

Development of an analytical methodology based on stable isotope ratios for air quality assessment in cultural heritage

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Abstract – The preservation and conservation of cultural heritage require a multidisciplinary approach related both to material and environmental science. The study focuses on an innovative application of stable isotope analyses to assess the air quality in cultural heritage sites both indoor (museums, churches, historical buildings) and outdoor (archeological sites). Results of our analysis showed that the value of stable carbon isotope varies with visitor presence or different concentrations of air pollutants. These findings suggest that the proposed methodology is suitable to identify problems related to air quality in cultural sites, thus helping preservation actions that must be done.

I. INTRODUCTION

In environmental and cultural heritage sciences, the understanding of the origin and the evolution of contaminants is necessary to guide the decisions taken by the museum committee of historical sites [1–3]. The remediation activities, with the possible temporary closure of visitor accesses, have a significant impact on the economy of the site and the public service. These problems highlighted the requirement of appropriate tools to identify pollutants and their sources as well as to verify the performance of the proactive actions on the historical sites [4,5]. The International Council Of Museum e Committee for Conservation (ICOM-CC) defined preservation as “all measures and actions aimed at avoiding and minimizing future deterioration or loss” [6]. These actions depend on the context and the surroundings of an item, but more often a group of items, according to the materials and structures. The assessment of air pollution permits to reduce the maintenance and restoration costs, an important topic in the conservation of Cultural Heritage.

Different air pollutants, comprising carbon dioxide (CO₂), nitrogen dioxide (NO₂), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), particulate matter, and some persistent organic pollutants, have negative effects on cultural heritage [7–15], and at high concentrations can pose risks to human health [16–19].

The growth in the level of carbon dioxide in the atmosphere has raised much interest in the chemical and physical implications [20–22]. In particular, recent studies focused on the possibility to use carbon dioxide as a reference parameter for air pollution and correlate the concentration range of other pollutants [23–26].

Carbon stable isotope ratio, expressed as $\delta^{13}\text{C}$, is a useful tool for the identification and classification of the origin of a sample [27–32], including CO₂ sources [26]. In fact, carbon stable isotope ratio permitted to discriminate between anthropogenic (e.g., vehicular traffic) and biogenic origin of CO₂ in urban environments [26]. $\delta^{13}\text{C}$ of atmospheric CO₂ resulted to have characteristic values, depending on the type of environment: in a rural area, $\delta^{13}\text{C}$ values ranged from –27 to –18.5 ‰; in an urban environment, $\delta^{13}\text{C}$ varied from –35 to –25.6 ‰ due to vehicular traffic (combustion processes of fossil fuels); in a common house kitchen, carbon stable isotope ratio was in the range from –45 to –40 ‰ because of the burning of methane and other hydrocarbons.

In the last years conservators and curators paid much attention to the variability of microclimate conditions, contaminations, air pollution and influence of visitors on the damage of cultural heritage sites. In this context, we developed an analytical methodology based on the measurement of carbon stable isotope ratios for air quality assessment in cultural heritage sites. In order to evaluate the applicability of this methodology in the field of cultural heritage, different types of environments

(indoor and outdoor) were studied. Specifically, we identified three sites of artistic and cultural interest: i) the refectory of Santa Maria delle Grazie in Milan (Italy), containing the Last Supper, one of Leonardo da Vinci's most famous paintings, characterized by a high influx of visitors and high control of environmental conditions; ii) the monumental complex of San Pietro a Corte, in Salerno (Italy), with a non-constant influx of visitors throughout the year and no control of air quality; iii) thermal springs of Contursi Terme (Salerno, Italy) as archaeological areas (outdoor environment), characterized by a high concentration of sulfur pollutants.

These cultural heritage sites differ from each other in the influx of visitors and its variability during the year, as well as the control of microclimatic conditions. For instance, due to its high artistic value, Leonardo's painting is protected by a sophisticated system of filtering and ventilation to control heating and humidity. However, many projects analyzed the risk of contamination from air pollution arising from its surrounding Milan area. The monumental complex of San Pietro a Corte, indeed, has no system to control these parameters, although it is located in the historic center of the city of Salerno. On the other hand, thermal springs are outdoor environments in which high concentrations of H₂S and SO₂ can cause the degradation of archeological objects.

Definitely, we measured the air concentration of different pollutants and the carbon stable isotope ratio of CO₂ collected by passive sampling in these sites in order to assess a possible correlation between these two parameters. Such a simple methodology could be very useful in the assessment of air quality in cultural heritage.

II. MATERIALS AND METHODS

A. Air monitoring

The air monitoring in the archaeological locations was conducted using passive samplers. RING® radial diffusive devices purchased from Aquaria (Aquaria Srl, Milan, Italy)[33–36] were located at a height of 1 m in the archaeological sites and museum environments. Three passive samplers were used for each determination 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.

Figure 1 shows the localization of the sampling points in the three sites: (a) two points inside and two outside the Refectory of Santa Maria delle Grazie; (b) one point near the source of the Thermal Spring of Contursi Terme and two points far from it; (c) two points inside the monumental complex of San Pietro a Corte and one point outside it. The monitoring was carried out during different seasonal periods: from September to November 2016 and May to July 2017 in the Refectory of Santa Maria delle Grazie; from October 2014 to January 2015

(during the social and cultural events) and from April 2015 to January 2016 in the monumental complex of San Pietro a Corte; and from January to April 2015 in the thermal environments.

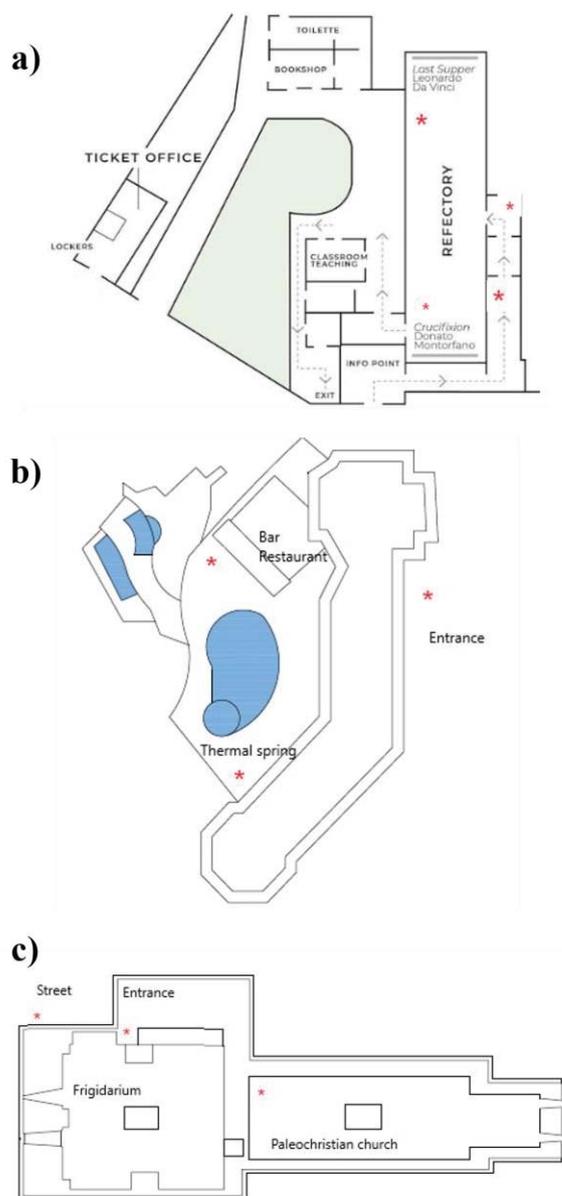


Fig. 1. Historical sites studied: a) Refectory of Santa Maria delle Grazie in Milan, Italy; b) Thermal springs in Contursi Terme, Salerno Italy; c) S. Pietro a Corte in Salerno Italy. Position of passive sampling are indicated by red asterisk (*).

B. Carbon stable isotope ratio measurement

$\delta^{13}\text{C}$ analysis was conducted by means of a HeliFANplus analyzer equipped with a single beam nondispersive infrared industrial photometer. After the exposure at the sampling locations, the sorbent materials

were placed into a glass flask and mixed with 2.5 mL of orthophosphoric acid to develop CO₂ from the carbonates. CO₂ was then gathered into the aluminized breath bags connected with the inlet ports of the NDIR spectrometer for sequential measurements. The NDIR device was connected to a computer, which enables the software-guided measurement and calculation of results. Three samples were analyzed for each determination.

The carbon isotope ratio was expressed in δ‰ relative to V-PDB (Vienna-Pee Dee Belemnite), according to the IUPAC protocol in:

$$\delta^{13}\text{C} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} * 1000 \quad (1)$$

where R is the ratio between the heavier isotope and the lighter one.

III. DISCUSSION

The most significant results obtained during the air monitoring campaigns in three different historical sites are shown in Figure 2. The values of carbon stable isotopic ratio δ¹³C (‰) of CO₂ collected by passive sampling vary in specific sampling times.

In the Refectory of Santa Maria delle Grazie, δ¹³C follows a daily trend, with different values depending on visitor attendance (Figure 2 a), i.e. during the visits and the closure of the museum. In particular, in the early morning δ¹³C value was -11.3 ‰, very close to the stable isotope value of carbon dioxide in the urban environments, while during a visit of 30 people the δ¹³C decreased to values associated with their presence. The same results were obtained in two important historical places in the old part of the city of Salerno, Italy: Fruscione Palace and S. Pietro a Corte. The cases study focused on the influence of tourists on environmental pollution correlated to indoor air quality during some social and cultural events. The δ¹³C (‰) values followed a clear seasonality trend (Figure 2 b): during the periods of the maximum presence of tourists (April, December, and January), there were very low levels, typical of the carbon isotopic composition of the human breath. Higher values are recorded in the other periods (June-October) corresponding to the increasing pollution due to vehicular traffic. During the monitoring campaigns, we observed that isotopic carbon composition varied with the increase in the concentration of air pollutants (e.g. ammonia, benzene, etc.), traffic, and visitors.

The isotope carbon composition variation during the winter, spring and summer seasons with the increase of visitors was noted also in the monitoring campaign of thermal springs under study (Figure 2 c). The δ¹³C value indoor ranged from -9.5‰ to -19.7‰, while stable carbon isotope composition outside values ranged from -24.0‰ to -31.2‰ due to the dilution effects of the carbon dioxide produced by the thermal spring, and the presence

of other sources, such as urban traffic, vegetation and respiration processes of plants.

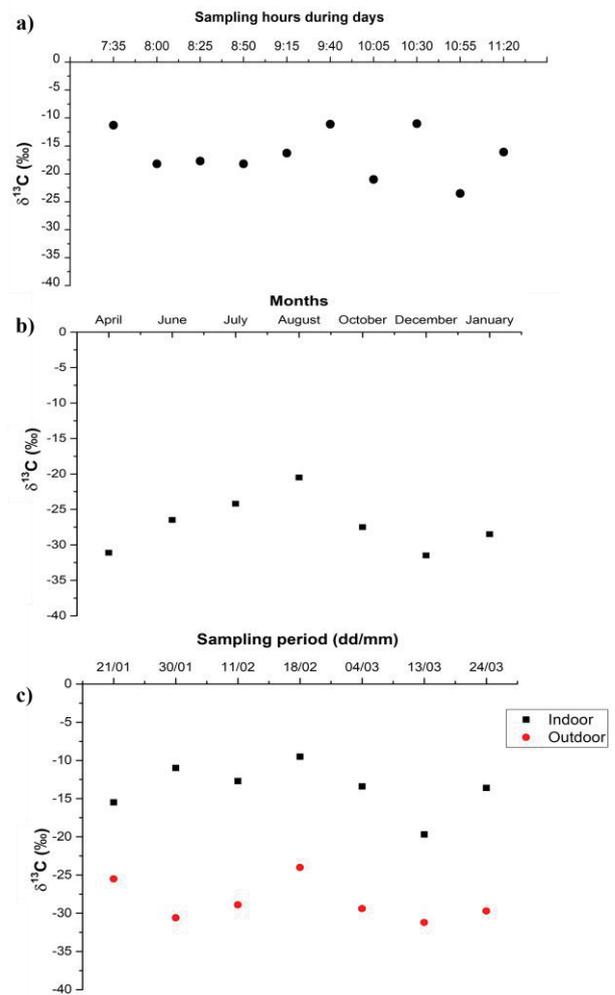


Fig. 2. Observed variation of δ¹³C in the different sites: a) Refectory of Santa Maria delle Grazie; b) S. Pietro a Corte; c) Thermal springs in Contursi Terme

During the monitoring campaigns, there was clear evidence of the variation of the isotopic composition of CO₂ with the presence of visitors. However, the variability of microclimate conditions, contaminations, air pollution and influence of visitors could be an important parameter for the conservation of historical structures and to evaluate the damage to place. The proposed methodology can be used as a supplemental and non-invasive tool to help in calibrating microclimatic conditions through the ventilation rate and air filtration systems in the museum and to manage the number of visitors per turn.

IV. CONCLUSIONS

The monitoring of air pollution and δ¹³C of atmospheric CO₂ was performed in three cultural heritage

sites at different sampling periods. Analysis of results on different types of cultural heritage sites (with or without controlled microclimatic conditions, indoor or outdoor) proves that the proposed analytical technique is valid for air quality assessment. In fact, variations in the value of the stable carbon isotope ratio were noted to be correlated with increasing or decreasing visitor presence (in the case of the Refectory of Santa Maria delle Grazie) or varying air quality (in the case of the monumental complex of San Pietro a Corte). These findings make it possible to identify problems related to air quality at cultural sites and improve the actions that must be put in place for preservation. This correlation revealed that $\delta^{13}\text{C}$ value could be used as a robust and non-invasive marker for the air quality in the archeological and museum sites and its monitoring could suggest a new analytical methodology to warn conservation of urban cultural heritage.

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