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ENVIRONMENTAL IMPACT ASSESSMENT ON THE MONZA CATHEDRAL (ITALY): A MULTI-ANALYTICAL APPROACH.

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Abstract

This research deals with the characterization of black crusts collected from the Dome of Monza (Milan, Italy). Air pollution is responsible for the degradation of historical buildings surfaces. In urban and industrial areas, the degradation process is accelerated, due to carbonaceous particles and heavy metals emitted by combustion processes which contribute to the formation of black crust (BCs). In this study the characterization of BC was performed using different analytical techniques such as: HRSEM-EDX, IC, LA-ICP/MS and digital image analysis. In particular, the research focused on the study of "heavy metals" which contribute to the identify the main sources of pollution responsible for the surface's deterioration over time. BCs variability in composition also depends on the exposure of the analyzed surfaces.

Keywords*: Black crust; Gypsum; Carbonate stone; Cultural Heritage; Conservation; Ion chromatography; Heavy metals; HRSEM-EDX*

Introduction

Numerous studies carried out on the degradation of stone materials have shown that air pollution is one of the main causes of the blackening of surfaces [1-6]. These researhes [1, 3, 7-8] deal with the chemical interaction of atmospheric pollutants with stone surfaces and led to an in-depth knowledge of both the relationships between pollution and architectural surfaces and the interaction whit other environmental factors (water, soluble salts, etc.). The action of pollutants on surfaces causes the formation of dark-colored deposits called black crusts (BCs). The main degradation mechanism is sulphation which takes place in areas exposed to atmospheric agents, but protected by an intense washout [9-14].

Several authors [15-23] have highlighted that the study of trace elements inside black crusts is a useful tool to identify the different pollutants acting in the formation processes of BC. This information can be useful for defining new strategies for the protection and maintenance of historical monuments.

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In this work, the results obtained from the analysis of BCs taken from the historical Monza cathedral, an important monument placed in Monza, a highly polluted city nearby Milan (N Italy), are discussed. Although BCs of Monza cathedral have already been studied from the point of view of their mineralogical and the carbonaceous fraction [24], this paper focuses on the crusts morphology, and the identification of their heavy metals and main ions contents.

Monza Cathedral

Monza cathedral is located in the homonymous city placed ca. 20 km NE of Milan (Italy). Monza covers an area of 33.09 km^2 and has 123,776 inhabitants, being the third largest city in the Lombardy region (N Italy). The city suffers from high pollution produced by the intense vehicular traffic, domestic heating, as well as industrial and agricultural activities typical of the Po Valley. Several BCs fragments have been sampled at different heights from the cathedral façade and then characterized. The façade of the cathedral is a remarkable example of the 15th century architecture. The building is divided into three parts, and was designed and finished by Matteo da Campione between 1300-1350 AD. It is characterized by alternating dark and white-colored rows of stone blocks. From 1700 to 1900 several restoration works were carried out, involving only some areas [24-25]. It is worth to notice that the pollutants accumulation period of the analyzed samples (see next paragraph) depends on the date of the last restoration, which took place in 2017.

Materials and methods

Sampling

During the last restoration in 2017, 9 samples of BCs developed onto marble stones were taken from the façade of the cathedral (Fig. 1) at different heights. The samples were divided in two groups on the basis of the period of pollutants accumulation, taking into account the last restoration of the surface:

- Group A formed by samples 1MD, 3MS and 4MS located at ca. 16m high (these BCs represent about 280 years of pollution accumulation);
- Group B formed by BCs taken from a height of ca. 12m, i.e. 5MC, 7MD, 8MD and 9MD, and from a height of ca. 5 m samples, i.e. 11MD and 12MD (these BCs represent about 650 years of pollution accumulation).

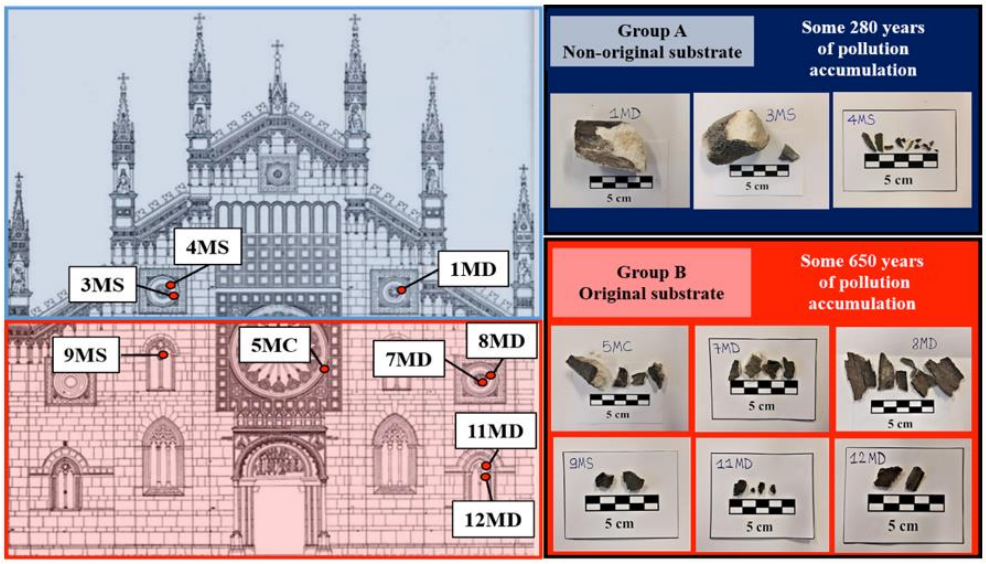


Fig. 1. Sampling sites and photographs of the black crusts collected from the façade of the Monza cathedral.

Analytical techniques

In order to obtain a complete characterization of BCs and the corresponding stone substrates, an integrated analytical study was conducted which involved the use of the techniques described below.

High Resolution Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy

HRSEM-EDX was used to characterize BCs micro texture and chemical composition. The instrument was a Supra 40Vp Carl Zeiss (Germany) furnished with BSE (backscattered electrons) and SE (secondary electrons) detectors (InLens) that deliver chemical and morphological images respectively, as well as a microanalysis system (Aztec 3) to provide elemental analyses by EDX (X-Max 50 mm detector). C-sputtered surfaces and cross sections obtained after embedding a 0.5x1x1 cm –fragment of each BC in styrene resin and cut and polished, were studied. The conditions of observation were accelerating potential of 15–20 kV, working distance of 9–11 mm and specimen current of 60 mA.

Ion Chromatography

The main ions present in BCs samples were quantified by IC analysis. The ionic species analyzed were Na^+, K^+, Ca^{2+}, Mg^{2+} and NH^{4+}, and NO_2^-, NO_3^-, SO_4^{2-}, Cl^- carried out by an ICS-1000 HPLC system equipped with a conductivity detector. The sample preparation and analytical procedure are reported elsewhere [22, 26-27]. PCA (principal components analysis) and consequent data elaborations have been carried out by means of Statistica software (by StatSoft).

Image analysis

A preliminary attempt to visualize and calculate the distribution of porosity (as % pore area measurement) within BCs samples was made by image processing procedure (by using a free IMAGEJ software) on cross section micrographs. Subsequently, the image analysis process was tested on SEM images acquired in BSE mode in selected BCs. Indeed, two selected BCs samples with different time of pollutants accumulation were chosen for this purpose, in particular 9MS and 1MD samples.

LA-ICP-MS

LA-ICP-MS has been used to determine trace elements. The instrument used was an Elan DRCe instrument (Perkin Elmer / SCIEX) connected to a New Wave UP213 solid state Nd-YAG laser probe (213nm). Spot resolution was around 40-50 μm [28-30] allowing in this way the identification of many trace elements. The analytical procedure to characterize BC is reported in literature [20-28]. PCA (principal components analysis) and consequent data elaborations have been carried out by means of Statistica software (by StatSoft).

Results and discussion

High Resolution Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy

The analysis was performed on representative samples (Group A and B).. Results showed that the stone substrates in all BCs samples were degraded. These substrates were crossed by a system of fissures into which gypsum precipitation was evident. Some examples on samples belonging to the two different groups are shown below in the text. HRSEM micrographs of bulk 1MD sample (Group A) showed that BCs were made of an interlocked structure of lenticular and/or hexagonal plate-like crystals arranged as rose-like clusters composed of Ca and S, which were attributed to gypsum (Fig. 2 a,b). X-ray maps acquired from 1MD cross section display the dissolution patterns of calcite crystals nearby the surface of the marble substrate, as well as the crystallization of acicular gypsum crystals inside calcite fissures (Fig. 2 c,d). Gypsum on the surface embeds minute particles of variable composition, such as silicates (Si/Al/Mg), Ba-sulfate, Ca- phosphate, Fe-rich and Pb-rich particles, as well as particles containing Zn (Fig. 2 e).

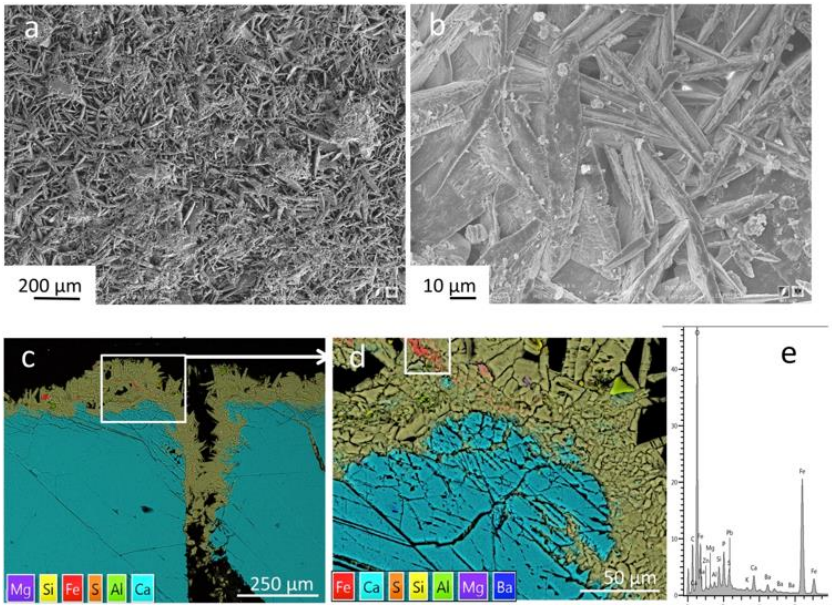


Fig. 2. (a and b) HRSEM micrographs showing 1MD BC sample; note the crust made of rose-like clusters of gypsum crystals and the tiny particles placed in the BC. (c and d) HRSEM-EDX false-color mineral map (thin section) of 1MD BC; note the dissolution patterns of the calcite crystals and the particles enclosed into the BC. (e) average EDX spectrum of the box shown in 2d.

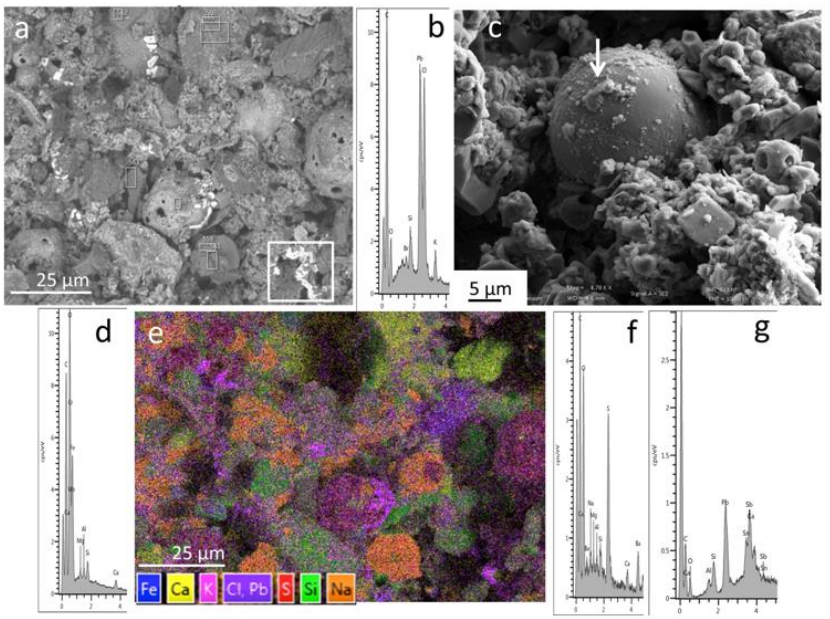


Fig. 3 SEM micrographs of 7MD and 9MS BCs (bulk samples). (a) 7MD crust made of granular and tabular gypsum crystals enclosing copious rounded spongy-like BCPs and metal particles (white box) made mostly of Pb and Cl. (b) EDX spectrum of 7MD-white box in 3a. (c) Smooth rounded BCP in 9MS crust. (d) EDX spectrum of metal particles (Fe, Cr) covering the CBP of image 3c (arrow). (e) HRSEM-EDX false-color mineral map of image 3a. Note the enrichment on Pb-Cl, Fe, K and Na elements. f) and g) are average spectra of metal particles composition.

Analysis of bulk 7MD and 9MS samples (Group B) by HRSEM show that crusts had a

powdered texture mostly made of granular and (hexagonal) plate-like gypsum crystals, as well as tabular crystals in lesser amount (Fig. 3a). Spheroidal spongy and/or smooth Black Carbonaceous Particles (BCP in Fig. 3a and c) as well as metal particles mainly rich in Pb and Br, in combination with K and Cl (Fig. 3b, e) were more abundant than in crusts from group A. As revealed by EDX analyses, clusters of tiny metal particles (e.g. Cr and Fe) covering the smooth rounded BCPs (Fig. 3c d) were also detected.

Other clusters of particles have variable composition such as: Ba-sulfate (Fig. 3f), glomerulus enriched by Sb, Sn, Pb and Al (Fig. 3g). Also K-sulfate, Ca-phosphate, and Al, Zn, Ti, and V were detected in the particles embedded into these BCs.

Ion Chromatography

Ion chromatography was used to quantify the main ions present in the BCs. In Fig. 4, it is shown the average ion concentrations obtained on the examined samples comparatively to those obtained in a recent study carried out on another monument built with a similar substrate, i.e. the Fontana di Trevi in Rome (Italy) [21], even if the period of crusts growth is different; BCs collected in Monza cathedral have grown during more decades than those found in Fontana di Trevi. Considering anions, with exception of NO_3^-, the concentration detected in Monza cathedral was notably lower. All cations concentrations (Na^{2+}, K^+, Mg^{2+} and Ca^{2+}) measured in the BCs of the Monza cathedral were lower than those collected in the Fontana di Trevi.

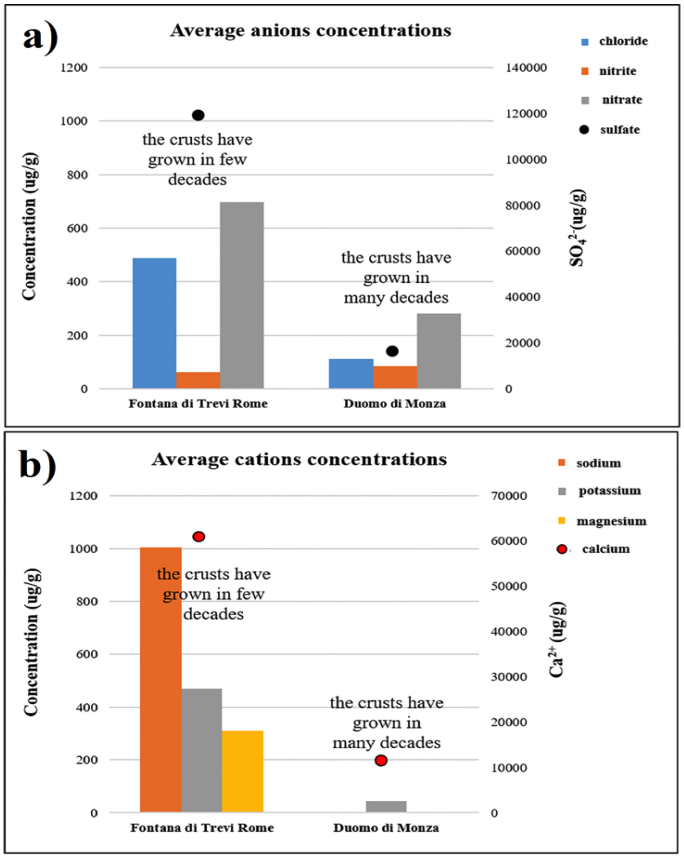


Fig. 4 Comparison of the (a) anions and (b) cations average concentrations (μg/g) obtained from the Monza cathedral and The Fontana di Trevi in Rome (Italy).

The different ion concentrations detected for the two monuments can be attributed to the different porosity of the BCs; since BCs from Monza cathedral have been developed during

longer time, they should be thicker and subsequently the porosity decreased over time as was suggested by other authors [31-33]. These conditions would lead to a minor interaction with the surrounding atmosphere and as a consequence a lower concentration of pollutants.

Image analysis

In order to confirm the hypothesis of a porosity decrease of BCs over time, analyses were carried out using image analysis in representative cross sections from two samples, i.e. 1MD and 9MD with different times of exposure to air pollution: 1MD (group A) (280 years and 650 years of exposure for group A and B respectively).

After converting the cross sections micrographs of the above samples from RGB image into 8-bit image (Fig. 5a), the images were binarized using thresholding procedure. This step is crucial in the image analysis process. When the proper threshold was selected only the pores should be colorful. The Otsu method [34] was used to calculate the threshold to minimize the intra-class variance in the gray scale (calculated threshold value is 142).

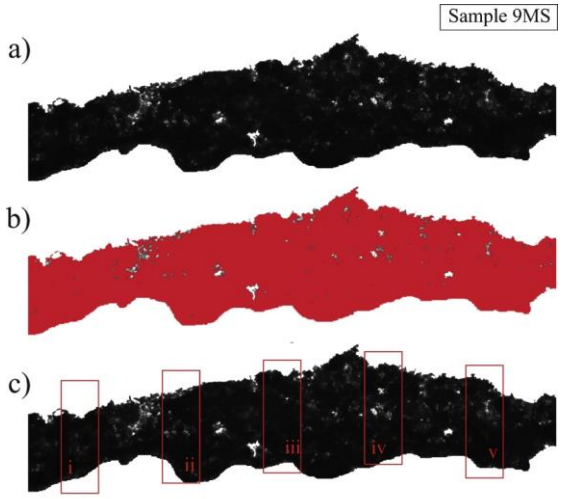


Fig. 5 Example of image processing for sample 9MS (a) conversion of the image from RGB to 8-bit; (b) binarization using thresholding procedure and calculation of the entire porosity; (c) calculation of the porosity on 5 subsections of the same image (i, ii, iii, iv and v) after binarization.

Table 1. Estimation of porosity values in BCs (1 MD, ca 250 years and 9MS, ca. 650 years) from the Monza cathedral using image analysis.

Subsection code	Porosity (% Area)	Subsection code	Porosity (% Area)
1 MD-i	11.28	9 MD-i	11.02
1 MD-ii	12.56	9 MD-ii	4.62
1 MD-iii	17.44	9 MD-iii	7.28
1 MD-iv	12.84	9 MD-iv	7.53
1 MD-v	17.37	9 MD-v	16.19
Mean value	14.298	Mean value	9.328
1 MD (whole crust)	15.18	9 MS (whole crust)	10.34

After the binarization procedure the measurement of % area of porosity was performed. In order to verify the reproducibility of the applied procedure, two different methods were chosen. The first one calculated the % area (i.e. porosity) on the entire binarized image (Fig. 5b), while the second method calculated the % area on five different subsections of the same image and therefore a mean value of porosity was obtained (Fig. 5c).

Values of calculated porosity are shown in Table 1 for both representative BCs samples chosen for image processing analysis.

As shown in Table 1 values obtained applying the two selected methodologies are rather similar. Furthermore, a slight difference in porosity was found in BCs samples from different periods of exposure to air pollution. In particular, the porosity for the BCs with longer exposure to air pollution (9MD, 650 years) is lower. These preliminary results agree with those reported in the literature [31-33].

LA-ICP/MS

Measurements by LA-ICP/MS were performed on five representative BCs samples in order to obtain information on trace elements with the aim of unraveling the heavy metals that could be tracers of combustion sources [35]. The selected samples were 1MD and 4MS from Group A and samples 7MD, 9MD and 12 MD from Group B.

It has been observed that all examined samples were enriched in: As, Ba, Cd, Cu, Fe, Mn, Ni, Pb, Sb, Sn, V and Zn, whose maximum (Max) and minimum (Min) values, expressed as average concentrations (ppm) are reported in Table 2.

Table 2 Maximum (Max) and minimum (Min) values, expressed in average concentrations (ppm), observed in the representative samples analysed by LA-ICP/MS

Element	Sample	Max (ppm)	Sample	Min (ppm)
As	7 MD	344	1MD	136
Ba	12 MD	4405	12 MD	426
Cd	12 MD	131	1 MD	13
Cu	12 MD	5017	1MD	118
Fe	12 MD	255657	1 MD	5584
Mn	12 MD	278	1 MD	156
Ni	12 MD	285	7 MD	157
Pb	12 MD	34554	1 MD	1464
Sb	12 MD	752	1 MD	47
Sn	12 MD	1033	1 MD	60
Sr	1 MD	870	7 MD	478
V	12 MD	550	1MD	55
Zn	12MD	3632	4 MD	462

The results show a different composition as regards as the trace elements analyzed. The average concentrations, reported in the histograms in Fig. 6, show that Fe, Pb and Zn are more aundant (Fig. 6a), while As, Ba, Cd, Cu, Mn, Ni, Sb, Sn and V are present in lower quantities (Fig. 6 b and c). These differences could be attributed to different factors (height of sampling, exposure).

Specifically, sample 12MD (group B) showed the highest concentrations of heavy metals, which is not surprising considering that it was taken from the lower part of the facade and that was most exposed to vehicular traffic in the past. On the contrary, 1MD and 4MS, showed lower concentration of heavy metals as they were taken from the higher part of the façade. Specimens 9MS and 7MD which were taken from a medium height compared to the other samples, displayed intermediate metal concentrations.

In general, all samples showed high contents of Fe (related to emissions from the numerous industries placed in the industrial area of Po valley [36-38] (Fig. 6a) in agreement with HRSEM -EDX results (see Fig. 2 and Fig. 3). Furthermore, Group B shows high concentrations in Pb, Fe, and Zn which demonstrated that the samples were most influenced by emissions produced by lead gasoline [10], employed until about 25 years ago. Elements such as Cu, Ni, Cr, Mn and V can be attributed to the fuels used after the abolition of lead gasoline (oil combustible, diesel, and gasoline) [10, 36-46], or could be linked to the industrial activities [46-47].

The enrichment in trace elements (mainly, Fe, Pb, Zn, Ba, Cu, Mn, Sb, Sn and V) observed in group B (7MD, 9MS and 12MD) can mainly be due to the high vehicular traffic that characterizes Monza, although the cathedral is located in a pedestrian zone since the last decades. On the contrary, group A (1MD and 4MS) samples collected from a high of 16 m from

the ground, often displayed lower concentrations of the same heavy metals. The detected elements using LA-ICP/MS agree with the results acquired with HRSEM -EDX. However other elements such as Cr and Al were detected with HRSEM-EDX since analyses were acquired from precise areas in the BCs.

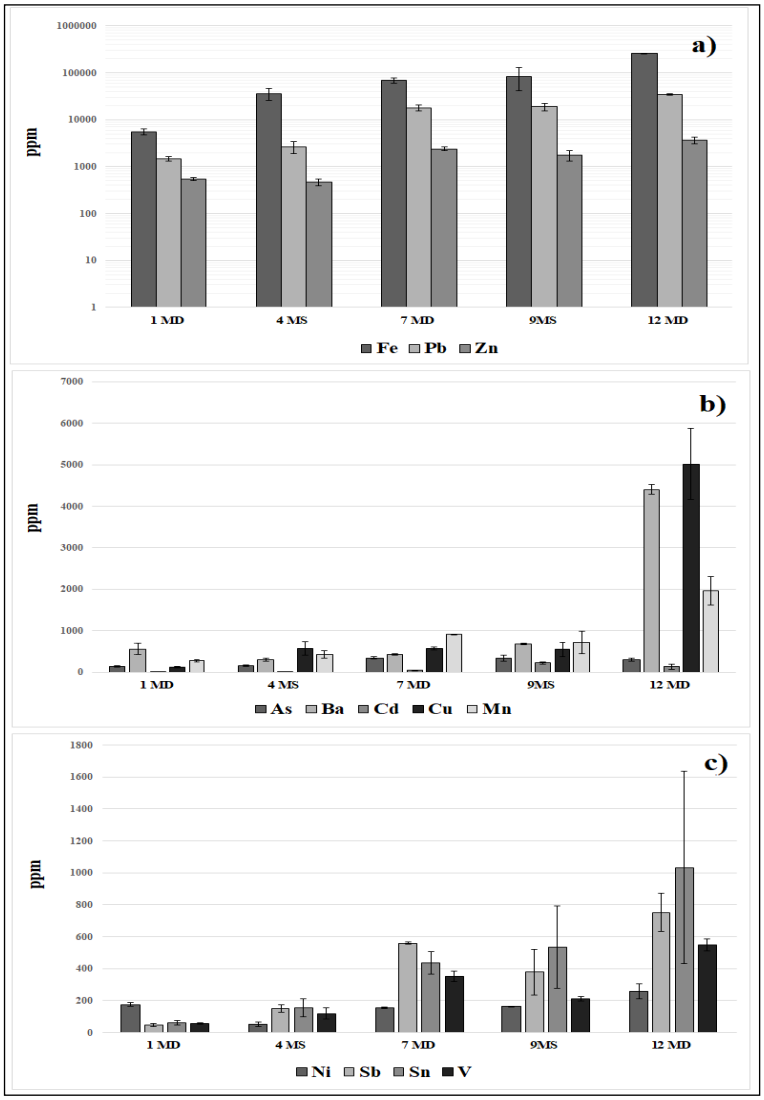
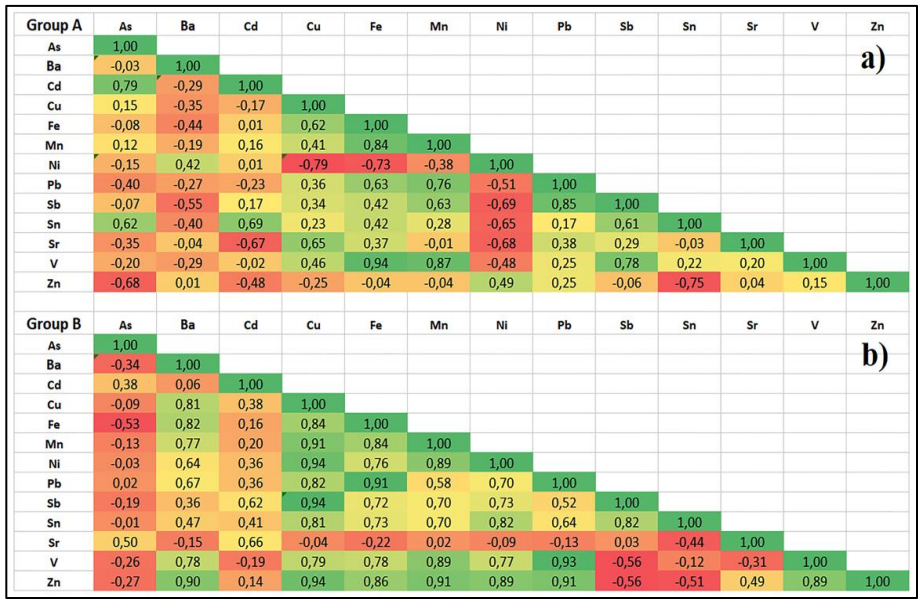


Fig. 6 Average concentrations (ppm) of heavy metals in the representative BCs collected in Monza cathedral: (a) Fe, Pb and Zn. (b) As, Ba, Cd, Cu and Mn. (c) Ni, Sb, Sn and V.

Further information on sources of air pollutants are provided by correlating the data of the main metals obtained for BCs (Fig. 7). For both groups A and B a good correlation between Fe and almost all metals, connected to heavy fuels combustion [17-22] and used mostly in industries and for domestic heating, is observable. A high correlation between Pb and Fe (0.91), Pb and Zn (0.91), Fe and Zn (0.86), Cu and Sb (0.94) and Zn and Ni (0.89) in group B confirmed that these elements were probably emitted by the same source such as vehicular traffic, as stated above. Cu and Sb could come from brake pad emissions and other parts of friction and machine wear [36-41,49-51] while Zn and Ni come from worn tires [52-53].



Group A	As	Ba	Cd	Cu	Fe	Mn	Ni	Pb	Sb	Sn	Sr	V	Zn
As	1,00												
Ba	-0,03	1,00											a)
Cd	0,79	-0,29	1,00										
Cu	0,15	-0,35	-0,17	1,00									
Fe	-0,08	-0,44	0,01	0,62	1,00								
Mn	0,12	-0,19	0,16	0,41	0,84	1,00							
Ni	-0,15	0,42	0,01	-0,79	-0,73	-0,38	1,00						
Pb	-0,40	-0,27	-0,23	0,36	0,63	0,76	-0,51	1,00					
Sb	-0,07	-0,55	0,17	0,34	0,42	0,63	-0,69	0,85	1,00				
Sn	0,62	-0,40	0,69	0,23	0,42	0,28	-0,65	0,17	0,61	1,00			
Sr	-0,35	-0,04	-0,67	0,65	0,37	-0,01	-0,68	0,38	0,29	-0,03	1,00		
V	-0,20	-0,29	-0,02	0,46	0,94	0,87	-0,48	0,25	0,78	0,22	0,20	1,00	
Zn	-0,68	0,01	-0,48	-0,25	-0,04	-0,04	0,49	0,25	-0,06	-0,75	0,04	0,15	1,00

Group B	As	Ba	Cd	Cu	Fe	Mn	Ni	Pb	Sb	Sn	Sr	V	Zn
As	1,00												
Ba	-0,34	1,00											b)
Cd	0,38	0,06	1,00										
Cu	-0,09	0,81	0,38	1,00									
Fe	-0,53	0,82	0,16	0,84	1,00								
Mn	-0,13	0,77	0,20	0,91	0,84	1,00							
Ni	-0,03	0,64	0,36	0,94	0,76	0,89	1,00						
Pb	0,02	0,67	0,36	0,82	0,91	0,58	0,70	1,00					
Sb	-0,19	0,36	0,62	0,94	0,72	0,70	0,73	0,52	1,00				
Sn	-0,01	0,47	0,41	0,81	0,73	0,70	0,82	0,64	0,82	1,00			
Sr	0,50	-0,15	0,66	-0,04	-0,22	0,02	-0,09	-0,13	0,03	-0,44	1,00		
V	-0,26	0,78	-0,19	0,79	0,78	0,89	0,77	0,93	-0,56	-0,12	-0,31	1,00	
Zn	-0,27	0,90	0,14	0,94	0,86	0,91	0,89	0,91	-0,56	-0,51	0,49	0,89	1,00

Fig. 7. Correlation values among the trace element concentrations; a) Group A and b) Group B.

All the chemical elements obtained were used to perform an analysis of the main components (PCA, principal component analysis). This method allow to identifie the directions in which the data express greater variability, therefore it allows to describe the data using fewer variables, synthesizing the information based on the correlation or covariance structure of the observed variables. Of the 4 factors identified, 1 and 2 explain 88% of the total variance.

Table 3 shows i loading values of the two first factors obtained through PCA. These data are graphically represented in Figure 8a.

Firstly, it can be seen that factor 1, which explains the 73% of the variance, is represented by Sr (with a positive weight). The rest of the elements have a negative weight regarding this factor 1. Factor 2 (which explains a 13% of the variance) is defined by the chemical elements Cu, Ba, V, Mn, Ni, Fe and Zn (with positive weights).

Table 3. Loading values of the two first factors obtained through PCA to the eccentricity of the variables (chemical elements) and of the cases (BCs).

Variables	Factor 1 eigenvalue	Factor 2 eigenvalue	Cases	Factor 1 eigenvalue	Factor 2 eigenvalue
Sr	0.378994	-0.833972	1MD	2.74362	0.78614
Cd	-0.526771	-0.835453	4MS	2.70094	0.44302
As	-0.685039	-0.489073	7MD	-0.47110	0.50272
Ni	-0.794216	0.048014	9MS	-0.06303	-2.39734
Ba	-0.887821	0.222185	12MD	-4.91043	0.66546
Cu	-0.899494	0.240892			
Sb	-0.952599	-0.013982			
Fe	-0.968695	0.044123			
V	-0.971774	0.126027			
Zn	-0.981016	0.008424			
Pb	-0.986037	-0.151311			
Mn	-0.986350	0.122310			
Sn	-0.986910	-0.126270			

If the cases (i.e. BC samples) were projected in the space defined by factors 1 and 2 (Figure 8b), it was verified that samples 1MD and 4MS fell alone within the space defined by the positive loading of factor 1 (corresponding to the element Sr), while the rest of BCs samples (7MD, 9MS and 12MD) fell within the space defined by the negative loading of factor 1 (i.e. the rest of the detected elements – metals).

It was also shown that the BCs differentiated following the factor 2 in two groups: one -composed by 12MD, 7MD, 1MD and 4MS- fell in the space defined by positive loadings (Cu, Ba, V, Mn, Ni, Fe and Zn elements) whereas 9MS sample fell in the space corresponding to the negative loading (Cd, As, Sb, Pb and Sn).

These results indicate that the differences, between the group formed by 1MD and 4MS and the group formed by 7MD, 9MS and 12 MD are related to heavy metals content; 1MD and 4MS (grouped within positive loadings of factor 1) were the BCs that contained a lower metal amounts. Conversely, 12MD, 7MD and 9MS (grouped within negative loading values of factor 1) were richer in metal elements. Particularly, 12MD (group B), which was the crust the most exposed to vehicular traffic in the past and the richest crust in heavy metals, was, consequently, characterized by the most negative loading value regarding factor 1.

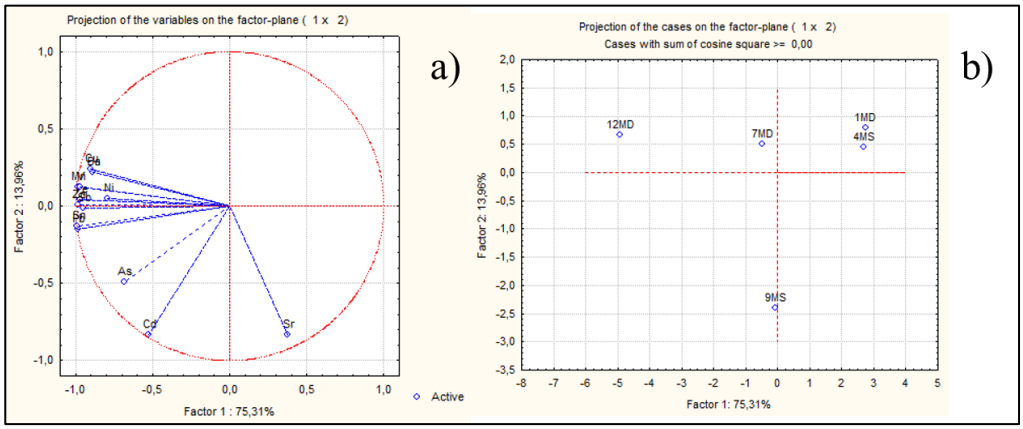


Fig. 8. Proyection in the space defined by the two first PCA factors of the variables (a) and of the cases (b).

Conclusions

Two types of BCs were collected from the facade of Monza cathedral, located in the homonymous city in Italy, and divided into two groups in order to study their morphology and metal contents, and consequently the potential air pollutants´ origin: BCs from Group A (the most recent formed crusts ca. 250 years ago) and BCs from Group B (crusts formed starting from about 650 years ago).The importance of this study is that it provides the opportunity to analyze BCs from the same monument but developed at different heights, exposed to different pollution sources exposure (industrial, domestic heating and vehicular traffic)

BCs are formed by gypsum that embedded minute BCPs of variable composition. The low values of ions concentration have been attributed to the diminishing porosity inside the crusts, hypothesis that has been confirmed by image analysis.

The study of the trace elements presents in BCs samples belonging to the two groups A and B have allowed some important considerations:

- The higher concentration of heavy metals was detected in BCs (650 years of air pollution exposure) taken at a lower height from the ground. This result indicates that mobile combustion sources (vehicles) had a major impact on the formation of these BCs.

- More recent BCs (about 280 years of pollutants accumulation) were characterized by the lower concentration of heavy metals even if these BCs located at about 16 m have been influenced by fixed combustion sources (e.g., industries, domestic heating).

This analytical approach combining different techniques has allowed identifying the air pollution sources responsible for the formation and decay of the stone material used in the Cathedral of Monza. The possibility of conducting these studies allows the identification of pollution involved in this type of degradation, in order to propose policies for reducing pollutants and improving air quality.

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