2020 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Trento, Italy, October 22-24, 2020

Correlation of indoor air quality and stable carbon isotope ratio of CO_2 in historical monuments of Italy: a case study

Concetta Pironti[1], Maria Ricciardi[1], Antonio Proto[2] ,

Raffaele Cucciniello[2], Antonino Fiorentino[2], Oriana Motta[1]

[1] Department of Medicine Surgery and Dentistry, University of Salerno, via S. Allende, 84081 Baronissi (SA), Italy
[2]Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy

Abstract **- Conservators and curators pay much attention to the variability of microclimate conditions, contaminations, air pollution, and the influence of visitors on the damage of museums since atmospheric and gaseous pollutants could affect the conservation of cultural heritage. This work has regarded the monitoring of indoor air quality to evaluate the effects of environmental pollution in the field of cultural heritage. In particular, two different archaeological places were analysed: *Fruscione Palace* and *S. Pietro a Corte* in Salerno, Italy. The work focused on the influence of tourists on environmental pollution correlated to indoor air quality during many social and cultural events. Moreover, it was also analysed the possible use of the carbon isotope composition of CO_2 as a tool for environmental studies in the field of cultural heritage. The results showed a good correlation between the isotopic composition of CO_2 and the variation of pollutants concentration in the air, demonstrating that it is a valid tool and non-invasive marker to monitor environmental pollution of museums and cultural heritage.**

Keywords environmental pollution, air quality, contaminants, cultural heritage

I. INTRODUCTION

Industrial and social evolution had influenced the degradation of built heritage, added to natural weathering and aging [1]. The preservation of cultural heritage has become an increasing concern over the past decades since it includes priceless cultural assets of identity and memorial value [2]. However, the preservation of historical constructions often contrasts with many factors that endanger them, putting cultural heritage at risk. In recent years, despite the improvement of air quality in urban areas, there was a real concern over the conservation of cultural heritage and the degradation of materials exposed to atmospheric pollution [3,4,5,6,].

The European Council has stated the effect of climate change on cultural heritage, highlighting the impact of climate and pollution acting together, causing many effects like decreasing pH value in precipitation and changes in pollutant deposition, which lead to effects such as stone recession, blackening of materials, corrosion of metals and bio-colonisation [7].

In environmental sciences, the understanding of the origin and the evolution of contaminants was necessary for the decisions that must be taken by industrial companies and international agencies of health. The identification of the pollution sources in cities and the remediation activities, with the possible temporary closure of industrial production, had a significant impact on the economy of the company. This problem highlighted the requirement of appropriate tools to identify pollutants and their sources as well as to verify the performance of the proactive actions.

Museums and historical buildings were considered in general as a major issue of concern for cultural heritage preservation. The exposure of artworks and materials to gaseous and particulate pollutants emitted from either indoor or outdoor sources contributes to their decay.

In cultural heritage, the most studied environmental pollutants are NO_2, SO_2, and CO_2 that have an effect on built heritage, which involves a chemical reaction between atmospheric pollutants and raw materials. For example, CO_2 produce a carbonation reaction, this is a natural effect, which can be aggravated by excessive atmospheric levels of CO_2 due to elevated global emissions, although localized attacks on concrete structures are more frequent. Average CO_2 levels in the atmosphere range just above 300 ppm, which is sufficient for carbonation to occur, although recent estimations show that CO_2 emissions have surpassed 400 ppm. In specific cases (e.g. road tunnels), CO_2 concentrations are even greater, possibly reaching over 2000 ppm.

In urban environments, carbon dioxide is emitted from

different anthropogenic and biogenic sources. For this reason in our work stable carbon isotope composition was investigated as a powerful tool for the identification and classification of the source of CO_2. In some scientific works, the isotopic composition of CO_2 was used to assess sources at a local scale to discriminate emissions from vehicles from emissions generated by the biological activity in the urban areas [8,9,10].

On the other hand, the disadvantage of this technique was that the $\delta^{13}CO_2$ value was often influenced by spatially and temporally specific parameters. In a previous work [8] the isotopic ratio $\delta^{13}CO_2$ was used as a marker of carbon dioxide collected in three different areas: a rural area where there were essentially plants and the contribution of carbon dioxide emission was attributed to the biological process of plants and $\delta^{13}C$ values ranged between −18.5 and −27‰; in an urban environment, $\delta^{13}C$ varied from −25.6 to −35‰ and the most important source was the combustion processes of fossil fuels; in civil inhabitation, near a kitchen, the burning of methane and other hydrocarbons was the source and stable carbon isotope value was from −40 to−45‰. This study has shown the reliability of $\delta^{13}C$ values as an environmental tool for the identification of pollutants [8].

Generally, isotopic compositions were used to set time constraints on processes and manufacturing of objects and to date human samples (e.g. the ^{14}C technique). Furthermore, the isotopic composition of metals like Sr and Pb isotopes were useful for tracing the origin of a component or a metal [11,12]. In our work we analysed the possible use of $\delta^{13}C$ values variation refer to atmospheric CO_2 as a simple tool for other specific pollutants of urban environments, such as SO_2 and NO_2.

SO_2 is produced from the combustion of solid fossil fuels and is considered the most relevant pollutant regarding material deterioration, especially in the corrosion of metals and stone recession. These corrosive effects are even greater with the presence of an oxidizer such as NO_2.

Fruscione Palace and *S. Pietro a Corte* are two important archaeological locations in Salerno and their preservation was the aim of a national project (DATABENC-SNECS) growing with different research centres, universities, and industries (see Figure 1). The excavations carried out by archaeologists in the Monumental Complex of *S. Pietro a Corte*, have brought to light a big space, in the hypogeum, where, successively two environments were evidenced, one with a temple of Priapus which then became a paleochristian church with wall frescos and a thermal structure with a frigidarium from the 1st or 2nd-century a.D. On the area above the excavations, starting from the current street level, the Lombard prince Arechi II, who elected Salerno as the capital of his kingdom, erected in the 8th century a.D. an autonomous structure intended for the function of a palatine chapel. The church of S. Pietro a Corte was situated in front of *Fruscione Palace* in a street near the city centre and together were a part of the same historical complex. The Church was composed of three levels: the first level was the frigidarium of ancient Roman thermal baths dating from the 1st -2nd a.D.; the second level was a Christian place of worship from the 5th to the 7th century according to holy paintings on the walls; the third structural phase of the building, promoted by the king Arechi, was represented by the autonomous structure of Cappella Palatina in the 8th-century a.D. In the *Fruscione Palace* are preserved the remains of a Norman building, ancient mosaics, and architectural elements of a Roman thermal bath. The project aimed to collect and publish scientific, artistic, archaeological, literary, historical, and philosophical knowledge of the local place supported by new technologies (mapping (GIS) modelling, aero-photogrammetric, toponomastics), to obtain interactive atlas with high definition and flexibility.

Fig. 1. Fruscione Palace and S. Pietro a Corte in Salerno

Concern about atmospheric pollution and damage on monuments highlighted the relationship between the presence of pollutants at low concentration and degradation events. In this work, during many social and cultural events as a biennial exhibition of contemporary art, Luci d'artista organised at *Fruscione Palace* and *S. Pietro a Corte*, it was analysed the influence of tourists on environmental pollution associated to indoor air quality and possible correlation with carbon isotope composition of CO_2.

These findings alongside with new archaeological studies, could be useful to address more specifically any restoration project of the entire monumental complex.

II. MATERIALS AND METHODS

A. Air monitoring

The air monitoring of archaeological locations was developed using passive samplers, RING® radial diffusive devices were purchased from Aquaria (Aquaria Srl, Milan, Italy). In particular, pollutants monitored were NH_3, NO_2, BTEX, H_2S, SO_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 methodologies used for the different pollutants:

- n° 2018, Aliphatic Aldehydes;
- n° 1500, Hydrocarbons, BP 36°-216° C;
- n° 6013, Hydrogen Sulfide;
- n° 6014, Nitric Oxide and Nitrogen Dioxide;
- n°6004, Sulfur Dioxide;
- n° 6015, Ammonia.

B. Preparation of high reactivity calcium oxide substrate for CO_2 capture

Calcium oxide-based sorbent was prepared as follows: 56.8 g of aluminium nitrate enneahydrate [$Al(NO_3)_3$ $9H_2O$] and 52.4 g of calcium oxide were added into a mixture of distilled water (1.5 L) and 2-propanol (260 mL) so that the weight ratio of calcium oxide to the newly formed mayenite ($Ca_{12}Al_{14}O_{33}$) would become 75:25 w/w. This solution was stirred for 1 h at 75 °C and successively dried at 120 °C for 18 h before being roasted at 500 °C for 3 h in the air. This method produced a fine and porous powder. After calcination, distilled water was added to the mixture and the obtained paste was dried at 120 °C for 2 h and then calcined in air at 800 °C for 1.5 h [9, 13].

All reagents were purchased at reagent grade from SigmaAldrich. Before exposure to CO_2, the sorbent was "activated" by hydrating with water vapor in a closed system for 7 days.

The crystalline structure of both hydrated and dehydrated sorbents was characterized by XRD analysis. Hydration was also necessary to avoid interferences due to variable atmospheric humidity during the exposition and to avoid potential errors in the quantitative evaluation of trapped CO_2.

Thermogravimetric analysis of the substrate after exposure. The quantitative determination of the captured CO_2 can be performed by thermogravimetric analysis (TGA) by evaluating the weight loss in the furnace during heating. Loss in sample weight between 500 and 800 °C in an inert atmosphere is directly correlated to the carbonate content of the sorbent, and hence to trapped carbon dioxide. The mass sample evolution was recorded, as a function of temperature, by using a Netzsch TG 209 apparatus. The analysis was carried out on samples with a mass of about 20 mg placed inside an aluminium crucible. The sample temperature was then increased with a heating rate of 10 °C min−1 from room temperature up to 900 °C under an inert atmosphere of nitrogen. The temperature of the sample and the reference were recorded by a platinum/rhodium thermocouple and a high-precision balance registered the weight loss due to the decomposition of the sample. Thermal analyses were repeated three times to test sample homogeneity and also the reproducibility of the instrument.

C. Field measurements

$\delta^{13}C$ measurements were performed in two autumn/winter campaigns during the period ranging from November 2014 to April 2015 and from April 2015 to January 2016, in two different environments in order to investigate spatial variations and a possible correlation with carbon dioxide concentration in air. The tested sites are two important archaeological locations in Salerno, *Fruscione Palace* and *S. Pietro a Corte*. An elevated density of traffic and population characterized the area during cultural events. Carbon dioxide for $\delta^{13}C$ measurements was collected through a diffusive sampling technique. The diffusive body was the commercial RING from Aquaria Srl, where the internal concentric steel cartridge was filled with 500.0 mg of a $CaO/Ca_{12}Al_{14}O_{33}$ 75:25 w/w hydrated sorbent.

The samplers were located at a height of 1 m of height in the archaeological sites. Three passive samplers were used for each determination.

D. Carbon isotopic ratio analysis

$\delta^{13}C$ 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 CO_2 from the carbonates. CO_2 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:

$$\delta^{13}C = [\ (R_{sample} - R_{standard}\ ) \setminus R_{13standard}\ ] \times 1000 \qquad (1)$$

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

III. RESULTS AND DISCUSSION

In the first part of the work it was analysed the effect of visitors in *Fruscione Palace* on the concentration of pollutants during contemporary art exhibition and cultural events, The air monitoring was conducted using passive samplers and the pollutants monitored were NH_3, NO_2, BTEX, H_2S, SO_2[13,14,15]. The results are reported in

Table 1.

Table 1. Concentrations of pollutants during and after cultural events.

	Before cultural events	During cultural events
NH_3 ($\mu g/m^3$)	0,22	0,58
NO_2 ($\mu g/m^3$)	0,67	1,74
CH_2O ($\mu g/m^3$)	3,78	3,86
Benzene ($\mu g/m^3$)	6,95	10,34
Toluene ($\mu g/m^3$)	2,08	12,11
Ethylbenzene ($\mu g/m^3$)	0,144	1,707
H_2S ($\mu g/m^3$)	0,068	0,042
$\delta^{13}C$ (‰)	-25,4	-29,2

The values show a strong correlation between greater presence of visitors during cultural events and increasing concentration of pollutants, such as ammonia raising from 0,22 to 0,58 $\mu g/m^3$ and toluene from 2,08 to 12,11 $\mu g/m^3$. However, the concentrations of pollutants reported in Table 1 always respected the limits reported in the literature. [16] In the same way the value of $\delta^{13}C$ (‰) was influenced, passing from -25,4 ‰ to -29,2 ‰. Indoor air quality (IAQ) is a well-known problem and its impact on human health has been addressed several times by the World Health Organization (WHO) in various documents and meetings and has been figured out at various levels [17,18,19,20]. Only in recent years, researches have highlighted the great importance that IAQ has in all environments (houses, schools, museums, banks, post offices, offices, hospitals, and public transport) [21,22].
The monitoring of NO_2, SO_2, and $\delta^{13}C$ was also performed in *S. Pietro a Corte* (see Table 2) from April 2015 to January 2016. During the period ranging from April to August values of pollutants decreased following seasonality, whereas they increased again during autumn and winter with the increasing pollution, traffic, and visitors, and $\delta^{13}C$ (‰) had the same trend.

Table 2. Atmospheric concentration of pollutants in S. Pietro a Corte.

	$\delta^{13}C$ (‰)	NO_2 ($\mu g/m^3$)	SO_2 ($\mu g/m^3$)
April	-31,1	3,88	0,56
June	-26,5	2,5	0,2
July	-24,2	0,507	1,4
August	-20,5	0,320	0,14
October	-27,5	2,9	1,2
December	-31,5	3,9	0,75
January	-28,5	2,8	0,83

IV. CONCLUSIONS

The monitoring of atmospheric pollutants demonstrated the influence of visitors on the preservation of archaeological sites.

The effects of degradation are visible after several years when the restoration of monuments is necessary and difficult. For this reason, good preservation of museums cannot leave out the control of the external environment into which they are exposed. Historically, it was studied the influence of environmental components – humidity and temperature – on the preservation of Fine artworks (monuments, paintings, manuscripts); only in recent years, researches are focused on degradation linked to chemical interactions with gases and aerosols present in the urban environment. The importance of the study is linked not only to the assessment of the concentration but also to the assessment of the presence of certain types of pollutants that, even at low concentrations, can have a lasting effect over time. In this work, we looked for the pollutants that are most representative of vehicular traffic and that can be linked to the presence of visitors. During the monitoring campaigns, we noted an increasing trend in the concentration of the chemicals analysed with a variation that in some cases were very important (ammonia concentration varied from 0,22 to 0,58 $\mu g/m^3$ and toluene concentration from 2,08 to 12,11 $\mu g/m^3$). These representative pollutants are strongly linked to an increasing in traffic and visitors in correspondence to cultural events and art exhibitions. Analogously the isotope carbon composition varied during the autumn and winter season with the increase of pollution, traffic, and visitors. This correlation revealed that $\delta^{13}C$ value could be used such as a robust and non-invasive marker for the air condition in the museum sites and its monitoring could suggest a strategy for the preventive conservation of urban monumental heritage. The chemical identification of pollutants is essential to reduce the damage on architectural structures and archaeological heritage preserved in them, suggesting new and correct procedures of restoration such as limitation of entrance or implementation of air filtration systems.

REFERENCES

[1] N. Ghedini, I. Ozga, A. Bonazza, M. Dilillo, H. Cachier, C. Sabbioni. Atmospheric aerosol monitoring as a strategy for the preventive conservation of urban monumental heritage: the Florence Baptistery, Atmos. Environ. 2011, 45,33, 5979–5987.

[2] T. Grøntoft. Conservation-restoration costs for limestone facades due to air pollution in Krakow, Poland, meeting European target values and expected climate change, Sustainable Cities and Society 2017, 29, 169–177.

[3] C. Di Turo, A. Proietti, M.F. Screpanti, I. Fornasier, G. Cionni, A. Favero, A. De Marco, Impacts of air pollution on cultural heritage corrosion at European level: What has been achieved and what are the future scenarios, Environ. Pollut. 2016, 218, 586-594

[4] L.T. Silva, B. Mendes, C. Oliveira, C. Reis, P. Silva, J. F. Silva Contribution of an environmental monitoring system to evaluate the potential effect of urban air pollution. Procedia Structural Integrity 2019, 22, 130-136.

[5] G. Vidorni, A. Sardella, P. De Nuntiis, F. Volpi, A. Dinoi, D. Contini, V. Comite, C. Vaccaro, P. Fermo, A. Bonazza. Eur. Phys. J. Plus 2019, 134-439

[6] F. Vidal, R. Vicente, J. M. Silva, Review of environmental and air pollution impacts on built heritage:10 questions on corrosion and soiling effects for urban intervention. Journal of Cultural Heritage 2019, 273–295

[7] C. Sabbioni, M. Cassar, P. Brimblecombe, R.A. Lefevre. Vulnerability of cultural heritage to climate change, Council of Europe report AP/CAT 2008, 44.

[8] A. Proto, R. Cucciniello, F. Rossi, O. Motta Stable carbon isotope ratio in atmospheric CO_2 collected by new diffusive devices Environ Sci. Pollut. Res. 2014, 3182-3186 doi: 10.1007/s11356-013-2369-3

[9] R. Cucciniello, A. Proto, D. Alfano, O. Motta, Synthesis, characterization and field evaluation of a new calcium-based CO2 absorbent for Radial diffusive sampler. Atmospheric Environment 2012. 60, 82-87
   a. doi: 10.1016/j.atmosenv.2012.06.023

[10] R. Zanasi, D. Alfano, C. Scarabino, O. Motta, R. Viglione, A. Proto Determination of $^{13}C/^{12}C$ carbon isotope ratio. Analytical Chemistry 2006, 79, 3080-3083.

[11] D. Alfano, A.R. Albunia, O. Motta, A. Proto, Detection of Diagenetic alterations by Spectroscopic Analysis on Archaeological Bones from the Necropolis of Poseidonia (Paestum): A case study", J. Cult. Heritage 2009, 10, 509-513 doi:10.1016/j.culher.2009.03.001

[12] A G Nord, K. Billström Isotopes in cultural heritage: present and future possibilities. Herit Sci 2018, 6-25 https://doi.org/10.1186/s40494-018-0192-3

[13] R. Cucciniello, A. Proto, F. Rossi, N. Marchettini, O. Motta, An improved method for BTEX extraction from charcoal Analytical Methods, 2015, 7, 4811 – 4815 doi:10.1039/C5AY00828J

[14] O. Motta, R. Cucciniello, C. Scicali, A. Proto A study on the applicability of zinc acetate impregnated silica substrate in the collection of hydrogen sulfide by active sampling. Talanta, 2014. 128,268-272 doi:10.1016/j.talanta.2014.04.031

[15] O. Motta, R. Cucciniello, R. La Femina, C. Pironti, A. Proto, Development of a new radial passive sampling device for atmospheric NOx determination Talanta, 2018, 19,199-203 doi.org/10.1016/j.talanta.2018.07.088

[16] F. Drougka, E. Liakakou, A. Sakka, D. Mitsos, N. Zacharias, N. Mihalopoulos, E. Gerasopoulos Indoor Air Quality Assessment at the Library of the National Observatory of Athens, Greece. Aerosol and Air Quality Research 2020, 20: 889–903,

[17] G. Settimo, M. Manigrasso, P. Avino Indoor Air Quality: A Focus on the European Legislation and State-of-the-Art Research in Italy. Atmosphere 2020, 11, 370

[18] M.J. Suess The Indoor Air Quality programme of the WHO regional office for Europe. Indoor Air 1992., 2,180–193.

[19] L. Mølhave; M. Krzyzanowski. The right to healthy indoor air: Status by 2002. Indoor Air 2003, 13, 50–53.

[20] M. Braubach; M. Krzyzanowski. Development and status of WHO indoor air quality guidelines. Syracuse, NY, USA, 2009.

[21] S. Tham, R. Thompson, O. Landeg, K.A. Murray, T. Waite. Indoor temperature and health: A global systematic review. Public Health 2020, 179, 9–17.

[22] C. Guerranti, F. Benetti, R. Cucciniello, D. Damiani, G. Perra, A. Proto, F. Rossi, N. Marchettini. Pollutants monitoring and air quality evaluation in a confined environment: The 'Majesty' of Ambrogio Lorenzetti in the St. Augustine Church in Siena (Italy). Atmos. Pollut. Res. 2016, 7, 754-76