with radial samplers (percentage differences from the control unit value of 4–20 % for axials and 52–64 % for radials). This phenomenon can be explained if we consider that in the case of axial samplers there is no impediment to the diffusive path that may occur in the case of radial samplers due to the presence of the external diffusive body. In addition, the tube geometry of this sampler (the high ratio *l/S*) makes it possible to minimize the influence of external environmental factors on the sampling rate. This allow the sampled pollutant concentration to be obtained directly from theoretical consideration, based on Fick's law, without the need for calibration [18]. These considerations may explain the evidence observed for axial samplers, whose measured concentration values fall within the acceptable level of ±25 % for percent relative error respect to the control unit values.

If on the one hand, passive samplers are often used to see the trend of concentrations rather than their absolute values, these data show how axial type samplers manage to give a concentration value much closer to the real one. The performance of the axial sampler CitiSense, although based on still preliminary data, were compared with the radial sampler used in this study (Ring®), the most used radial sampler (Radiello™), and the most widely used axial sampler, the Palmes tube, considering an exposure period of two weeks (Table 3).

As expected, radial samplers have lower detection limits (0.5–0.9 µg/m^3), thanks to their higher flow rate, whereas CitiSense samplers reach a value (1.6 µg/m^3) close to that of Palmes tube (1.4–2 µg/m^3). An estimation of precision is given by the measure of relative standard deviation, which is higher for CitiSense than for other samplers but, even so, close to the acceptable value reported in literature (~20 %) [19]. This highlights the fact that these samplers need further studies to be validated. However, the results of this study are encouraging in that the use of very simple sampler makes it possible to obtain concentration values close to those measured by the central unit. It should also be pointed out that the passive axial sampler CitiSense is cheaper than those on the market (the price is about a quarter of that of Radiello™, the most widely used passive sampler), leaving room for very wide use, such as in Citizen Science. The use of these systems for other types of air pollutants is also desirable, so future research will be directed in this regard.

Focusing on the case study, the indoor concentrations of NO_2 are not only much higher than the recommended limit values to achieve proper conservation of artefacts, but, in the case of axial samplers, also higher than the values for human health preservation, suggesting the need of proper strategy to improve indoor air quality inside the Sanctuary.

4. Conclusions

In this study NO_2, SO_2, H_2S, NH_3 and BTEX concentrations inside the Sanctuary of the Beata Vergine dei Miracoli and outside of it were determined by using radial passive air samplers, along with the monitoring of particulate matter (PM10 and PM2.5) using Sensy sensors. SO_2 concentrations in the range 0.8–3.1 µg/m^3 were observed, with outdoor values higher than indoor ones, indicating transport of this pollutant from outside to inside the Sanctuary. The opposite situation happens for NH_3, where indoor concentrations are higher than outdoor ones (3.6–5.5 vs 2.7–3.1 µg/m^3), since ammonia is a pollutant often linked to the presence of humans in indoor environments. Toluene results as the most abundant hydrocarbon (1.7–2.3 µg/m^3) in outdoor environments, whereas, in indoors, benzene has the higher concentration (6–9 µg/m^3), statistically different (*p-value* < 0.05) from that found in outdoors. The T/B ratio suggests vehicular traffic emission as sources in outdoors, while other origins must be assumed for benzene in indoors (e.g. incense, candle burning and cigarettes). Indoor NO_2 concentrations (15.4–22.2 µg/m^3), were always higher than outdoor ones (6.6–8.1 µg/m^3), with an I/O ratio from 1.9 to 3.3 that indicate indoor sources of NO_2 inside the sanctuary (e.g. candle burning during religious rites). It should be noted that indoor concentrations of SO_2 and NO_2 inside the Sanctuary are higher than the recommended limit values to guarantee proper conservation of artefacts (1 µg/m^3 and 5 µg/m^3 respectively).

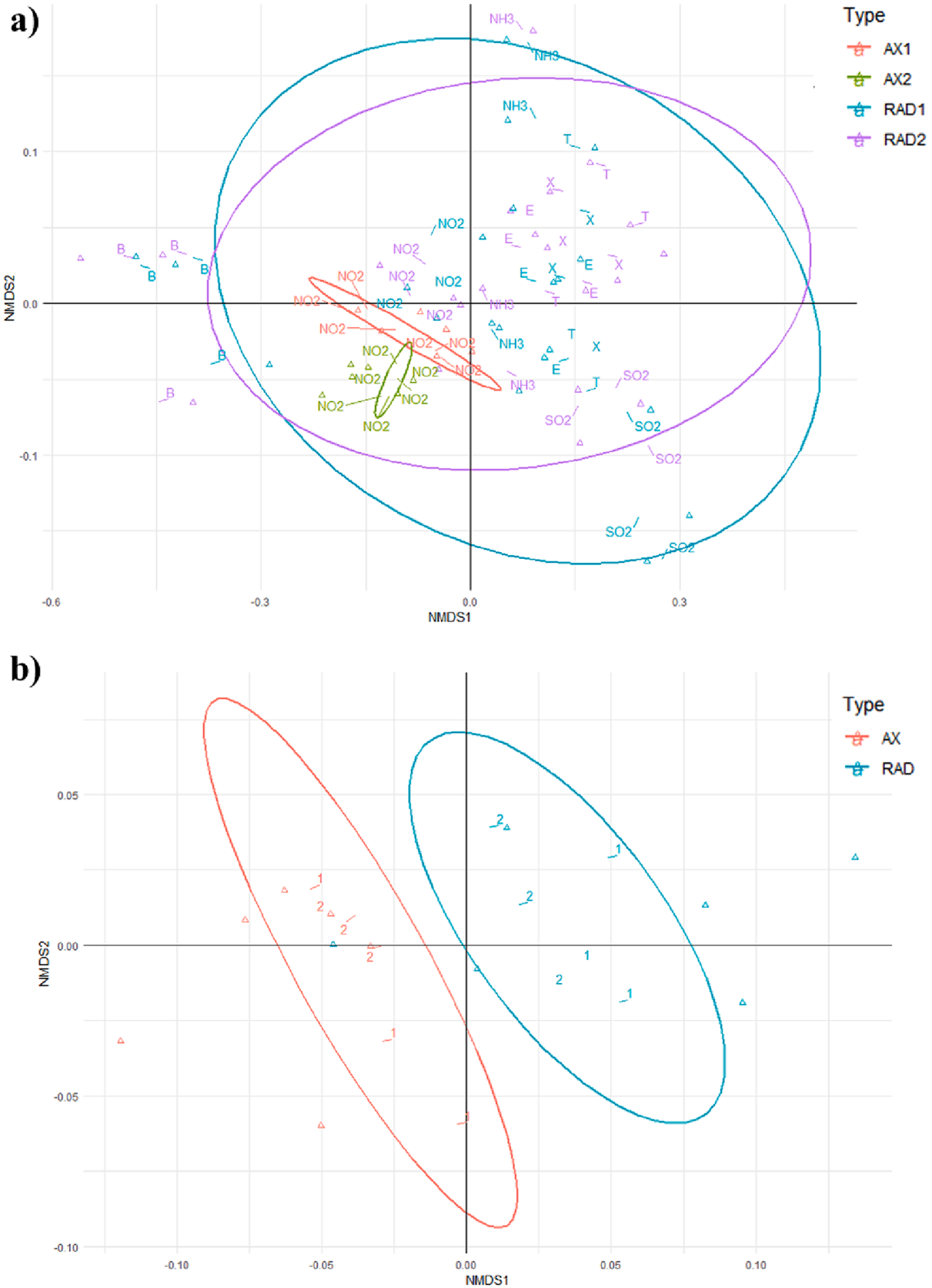

Fig. 11. NMDS plots including 95% confidence interval ellipses for the comparison between: (a) the sampling periods 1(April 27 to May 11, 2022) and 2 (from May 11 to May 25, 2022) for both axial (AX) and radial (RAD) type samplers; (b) all results from axial and the radial samplers for NO_2.

Table 3
Characteristic of passive air samplers relative to an exposure period of two weeks.

Diffusive sampler	Precision as relative standard deviation (%)	Detection Limit (ug/m^3)	Reference
CitiSense	2–25 (10.5 ± 8.9)	1.6	This study
Ring®	1–11 (7.0 ± 4.2)	0.5	This study
Palmes[#]	5–8	1.4–2	[22]
Radiello™[#]	8.7–11.4	0.9	[22]

This is true also for indoor PM10 and PM2.5 concentrations, suggesting the need of proper strategy to improve indoor air quality inside this Sanctuary. Moreover, the proximity of this sanctuary to an air monitoring central unit, allowed us to evaluate the performance of a new axial-type sampler for NO_2. This axial sampler returns NO_2 concentrations 2.5–3 times higher than radial ones, and, in the case of outdoor environments, axial values are closer to those of the control unit than the radial ones (percentage differences from the control unit value of 4–20 % for axials and 52–64 % for radials). The obtained results are encouraging in the use of the proposed very simple and cheap air sampler that makes it possible to obtain concentration values close to those measured by the central unit.

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CRediT authorship contribution statement

Maria Ricciardi: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Daniele Sofia:** Validation, Methodology, Formal analysis, Conceptualization. **Antonio Faggiano:** Formal analysis, Data curation. **Andrea Bergomi:** Writing – review & editing, Methodology, Investigation. **Valeria Comite:** Validation, Conceptualization. **Vittoria Guglielmi:** Validation, Conceptualization. **Paola Fermo:** Validation, Supervision, Project administration, Funding acquisition, Conceptualization. **Antonio Proto:** Validation, Supervision, Project administration, Funding acquisition, Conceptualization. **Oriana Motta:** Writing – review & editing, Validation, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2024.110593.

References

[1] B. Xiao, L. Ning, Z. Lin, S. Wang, H. Zang, The impact of air pollution on the protection of world cultural heritage in China, Int. J. Environ. Res. Public Health. 19 (2022) 10226, https://doi.org/10.3390/ijerph191610226.
[2] M. Ricciardi, C. Pironti, O. Motta, R. Fiorillo, F. Camin, A. Faggiano, A. Proto, Investigations on historical monuments' deterioration through chemical and isotopic analyses: an Italian case study, Environ. Sci. Pollut. Res. 29 (2022) 29409–29418, https://doi.org/10.1007/s11356-021-15103-x.
[3] C. Pironti, O. Motta, M. Ricciardi, F. Camin, R. Cucciniello, A. Proto, Characterization and authentication of commercial cleaning products formulated with biobased surfactants by stable carbon isotope ratio, Talanta 219 (2020) 121256, https://doi.org/10.1016/j.talanta.2020.121256.
[4] C. Pironti, M. Ricciardi, O. Motta, F. Camin, L. Bontempo, A. Proto, Application of 13C quantitative NMR spectroscopy to isotopic analyses for vanillin authentication source, Foods 10 (2021) 2635, https://doi.org/10.3390/foods10112635.
[5] C. Pironti, M. Ricciardi, O. Motta, M. Venier, A. Faggiano, R. Cucciniello, A. Proto, Sulphurous air pollutants and exposure events of workers in thermal-mineral springs: a case study of Contursi Terme (Salerno, Italy), Environ. Sci. Pollut. Res. 30 (2023) 3112–3120, https://doi.org/10.1007/s11356-022-22432-y.
[6] A. Faggiano, C. Pironti, O. Motta, Y. Miele, A. Fiorentino, N. Marchettini, M. Ricciardi, A. Proto, Insight on the deterioration of cultural objects: a multi-analytical approach to characterize degradation products of lead weights from a Steinway & sons piano, Environ. Sci. Pollut. Res. 30 (2023) 104633–104639, https://doi.org/10.1007/s11356-023-29790-1.
[7] S. Oesch, M. Faller, Environmental effects on materials: the effect of the air pollutants SO2, NO2, NO and O3 on the corrosion of copper, zinc and aluminium. A short literature survey and results of laboratory exposures, Corros. Sci. 39 (1997) 1505–1530, https://doi.org/10.1016/S0010-938X(97)00047-4.
[8] J.S. Pozo-Antonio, M.F.C. Pereira, C.S.A. Rocha, Microscopic characterisation of black crusts on different substrates, Sci. Total Environ. 584–585 (2017) 291–306, https://doi.org/10.1016/j.scitotenv.2016.12.080.
[9] M. Ricciardi, A. Faggiano, C. Pironti, O. Motta, M. Carotenuto, V. Comite, P. Fermo, A. Proto, Analysis of PAHs (polycyclic aromatic hydrocarbons) and other main components in black crusts collected from the Monumental Cemetery of Milan (Italy), J. Phys. Conf. Ser. 2204 (2022) 012027, https://doi.org/10.1088/1742-6596/2204/1/012027.
[10] V. Comite, J.S. Pozo-Antonio, C. Cardell, L. Randazzo, M.F. La Russa, P. Fermo, A multi-analytical approach for the characterization of black crusts on the facade of an historical cathedral, Microchem. J. 158 (2020) 105121, https://doi.org/10.1016/j.microc.2020.105121.
[11] D.M. 2001. DECRETO 10 maggio 2001. Atto di indirizzo sui criteri tecnico-scientifici e sugli standard di funzionamento e sviluppo dei musei (Art. 150, comma 6, D.L. n. 112/1998), (2001). https://www.gazzettaufficiale.it/atto/serie_generale/caricaDettaglioAtto/originario?atto.dataPubblicazioneGazzetta=2001-10-19&atto.codiceRedazionale=001A8406&elenco30giorni=false (accessed August 4, 2022).
[12] A. Schieweck, T. Salthammer, Indoor air quality in passive-type museum showcases, J. Cult. Herit. 12 (2011) 205–213, https://doi.org/10.1016/j.culher.2010.09.005.
[13] B. Krupińska, A. Worobiec, G. Gatto Rotondo, V. Novaković, V. Kontozova, C.-U. Ro, R. Van Grieken, K. De Wael, Assessment of the air quality (NO2, SO2, O3 and particulate matter) in the Plantin-Moretus Museum/Print Room in Antwerp, Belgium, in different seasons of the year, Microchem. J. 102 (2012) 49–53. https://doi.org/10.1016/j.microc.2011.11.008.
[14] B. Krupińska, R. Van Grieken, K. De Wael, Air quality monitoring in a museum for preventive conservation: results of a three-year study in the Plantin-Moretus Museum in Antwerp, Belgium, Microchem. J. 110 (2013) 350–360, https://doi.org/10.1016/j.microc.2013.05.006.
[15] C.K. Varshney, A.P. Singh, Passive samplers for NOx monitoring: a critical review, Environmentalist 23 (2003) 127–136, https://doi.org/10.1023/A:1024883620408.
[16] J.N. Cape, The use of passive diffusion tubes for measuring concentrations of nitrogen dioxide in air, Crit. Rev. Anal. Chem. 39 (2009) 289–310, https://doi.org/10.1080/10408340903001375.
[17] R.H. Brown, The use of diffusive samplers for monitoring of ambient air (Technical Report), Pure Appl. Chem. 65 (1993) 1859–1874, https://doi.org/10.1351/pac199365081859.
[18] M.R. Heal, D.P.H. Laxen, B.B. Marner, Biases in the measurement of ambient nitrogen dioxide (NO2) by palmes passive diffusion tube: a review of current understanding, Atmosphere 10 (2019) 357, https://doi.org/10.3390/atmos10070357.
[19] V.P. Campos, L.P.S. Cruz, R.H.M. Godoi, A.F.L. Godoi, T.M. Tavares, Development and validation of passive samplers for atmospheric monitoring of SO2, NO2, O3 and H2S in tropical areas, Microchem. J. 96 (2010) 132–138, https://doi.org/10.1016/j.microc.2010.02.015.
[20] S. Bootdee, P. Chalemrom, S. Chantara, Validation and field application of tailor-made nitrogen dioxide passive samplers, Int. J. Environ. Sci. Technol. 9 (2012) 515–526, https://doi.org/10.1007/s13762-012-0074-2.
[21] Ö.Ö. Üzmez, E.O. Gaga, Ö. Ercan, Ö. Ceylan, T. Döğeroğlu, Performance evaluation of a new three-in one diffusive sampler for monitoring NO2, SO2 and O3, Talanta 214 (2020) 120829, https://doi.org/10.1016/j.talanta.2020.120829.
[22] T. Hafkenscheid, A. Fromage-Mariette, E. Goelen, M. Hangartner, U. Pfeffer, H. Plaisance, F. de Santis, K. Saunders, W. Swaans, Y.S. Tang, J. Targa, C. van Hoek, M. Gerboles, Review of the application of diffusive samplers in the European Union

for the monitoring of nitrogen dioxide in ambient air, (2009). https://nora.nerc.ac.uk/id/eprint/9558/ (accessed July 12, 2023).
[23] M. Ricciardi, R. Cucciniello, J. Barrault, A. Faggiano, C. Capacchione, A. Proto, A step towards bio-surfactants: monoalkylglyceryl ethers synthesis through glycidol alcoholysis with long-chain alcohols catalyzed by Al(OTf)3, Sustain. Chem. Pharm. 17 (2020) 100281, https://doi.org/10.1016/j.scp.2020.100281.
[24] F. Della Monica, M. Ricciardi, A. Proto, R. Cucciniello, C. Capacchione, Regioselective ring-opening of glycidol to monoalkyl glyceryl ethers promoted by an [OSSO]-FeIII triflate complex, ChemSusChem 12 (2019) 3448–3452, https://doi.org/10.1002/cssc.201901329.
[25] M. Ricciardi, L. Falivene, T. Tabanelli, A. Proto, R. Cucciniello, F. Cavani, Bio-glycidol conversion to solketal over acid heterogeneous catalysts: synthesis and theoretical approach, Catalysts 8 (2018) 391, https://doi.org/10.3390/catal8090391.
[26] X.-Q. Wang, J.-W. Zhao, K.-D. Zhang, W.-J. Yu, J. Wang, Y.-Q. Li, X. Cheng, Z.-H. Li, Y.-C. Mao, C.-Y. Hu, K. Huang, K. Ding, X.-J. Yang, S.-S. Chen, X.-J. Zhang, X.-H. Kan, Short-term effect of sulfur dioxide (SO2) change on the risk of tuberculosis outpatient visits in 16 cities of Anhui Province, China: the first multi-city study to explore differences in occupational patients, Environ. Sci. Pollut. Res. (2022), https://doi.org/10.1007/s11356-022-19438-x.
[27] W.J. Lee, K. Teschke, T. Kauppinen, A. Andersen, P. Jäppinen, I. Szadkowska-Stanczyk, N. Pearce, B. Persson, A. Bergeret, L.A. Facchini, R. Kishi, D. Kielkowski, B.A. Rix, P. Henneberger, J. Sunyer, D. Colin, M. Kogevinas, P. Boffetta, Mortality from lung cancer in workers exposed to sulfur dioxide in the pulp and paper industry, Environ. Health Perspect. 110 (2002) 991–995, https://doi.org/10.1289/ehp.02110991.
[28] Y. Shang, Z. Sun, J. Cao, X. Wang, L. Zhong, X. Bi, H. Li, W. Liu, T. Zhu, W. Huang, Systematic review of Chinese studies of short-term exposure to air pollution and daily mortality, Environ. Int. 54 (2013) 100–111, https://doi.org/10.1016/j.envint.2013.01.010.
[29] C. Pironti, M. Ricciardi, A. Proto, R. Cucciniello, A. Fiorentino, R. Fiorillo, O. Motta, New analytical approach to monitoring air quality in historical monuments through the isotopic ratio of CO2, Environ. Sci. Pollut. Res. 29 (2022) 29385–29390, https://doi.org/10.1007/s11356-020-12215-8.
[30] O. Motta, C. Pironti, M. Ricciardi, C. Rostagno, E. Bolzacchini, L. Ferrero, R. Cucciniello, A. Proto, Leonardo da Vinci's "Last Supper": a case study to evaluate the influence of visitors on the Museum preservation systems, Environ. Sci. Pollut. Res. 29 (2022) 29391–29398, https://doi.org/10.1007/s11356-021-13741-9.
[31] S. López-Aparicio, J. Smolík, L. Mašková, M. Součková, T. Grøntoft, L. Ondráčková, J. Stankiewicz, Relationship of indoor and outdoor air pollutants in a naturally ventilated historical building envelope, Build. Environ. 46 (2011) 1460–1468, https://doi.org/10.1016/j.buildenv.2011.01.013.
[32] Decreto Legislativo 13 agosto 2010, n.155. Attuazione della direttiva 2008/50/CE relativa alla qualità dell'aria ambiente e per un'aria più pulita in Europa, (n.d.). https://web.camera.it/parlam/leggi/deleghe/testi/10155dl.htm (accessed July 29, 2022).
[33] D. Sanjuán-Herráez, S. de la Osa, A. Pastor, M. de la Guardia, Air monitoring of selected volatile organic compounds in wineries using passive sampling and headspace-gas chromatography–mass spectrometry, Microchem. J. 114 (2014) 42–47, https://doi.org/10.1016/j.microc.2013.11.017.
[34] A. Bergomi, V. Comite, V. Guglielmi, M. Borelli, C.A. Lombardi, R. Bonomi, C. Pironti, M. Ricciardi, A. Proto, C. Mariani, P. Fermo, Preliminary air quality and microclimatic conditions study in the Santuario della Beata Vergine dei Miracoli in Saronno (VA), Molecules 28 (2023) 1615, https://doi.org/10.3390/molecules28041615.
[35] M. Caselli, G. de Gennaro, A. Marzocca, L. Trizio, M. Tutino, Assessment of the impact of the vehicular traffic on BTEX concentration in ring roads in urban areas of Bari (Italy), Chemosphere 81 (2010) 306–311, https://doi.org/10.1016/j.chemosphere.2010.07.033.
[36] T. Martellini, C. Berlangieri, L. Dei, E. Carretti, S. Santini, A. Barone, A. Cincinelli, Indoor levels of volatile organic compounds at Florentine museum environments in Italy, Indoor Air 30 (2020) 900–913, https://doi.org/10.1111/ina.12659.
[37] J.G. Ceron-Breton, R.M. Cerón Bretón, J.D.W. Kahl, G. Sánchez Rico, S.E. Carranco Lozada, M. de la Luz Espinosa Fuentes, M.P. Uc Chi, Concentrations, sources, and health risk associated with exposure to BTEX at ten sites located in an urban-industrial area in the Bajio Region, Mexico, Air Qual. Atmos. Health 14 (2021) 741–761, https://doi.org/10.1007/s11869-021-00976-1.
[38] S.A. Hosseini, M. Abtahi, S. Dobaradaran, H. Hassankhani, A. Koolivand, R. Saeedi, Assessment of health risk and burden of disease induced by exposure to benzene, toluene, ethylbenzene, and xylene in the outdoor air in Tehran, Iran, Environ. Sci. Pollut. Res. (2023), https://doi.org/10.1007/s11356-023-27889-z.
[39] C.-C. Lin, G.-W. Yen, Y.-H. Cheng, R.-H. Shie, Exposure levels of volatile organic compounds and potential health risks for passengers and workers at an intercity bus terminal, Atmos. Pollut. Res. 11 (2020) 1820–1828, https://doi.org/10.1016/j.apr.2020.07.024.
[40] L.P.S. Cruz, D.F. Santos, I.F. dos Santos, Í.V.S. Gomes, A.V.S. Santos, K.S.P.P. Souza, Exploratory analysis of the atmospheric levels of BTEX, criteria air pollutants and meteorological parameters in a tropical urban area in Northeastern Brazil, Microchem. J. 152 (2020) 104265, https://doi.org/10.1016/j.microc.2019.104265.
[41] A. Cincinelli, T. Martellini, A. Amore, L. Dei, G. Marrazza, E. Carretti, F. Belosi, F. Ravegnani, P. Leva, Measurement of volatile organic compounds (VOCs) in libraries and archives in Florence (Italy), Sci. Total Environ. 572 (2016) 333–339, https://doi.org/10.1016/j.scitotenv.2016.07.201.
[42] A. Monod, B.C. Sive, P. Avino, T. Chen, D.R. Blake, F. Sherwood Rowland, Monoaromatic compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene, Atmos. Environ. 35 (2001) 135–149, https://doi.org/10.1016/S1352-2310(00)00274-0.
[43] M.T. Latif, H.H. Abd Hamid, F. Ahamad, M.F. Khan, M.S. Mohd Nadzir, M. Othman, M. Sahani, M.I. Abdul Wahab, N. Mohamad, R. Uning, S.C. Poh, M. F. Fadzil, J. Sentian, N.M. Tahir, BTEX compositions and its potential health impacts in Malaysia, Chemosphere 237 (2019) 124451, https://doi.org/10.1016/j.chemosphere.2019.124451.
[44] P. Ielpo, C. Mangia, G. de Gennaro, A. Di Gilio, J. Palmisani, A. Dinoi, A. Bergomi, V. Comite, P. Fermo, Air quality assessment of a school in an industrialized area of southern Italy, Appl. Sci. 11 (2021) 8870, https://doi.org/10.3390/app11198870.
[45] H. Wang, S. Lou, C. Huang, L. Qiao, X. Tang, C. Chen, L. Zeng, Q. Wang, M. Zhou, S. Lu, X. Yu, Source profiles of volatile organic compounds from biomass burning in Yangtze River Delta, China, Aerosol Air Qual. Res. 14 (2014) 818–828, https://doi.org/10.4209/aaqr.2013.05.0174.
[46] A. Manoukian, E. Quivet, B. Temime-Roussel, M. Nicolas, F. Maupetit, H. Wortham, Emission characteristics of air pollutants from incense and candle burning in indoor atmospheres, Environ. Sci. Pollut. Res. 20 (2013) 4659–4670, https://doi.org/10.1007/s11356-012-1394-y.
[47] S.-C. Lee, B. Wang, Characteristics of emissions of air pollutants from burning of incense in a large environmental chamber, Atmos. Environ. 38 (2004) 941–951, https://doi.org/10.1016/j.atmosenv.2003.11.002.
[48] W. Tirler, G. Settimo, Incense, sparklers and cigarettes are significant contributors to indoor benzene and particle levels, Ann. Ist. Super. Sanita 51 (2015) 28–33, https://doi.org/10.4415/ANN_15_01_06.
[49] M.A. El-Hashemy, H.M. Ali, Characterization of BTEX group of VOCs and inhalation risks in indoor microenvironments at small enterprises, Sci. Total Environ. 645 (2018) 974–983, https://doi.org/10.1016/j.scitotenv.2018.07.157.
[50] A. Lozano, J. Usero, E. Vanderlinden, J. Raez, J. Contreras, B. Navarrete, H. El Bakouri, Optimization of the design of air quality monitoring networks and its application to NO2 and O3 in Jaen, Spain, Microchem. J. 96 (2010) 406–411, https://doi.org/10.1016/j.microc.2010.07.002.
[51] M. Stranger, A. Krata, V. Kontozova-Deutsch, L. Bencs, F. Deutsch, A. Worobiec, I. Naveau, E. Roekens, R. Van Grieken, Monitoring of NO2 in the ambient air with passive samplers before and after a road reconstruction event, Microchem. J. 90 (2008) 93–98, https://doi.org/10.1016/j.microc.2008.04.001.
[52] O. US EPA, Basic Information about NO2, (2016). https://www.epa.gov/no2-pollution/basic-information-about-no2 (accessed June 26, 2023).
[53] Y. Hu, B. Zhao, Relationship between indoor and outdoor NO2: A review, Build. Environ. 180 (2020) 106909, https://doi.org/10.1016/j.buildenv.2020.106909.