2022 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
University of Calabria, Italy, October 19-21, 2022

Monitoring of the concentration of particulate matter, volatile organic compounds and nitrogen dioxide in the Vesuvius National Park

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***Abstract* – In this work, the air concentration of particulate matter (PM10, PM2.5), nitrogen dioxide (NO_2), benzene, toluene, ethylbenzene and xylenes (BTEX) in the area of the Vesuvius National Park (Naples, Southern Italy) was monitored. These values are fundamental to evaluate the effects of these pollutants on both the works of archaeological, historical and artistic interest and the numerous people who visit these sites. The atmosphere in the considered area was characterised by high PM pollution (average concentrations: 59.1 μg/m^3 and 50.1 μg/m^3 for PM10 and PM2.5 respectively), a quite high concentration of BTEX (average total concentration of 8.25 μg/m^3), and an average concentration of 10.3 μg/m^{3}of NO_2.**

I. INTRODUCTION

Air pollution, such as NOx, PM10, PM2.5 and volatile organic compounds (VOCs), has evolved in both urban and rural regions around the world over the last one hundred years [1]. The ambient air pollutants (e.g., CO_2, NOx, SOx, PM and VOCs) have a potential adverse impact on buildings, artifacts and biochemical parameters, which further leads, for example, to a reduction in plant growth and development [2–4]. Moreover, a high concentration of specific pollutants can pose risks to human health [5–8].

In recent years, urban air pollution represents one of the greatest environmental challenges in the 21st century [9,10]. In particular, urban fine PM has been associated with negative human health impacts [10]. PM effects on human health range from aggravating allergies to the development of serious chronic diseases and premature death [11–14]. The PM toxicity derives from the toxic effects of its constituents, including VOCs, NOx, polychlorinated biphenyls (PCBs), crustal materials, metals and also microplastics [15–19].

In urban areas, air pollution is a great problem that manifests itself differently in countries on the basis of economical, technological, political development and nature and energy sources [20]. It is well known that air pollutants cause a reduction of the lifespan of materials and coating leading to corrosion of cultural heritages, which is an inestimable damage due to the original material loss and the damage to aesthetic purpose and message [21–23]. In particular, stone materials are strongly damaged by air pollution in urban areas characterized by high anthropogenic emissions [24]. In the limestone's case, for example, black crusts are a common alteration of this material, due to the interaction of sulphur dioxide, PM10, and acidic rain [25,26]. It is well known that NOx concurr in the acidification of rain, thus these Major degradation results in cultural heritagescompounds are important in the degradation of limestone, [27]. Regarding the influence of PM on cultural heritage degradation, the most important characteristics are the size and the chemical composition [28]. It is known that atmospheric PM can damage stone artifacts by crystallization of salts from solution and hydration of salts that have more than one hydration state [29]. This study is focused on the analysis of different pollutants (PM10, PM2.5, VOCs, and NOx) in the area of Vesuvius National Park (Naples, Italy).

The territory of Vesuvius National Park [30] is a concentration of naturalistic riches, history of volcanology, breath-taking landscapes, centuries-old crops, and traditions that make the Vesuvius area one of the most fascinating and among the most visited places in the world. Vesuvius National Park was officially established on June 5, 1995, to conserve animal and plant species, plant and forest associations, geological singularities, paleontological formations, biological communities, biotopes, scenic and panoramic values, natural processes, hydraulic and hydrogeological balances, and ecological balances of the Vesuvius area. In addition to its natural heritage, the park is home to several works of archaeological, historical and artistic interest, the most important of which are: i) the Herculaneum excavations; ii) the Herculaneum antiquarium; iii) the Boscoreale antiquarium; and iv) Villa Augustea in Somma Vesuviana.

In this work, the atmospheric concentrations of PM, VOCs (especially benzene, toluene, ethylbenzene and xylenes, i.e., BTEX) and NO_2 were monitored in the urban area of San Giuseppe Vesuviano and San Gennaro Vesuviano, located in the borders of Vesuvius National Park (Neaples, Italy) and near some of the most important cultural heritage sites.

II. MATERIALS AND METHODS

A. Particulate matter sampling

Particulate matter (PM) analyses were carried out with the gravimetric method. Air is drawn through a size-selective inlet and then through a preweighed quartz-fiber filter, and particles collect in the filter. The filter is then removed and reweighed. The pump worked in the sampling site for 24 h per sampling and the air flux was set at 2.3 m^3/h. After this time, the filter was stored at 4 °C. Then, the filter was dried and weighed to obtain the mass in µg of PM.

The air concentration in µg/m^3 of PM was calculated using the equation (1):

$$C\left(\frac{\mu g}{m^3}\right) = \frac{m_{PM}}{F * t_{PM}} \qquad (1)$$

where m_{PM} is the mass of PM in µg, t_{PM} is the sampling time in hours and F is the air flux in m^3/h.

B. Passive air sampling

NO_2 and BTEX were collected through passive sampling techniques. Passive samplers, RING® radial diffusive devices were purchased from Aquaria (Aquaria Srl, Milan, Italy). Activated carbon was used as sorbent materials for BTEX, while triethanolamine for NO_2. The pollutants were monitored according to the National Institute for Occupational Safety and Health (NIOSH) methodologies: NIOSH n° 6014 for NO_2 and NIOSH n° 6014 n° 1500 for BTEX. Sampling time was in the range of 7-15 days. Three passive samplers were used for each determination and the analyses were performed in triplicate.

The detection of NO_2 was performed through a Spectroscopic assay using a Varian Cary® 50 UV-VIS spectrophotometer [31–33]. BTEX determination was carried out by gas chromatography with a flame ionization detector (Agilent Technologies) [34,35] on carbon disulfide extracts.

The air concentration (µg/m^3) of NO_2 was determined from the equation (2):

$$C\left(\frac{\mu g}{m^3}\right) = \frac{m_{NO2}}{t_{NO2}} * K \qquad (2)$$

where m_{NO2} is the mass of NO_2 in µg, t_{NO2} is the exposure time in hours and K=157.82 h/m^3.

The air concentration (µg/m^3) of BTEX was calculated using the equation (3):

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

where m_{BTEX} is the mass of each BTEX in µg, t_{BTEX} is the exposure time in minutes and F is the sampling flow rate (73, 66, 60 and 64 mL/min for benzene, toluene, ethylbenzene and xylene respectively).

III. RESULTS AND DISCUSSION

The concentration of air pollutants such as PM, nitrogen oxides and VOCs, that cause deterioration of cultural heritage and can be potentially harmful to human health, is an important task of research. In this study, PM was monitored using the gravimetric method, whereas NO_2 and BTEX were collected using passive sampler devices.

Results of gravimetric analyses showed that the average PM 10 and PM 2.5 concentrations were 59.1 and 50.1 respectively (Figure 1). Sample 2, Sample 3 and Sample 4 exceed the annual average Italian concentration limit [36], which is set at 40 µg/m^3 for PM 10 and 25 µg/m^3 for PM 2.5. Sample 1, instead, exceeds only the limit for PM 2.5. Sample 4 exceed also the recommended limit of PM 2.5 for the proper conservation of cultural heritage regulated by UNI 10586/97 (<50 µg/m^3) [37].

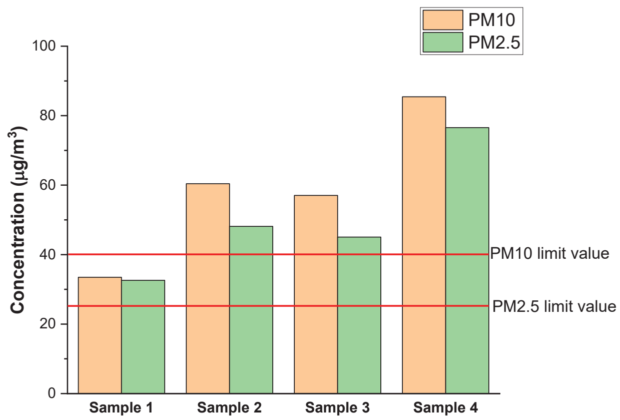

Figure 1 – Air concentration (µg/m^3) of PM 10 and PM 2.5; four samples are shown. Red lines indicate the annual average Italian concentration limits.

The high concentrations of PM may be due on the one hand to the very intense vehicular traffic in the area under consideration and on the other hand to the high density of commercial activities that require the use of wood-fired ovens for the production of foodstuffs (e.g., pizzerias, ovens, pastry shops etc.) as well as the high population density of the place (an average of 2672 inhabitants / km² in the entire province of Naples).

One of the meeting points of the ancient Herculaneum people was certainly the public fountains placed at street crossings. These were limestone basins decorated with figures of deities among which Neptune, Hercules, Minerva and Venus can be recognized. Figure 2 clearly shows the signs of degradation on the Neptune fountain. The white limestone, in addition to signs of degradation due to wear over time, shows clear deposits of black dust.

Figure 2 – Neptune Fountain in the Herculaneum excavations, with black patina showing signs of degradation due to particulate matter

The NO_2 concentrations (Figure 3) were in the range of 7.2-12.7 μg/m^3, with an average value of 10.3 μg/m^3. Despite the high vehicular traffic in the Vesuvius National Park, all these concentration values are lower than the Italian annual average regulatory limit (40 μg/m^3) [36]. All values, however, exceed the UNI 10586/97 recommended limit for the proper preservation of cultural heritages (< 2 μg/m^3).

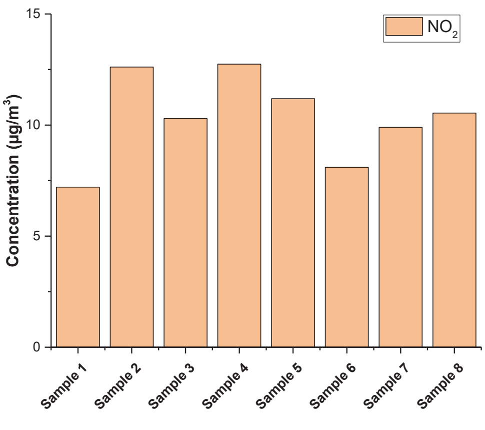

Figure 3– Air concentration (μg/m^3) of NO_2; eight samples are shown.

The chemical analyses of BTEX passive air samplers showed that the average concentrations for benzene, toluene, ethylbenzene, and xylenes were 2.55, 3.54, 0.47 and 1.69 μg/m^3 respectively, while the average total concentration was 8.25 μg/m^3 (Figure 4).

Among these pollutants, only benzene is regulated by an Italian annual average regulatory limit (5 μg/m^3) [36]. In all samples this limit is not exceeded but, the sum of all pollutants leads to high exposure for visitors to the archaeological sites.

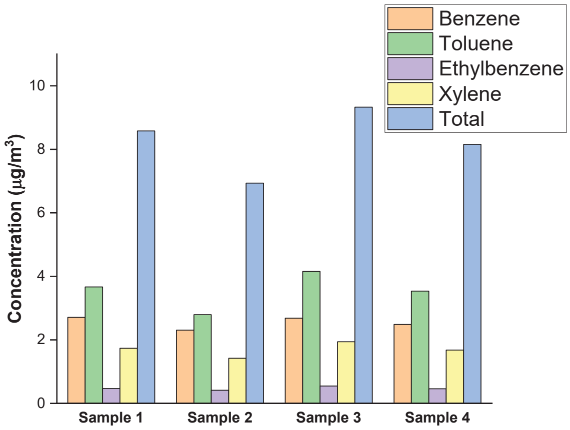

Figure 4 – Air concentration (μg/m^3) of BTEX; four samples are shown.

Monitoring the concentration of BTEX at heavily visited archaeological sites is of paramount importance as these pollutants have an adverse effect on human health and prolonged exposure to high concentrations can cause serious health complications.

This work is only a preliminary analysis and more detailed characterizations are required. Often the results of degradation of cultural properties and buildings may be visible after several years, which makes restoration more difficult and expensive. For this reason, the identification of such pollutants and control of external environmental conditions are essential to reduce the damage to heritage, suggesting new and correct procedures for restoration.

IV. CONCLUSIONS

In this work, PM10, PM2.5, NO_2 and BTEX concentrations have been analysed in the area of Vesuvius National Park, a site plenty of cultural, historical, archaeological and natural heritage of national importance in Italy. High particulate matter concentration was detected in the area under study, with an average concentration of 59.1 μg/m^3 for PM10 and 50.1 μg/m^3 for PM2.5. Moreover, three out of four samples exceed the

Italian regulatory limits (annual average concentrations of 40 mg/m^3 for PM 10 and 25 μg/m^3 for PM 2.5). Indeed, nitrogen dioxide concentrations (range 7.2-12.7 μg/m^3) are always lower than the Italian annual average regulatory limit. Concerning BTEX, the benzene concentration is below the regulatory limit (annual average concentration of 5 μg/m^3) for all samples, but the sum of the four is quite high for all four samples (average concentration of 8.25 μg/m^3).

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