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Review

The Impact of Air Pollution on Stone Materials

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Abstract: Air pollution can have a significant impact on stone materials used in monuments, buildings, and sculptures. Sulfur and nitrogen oxides are particularly harmful pollutants, especially in carbonate stones. These oxides, reacting with moisture in the air, result in the formation of acids able to erode the stone surface and gradually compromise its structural integrity. The acids can also combine with airborne particulate matter, heavy metals, and salts, leading to the development of black crusts. These not only have detrimental effects on the stone's integrity but also affect the original appearance of the surfaces, threatening the conservation of important monuments and buildings. This review discusses the characteristics of black crusts and their relation to the environment and stone materials.

Keywords: air pollution; stone degradation; black crusts

1. Introduction

The degradation of stone materials has been a subject of research for several decades [1], as it is closely tied to the conservation of built cultural heritage. In fact, the comprehension of the mechanisms and processes regulating this phenomenon is crucial for developing effective and durable conservation strategies.

Stone decay can be caused by chemical, physical, and biological factors and often by their combined action. Water plays a significant role as a weathering agent or co-agent. It acts as a solvent able to solubilize specific components of stones, such as calcium carbonate or gypsum, due to their inherent solubility in water. Additionally, water can transport salts or pollutants onto the stone surface or within its porous structure, contributing to physical processes and reactions that lead to degradation. Furthermore, water promotes biological decay favoring the suitability of nutrients for microorganisms. This occurs when it combines with compounds from the stone substrate (i.e., carbonatic ones) or with the NOx pollutants from the atmosphere. Overall, degradation processes are influenced by environmental factors, materials, design, construction procedures, and maintenance [2]. The first of these have a profound impact on stone decay processes, while factors such as orientation and architectural details influence the extent to which moisture supply and drying affect degradation [3].

It is important to point out that all stone materials are prone to these phenomena, although certain human activities, such as pollutant emissions, can accelerate their development. This review will focus on the processes at the stone–atmosphere interface relating to air pollution, with particular emphasis on the blackening of architectural surfaces observed in highly polluted urban environments. This phenomenon takes two forms. The first is soiling, which involves the accumulation of dust on the surface, characterized by its black color due to high carbon content. The second mechanism consists of a chemical alteration of the surface, resulting in the formation of black crusts.

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2. Air Pollution and Stone

Since the industrial revolution, air pollution has had a deep impact on human health, ecosystems, and stone materials. It is primarily caused by anthropic activities, particularly combustion processes involving fossil fuels and wood, which release various inorganic and organic gaseous and solid compounds into the air. It is widely acknowledged that the primary compounds that negatively affect the integrity of stone materials are the oxides that can react with water, leading to acid formation: carbon dioxide (CO_2), nitrogen oxides (NOx), and sulfur oxides (SOx) [4,5]. These acids react with stone, especially carbonate-based materials such as marbles and limestones, resulting in deterioration.

Carbon dioxide (CO_2) dissolves in water according to

$$CO_2 + H_2O \leftrightarrow CO_2 \cdot H_2O \tag{1}$$

$$CO_2 \cdot H_2O \ \leftrightarrow H^+ + HCO_3^- \tag{2}$$

This indicates that a gain in atmospheric CO_2 leads to higher CO_2 concentrations in water becoming chemically more acidic. Calcium carbonate, a common component of stone materials, exhibits slight solubility in water that increases with dissolved CO_2.

$$CaCO_3 + CO_2 \cdot H_2O \ \leftrightarrow Ca(HCO_3)_2 \tag{3}$$

According to Henry's law, the amount of CO_2 dissolved in water depends on the atmospheric CO_2 concentration and the water temperature. Lower temperatures enhance dissolution. Therefore, in urban environments (where CO_2 concentrations are typically higher) and during winter (when lower temperatures prevail), carbonate dissolution reaches its maximum. However, Equation (3) represents an equilibrium that can be shifted toward the reagents through water evaporation or an increase in temperature, causing the reformation of calcium carbonate. Actually, calcium carbonate dissolves and then precipitates in the same or different locations. In both cases, the microstructure of the stone in the dissolved areas undergoes significant changes, rendering the stone more susceptible to further degradation. It is well established that the atmospheric CO_2 concentration is raising according to the Keeling curve [6], and the predicted concentration in 100 years is approximately 700 ppm (it is currently around 420 ppm). This increased effect can be considered relatively modest if compared with the 2500 ppm reached by CO_2 in indoor environments. Here, the dissolution linked to CO_2 can pose a threat, for example, if affecting the delicate and valuable surfaces of wall paintings where calcium carbonate is commonly an important component of the setting layers or pigments.

Nitrogen oxides (NOx) are primarily present in the atmosphere as nitric oxide (NO) and nitrogen dioxide (NO_2). The most significant mechanism for NO formation is described by the Zeldovich reaction [7]:

$$O_2 \leftrightarrow 2\,O \tag{4}$$

$$N_2 + O \ \leftrightarrow NO + N \tag{5}$$

$$O_2 + N \ \leftrightarrow NO + O \tag{6}$$

$$OH + N \ \leftrightarrow NO + H \tag{7}$$

The first reaction (Equation (4)) takes place at a temperature above about 2200 K (~1900 °C), and then the reactions (Equations (5)–(7)) follow. Hence, the formation of NO requires a high temperature and local excess of oxygen; this occurs, for example, in internal combustion engines.

NO can be converted to NO_2 by reacting with ozone:

$$NO + O_3 \leftrightarrow NO_2 + O_2 \tag{8}$$

Nitrogen dioxide can be further oxidized to dinitrogen pentoxide (N_2O_5), which reacts with water to form nitric acid.

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{9}$$

This acid can react with calcium carbonate:

$$2HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \tag{10}$$

Nitric acid corrodes the stone substrate, resulting in the production of calcium nitrate, which is more soluble than carbonates. Unlike Equation (3), this reaction is irreversible, and there is no re-precipitation of carbonates at the end of the process.

Sulfur dioxide (SO_2) represents the most dangerous compound for the conservation of stone materials. The main source of anthropogenic emissions is the combustion of fossil fuels, such as coal and heavy fractions of mineral oil. The sulfur of SO_2 can be oxidized from S(IV) to S(VI) by means of several pathways involving O_3, NO_2, particulate matter, and metals [8–10], leading to the formation of SO_3 (sulfur trioxide), and H_2SO_4 (sulfuric acid) once SO_3 reacts with water. Sulfuric acid reacts with calcium carbonate producing calcium sulfate:

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O \tag{11}$$

Calcium sulfate (usually in the hydrated form of gypsum $CaSO_4{\cdot}2H_2O$) has a similar solubility to that of calcium carbonate, so as $CaSO_4$ precipitates, it creates a crust.

In recent decades, the trend of emissions of NOx and SO_2 is decreasing, although in some countries such as China and developing countries, the emissions are still high [11,12]. This means that in those areas the process described in Equation (11) is still crucial.

A component of the air pollutant is particulate matter (PM), which is a complex mixture of extremely small particles and liquid droplets made up of acids, organic chemicals, metals, and soil or dust particles. Sources of PM are both natural (e.g., volcanoes, dust storms, sea spray) and anthropogenic, the latter including combustion in mechanical and industrial processes and vehicle emissions [13].

All the above-mentioned pollutants can reach the surface of the stone by dry or wet deposition. Dry deposition is a process in the absence of water in which gases and particulate matter reach the surface, while wet deposition is the process whereby atmospheric gases and PM mix with suspended water in the atmosphere and are then washed out through rain or fog. Dry deposition is slower but more continuous with respect to wet deposition, which is faster and also more "efficient". In fact, it provides water to the surface as a solvent and sometimes as a reactant, allowing the above-mentioned reactions with the substrate (Equations (3), (10), and (11)) [14].

Calcium sulfate can be removed from the stone surfaces by washout, since it is more soluble than calcium carbonate. However, such deposits can grow and embed PM (commonly blackish in color) in the areas protected from rain, creating black crusts. However, the color of such degradation products can be grey or even white, depending on the content of the particulate matter. The term "black crust" is also included in the ICOMOS Glossary [15], which describes this degradation form as "Generally coherent accumulation of materials on the surface. A crust may include exogenic deposits in combination with materials derived from the stone. A crust is frequently dark colored (black crust) but light colors can also be found. Crusts may have a homogeneous thickness, and thus replicate the stone surface, or have irregular thickness and disturb the reading of the stone surface details" [15] (p. 42).

3. The Study of Black Crusts

3.1. The Sampling Methodology

The choice of the points to sample is fundamental in the study of black crusts and in the subsequent elaboration and interpretation of the data. All the information collected can be useful to define the processes of growth of the black crusts. Firstly, it is necessary to select suitable tools for sampling, generally stainless-steel lancets and small chisels. The operations of sampling on built cultural heritage follow some precise criteria: the material taken should be a sufficiently representative portion, preferably consisting both of black crust and unaltered substrate, but without compromising the original aesthetic aspect of the surface. It is crucial to select the position of the samples because it can determine the enrichment of pollutants. In this regard, it is important to consider the height of the sampling; the incline, morphology, and composition of the original substrate; the exposure to the pollutant sources; and the environmental and climatic surrounding conditions (e.g., temperature and exposure to agents such as sunlight, wind, and rainfall). It is also valuable to reconstruct the history of the monuments with black crusts, identifying past restoration interventions such as rebuilding, substitution of stone elements, or other cleaning procedures. However, it is often difficult to recover this kind of information in the cultural heritage field because of the absence in the past of "good practices" aimed at the documentation (a sort of anamnesis) of all the interventions on the monuments over time.

3.2. Structure and Main Components

Macroscopically, black crusts can be classified as laminar (Figure 1) and/or dendritic (Figure 2) [16]. The first type is described as parallel layers, black to dark grey in color, and adherent to the stone; it does not change the morphology of the surface. It can cover large portions and develops most commonly on vertical areas, which are sheltered from direct rain wash. The dendritic type is also known as globular [17], ropey [18], framboidal [19,20], or cauliflower-like [21] black crust. It develops on protected and sheltered parts of buildings, where the dust is rarely swept away. The morphology of this crust type is highly variable; its thickness ranges between a few millimeters and 2–3 cm.

Figure 1. Architectural element (artificial stone) affected by black crust (laminar), together with blistering phenomena. Blistering is evidenced by the lack of black crusts in some areas. Image from the Monumental Cemetery of Milan (Italy).

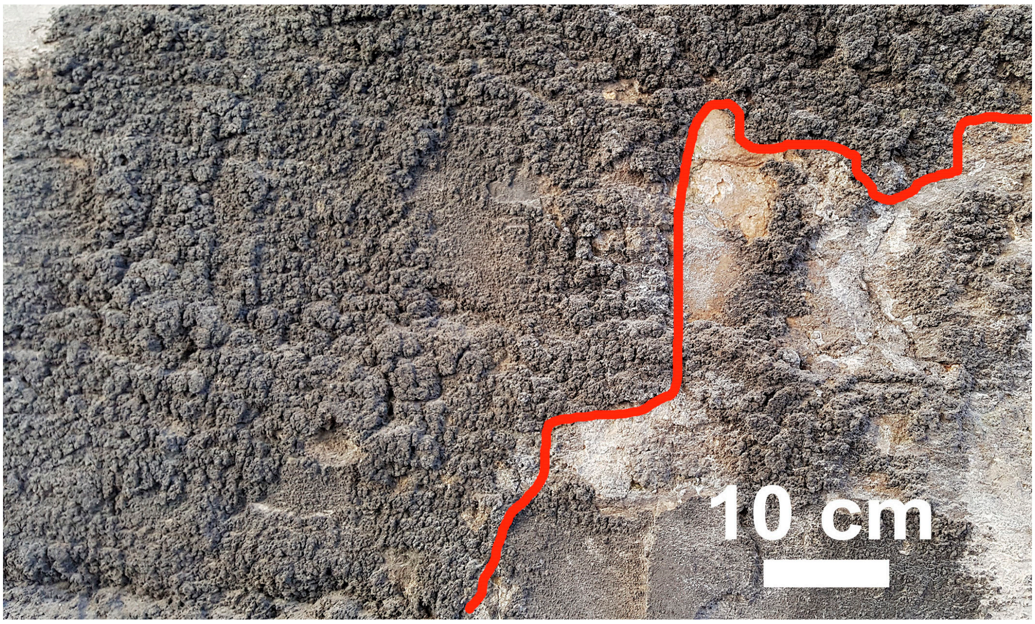

Figure 2. Example of dendritic black crust on a plastered wall. The red line shows the "front" of the blistering. Image from ancient walls of the town of Como (Italy) and modified from [1].

The formation of black crusts leads to a detachment of the degraded layer because these newly formed materials have different properties from the substrate in terms of texture and porosity. Then, the adhesion between them is compromised, which is why black crusts are often observed together with detachments (usually blistering) (Figure 1) and powdering as well.

The chemical fundamentals of the effects of pollutants on stone have been known since the 1960s [22,23]. Moreover, several studies have assessed the ability of the stone to absorb SO_2 [24], and it has even been speculated that this process could have a significant effect in cleaning the surrounding air [25]. The studies, which specifically focused on black crusts, began in the early 1980s [26–35]. In these studies, the black crusts on carbonate-based stones from different cities were studied by collecting samples from degraded surfaces and were analyzed to understand their microstructure and composition. For this purpose, several complementary techniques, such as optical microscopy, scanning electron microscopy (SEM), energy-dispersive X-ray microanalysis (EDX), X-ray fluorescence (XRF), X-ray diffraction (XRD), infrared spectroscopy (FTIR), Raman spectroscopy, and ion chromatography (IC), have been applied.

Specifically, ion chromatography analysis reveals the presence of sulfate ions ascribable to gypsum since it is quite soluble in water. In many cases, significant amounts of nitrate ions can be found as well. This provides evidence of the occurrence of Equation (9) in which nitric acid from NOx reacts with carbonates, forming nitrate salts, which are soluble. Regarding the composition from a mineralogical as well as geochemical point of view, the black crusts commonly consist of gypsum, up to about 80% [36]. The other components are particulate matter, mainly made of carbon, and other elements such as silicon, aluminum, iron, and zinc (Figure 3). Calcite crystals, generally from the substrate, are also present. Usually, a portion of altered substrate is visible between the substrate and the crust, the so-called "front" of the sulfation process. This area favors the penetration of black crust into the intergranular spaces, causing cracks. This weathering depends on the exposure of the stone to pollution as well as on its porosity: the more porous the stone, the more the penetration of the sulfate occurs.

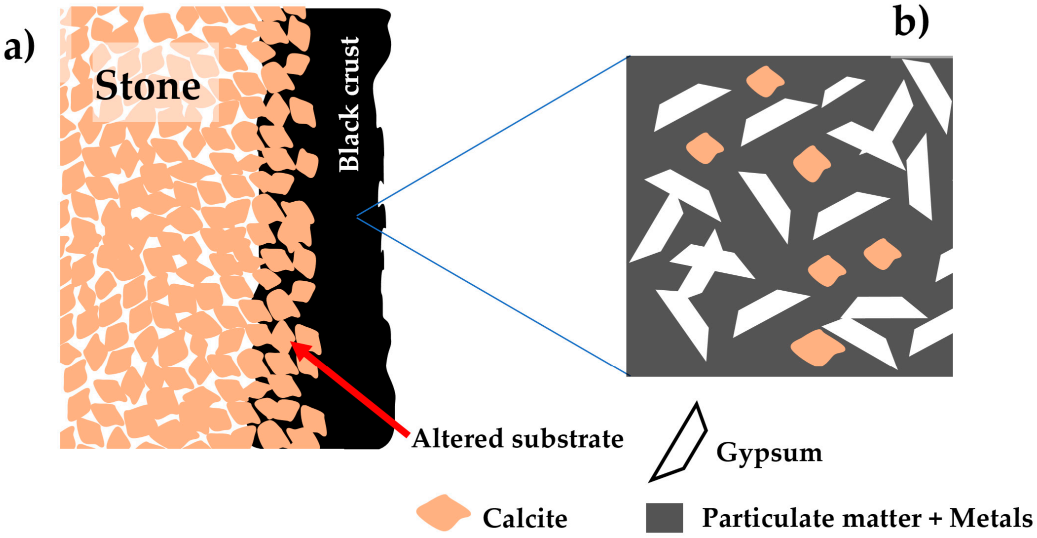

Figure 3. Schematization of a typical structure of black crust. (**a**) Cross section of a calcite-based stone with a black crust superimposed together with the altered substrate. (**b**) Thin section of the black crust. The figure is not to scale.

By optical microscopy, SEM-EDX, XRD, and FTIR, it was possible to identify, in many case studies, the presence of calcium oxalates together with black crusts [37,38]. The occurrence and the formation of calcium oxalate are debated but are generally considered to be due to the partial oxidation of organic carbon [39,40]. This could come from organic protective products applied during previous restoration work, from the activity of microorganisms colonies, or from pollutants [41,42].

The presence of black crusts was also observed on substrates with relatively low calcium content, such as granite, tuff, andesite, and trachyte [43–45]. In these rocks, calcium is released from minerals, such as plagioclase, if they undergo weathering, such as acid leaching. In some cases, the lack of a significant intrinsic calcium and sulfur source for the formation of the gypsum crusts suggests an external source of calcium ions, e.g., pollution, mortars, and neighboring carbonate stones [45–49]. Other authors suggested that Ca^{2+} may come from the hydrolysis processes of plagioclase mineral grains under acid environments [50].

3.3. Analysis of Metals

Another aspect that has been widely investigated by several researchers is the content of metals, including both major and trace metals. Those metals with a concentration of about 1 percent in weight as an order of magnitude can be analyzed by EDX, while more sensitive equipment is required for traces. For these reasons, starting from the first decade of this century, the inductively coupled plasma mass spectrometry (ICP-MS) technique has been applied for the study of black crusts, in particular the laser ablation ICP-MS [51]. The latter allows one to perform spot analysis on a ~60 × 60 square micron area and measure the content of many metals, and elements in general, with a concentration of about a few parts per million (ppm).

Firstly, it is important to determine the origin of the metals to determine their role in and contribution to the formation of the black crust: endogenous (from the stone) or exogenous (from the environment).

This assessment can be achieved by evaluating the enrichment factor (EF) for each detected element, namely the ratio between the concentration of the element in the crust and the concentration of the element in the unaltered substrate (Equation (12)).

$$EF = \frac{C_{Crust}}{C_{Substrate}} \tag{12}$$

If the EF is significantly higher than 1, it is reasonable to suppose that the element comes from the environment and is usually identified as a pollutant; otherwise, the element is ascribable to the substrate. The analysis of metals in the black crusts has allowed the evaluation in many case studies of the source of the pollutants of the surrounding environment.

Metals such as Pb, Zn, Fe, and Cu are usually found in the crust at concentrations between 100 and 3000 ppm, while the concentrations of As, Cd, Cr, Ni, Sb, Sn, and V are usually lower than 100 ppm [52–54].

Table 1 shows the concentrations (expressed as mean values) of trace metals within black crusts taken from some of the most representative European monuments exposed to urban pollution sources (e.g., vehicular traffic, domestic heat, industrial activity) and analyzed by LA-ICPMS. It is worth clarifying that the conditions of the sampling can influence the concentrations of the metals. Their contribution to the crust can be affected by different factors: the height of the sampling, incline of the surface, direct or indirect exposure to the pollutant sources, age and thickness of the crust, past restoration works, and climatic conditions linked, for example, to wind circulation or the intensity of rainfall.

Table 1 collects the data of black crusts from heterogeneous contexts: the host rocks, for example, change from the German or Padua trachyte to the various typologies of the limestones of Venetian, London, St. Eustache, and St. Mechelen monuments to the marbles of St. Cosimato and Naples monuments; the building ages are different and consequently the time of accumulation of the deposits; and the surrounding environmental conditions change too. Nevertheless, it is possible to observe general similarities such as the predominant content of Pb and Zn in almost all the monuments analyzed, reflecting the widespread use of leaded petrol until the 1990s.

In addition, some metals, or a group of them, can be considered as proof of a certain pollution source. For example, the presence of Pb, Zn, V, Cr, Cu, Sb, As, and Ni can be attributed to the combustion of fossil fuels [55] and particles released from the friction and wear of the mechanical parts of vehicles [56] and the wear of the asphalt [57]. Cu and Sb are related to the emissions from brake pads and to other friction parts [58,59]. As, Cu, Ni, Cr, and V may be associated with the use of heavy oil fractions, and Pb can be attributed mainly to leaded gasoline, which was used until the end of the 1990s [60]. LA-ICPMS allows the evaluation of the spatial variation in the metals' concentrations within the crust and punctual analyses from the outermost part of the crust to the unaltered substrate. Thanks to this, it was possible to observe that in many cases the amount of Pb was higher closer to the substrate than in the outer portions of the black crust [52,54]. This could be because Pb emissions dropped in the 1990s, so the inner layers represent the oldest deposits. Another reasonable explanation is the differential geochemical mobility of the elements under certain environmental conditions [61] and the strong affinity of Pb with calcite, especially in the black crusts on carbonatic substrates.

Table 1. Concentration in ppm of heavy metals in the black crusts sampled on several European monuments.

Sampling	Country	As	Ba	Cd	Cr	Cu	Mn	Ni	Pb	Sb	Sn	V	Zn	Ref
Tower of London	England	57.2		4.4	41.2	185.6	275.0	56.5	807.6	20.2	38.2	116.8	384.1	[52]
Mechelen Cathedral	Belgium	35.6		0.2	58.6	182.2	120.9	29.7	1721.3	10.1	9.7	320.2	3436.8	[53]
St. Eustache Paris	France	58.1		12.2	15.0	89.4	68.4	33.2	813.3	17.0	165.7	66.8	451.8	[53]
Seville Cathedral	Spain	85.5		15.3	213.7	125.1	255.0	18.4	378.2	8.7	819.3	43.5	226.7	[54]
La Galea Fortress, Getxo, Basque Country	Spain	16.3	110.7	0.3	20.3	19.0	74.0	10.0	299.3	2.0	6.7	19.0	184.7	[21]
Altenberg Cathedral	Germany	28.0							890.0	12.0				[45]
Cologne Cathedral	Germany	365.0							1849.0	37.0				[45]
Xanten Cathedral	Germany	50.0							1944.0	16.0				[45]
Corner Palace in Venice	Italy	125.4		4.2	54.2	98.3	327.9	49.5	2613.1	41.7	31.1	106.4	712.5	[53]
Fontana di Trevi Rome	Italy	58.2	620.3	49.3		122.8		26.8	557.3	34.0	45.4	103.9	337.0	[62]
Monza Cathedral	Italy	240.0	2415.5	72.0		2567.5	217.0	221.0	9009.0	399.5	546.5	302.5	2047.0	[31]
Historical center of Naples	Italy	21.5	532.2	0.9	16.4	89.8		7.9	1395.1	9.6		22.9	628.0	[34]
Historical center of Venice	Italy	170.2	836.2	8.1	65.2	160.8		179.9	696.5	40.7	604.0	98.6	1848.2	[35]
St. Cosimato Cloister, Rome	Italy	34.5	772.9	2.6	21.3	60.1	248.5	9.2	598.4	7.1	25.3	56.1	210.7	[51]
Cemetery Pessago con Bornago (Milan)	Italy	44.8	202.7	19.0	55.1	64.6	250.1	13.0	2821.2	62.0	222.7	123.5	414.2	[51]
Renaissance city walls of Padua	Italy	47.8		8.7	68.9	489.8		46.4	6738.2	17.8	38.7	143.1	4171.3	[44]

Since the contents of the metals in the black crusts reflect the presence of such metals in the air, chiefly referring to the past, some researchers have hypothesized that black crusts themselves can be considered as passive samplers of past air quality [21,52]. In this regard, the fingerprints of the elements inside the crust and the air measured in the last 20–30 years were compared. The results indicate a good correlation between the two datasets, suggesting that the concentrations of the metals in the crusts reflect those of the surrounding air. Figure 4 compares the metal contents measured in black crusts from Seville Cathedral and in particulate matter. The coherence of the concentrations is evident, especially for the older monitoring campaign.

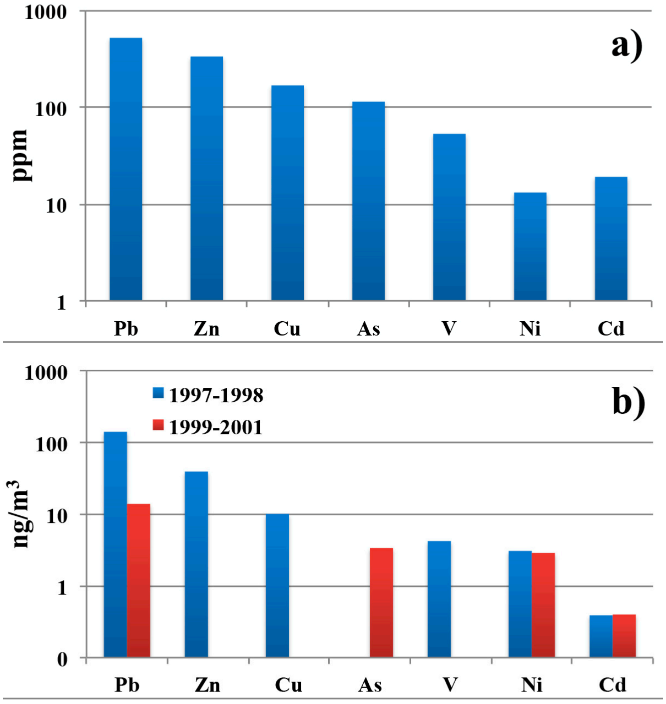

Figure 4. Histograms showing the average concentrations of the heavy metals detected (**a**) in the black crusts taken from the Cathedral of Seville and (**b**) in the particulate matter collected in 1997–1998 and 1999–2001. Taken from Ruffolo and coworkers [52].

3.4. Particulate Matter and Organic Fraction

Carbon-based compounds are a mixture of many components that researchers determine by evaluating the following parameters: total carbon (TC), carbonate carbon (CC), organic carbon (OC), and elemental carbon (EC). These are measured by means of CHN (carbon, hydrogen, nitrogen) and TOC (total organic carbon) analyzer equipment, following a specific workflow [63].

TC is the total amount of carbon in all forms within the crust, while CC is the fraction of carbon related mainly to the substrate. EC is the black carbon, which gives the dark color to the crust. It is emitted in urban environments by combustion processes, such as traffic and biomass burning [64], and it is the main cause of the soiling of monument surfaces [65]. OC is emitted by combustion processes, but it can have a primary (directly emitted) or secondary origin (in this case, it forms in the atmosphere because of different kinds of reactions starting from the volatile organic precursors), also known as VOC, volatile organic compounds.

The EC parameter has been measured in several case studies and is usually between 0.1 and 3%, while values of OC up to about 7% have been observed [62,63,66]. An important component of the OC fraction is polycyclic aromatic hydrocarbons (PAHs), a group of organic compounds that are formed from the incomplete combustion of fossil fuels, wood, and other organic matter. They are composed of multiple fused aromatic rings and have a characteristic planar structure. PAHs are persistent environmental pollutants and can be found in black crusts and stone [67,68]; these molecules can be extracted from the matrix and then analyzed by high-performance liquid chromatography (HPLC) [69]. The amount of PAHs found in black crust can be up to 20 ppm [70]. Three processes can generate polycyclic aromatic compounds: (a) combustion at high temperature [71], (b) release of petroliferous products, and (c) degradation of organic matter [72,73]. The fingerprinting of the amounts of different PAHs can provide information on their source. Combustion-type sources are characterized by a wide range of PAHs, while petroleum and organic sources produce lighter PAH molecules. All studies have suggested that the combustion source is the predominant one [69–73].

4. Intervention Strategies

The data collected in this document clearly explain how products of degradation such as black crusts are closely connected to the increase in pollution rates in large cities, making the issue of built heritage conservation ever more urgent.

There are currently two approaches that can be adopted: a longer-term and larger-scale one with the implementation of national and international green policies aimed at reducing emissions into the atmosphere; and a short-term and local-scale one, removing the crusts from monuments by suitable cleaning procedures and developing durable conservative strategies.

In the first case, the institutions could promote more sustainable lifestyles by encouraging citizens to take public transport and limiting the use of private cars, or they could reduce the vehicular traffic around the monuments. In addition, they could encourage the productive sectors to adopt green and circular strategies to significantly decrease the emissions into the atmosphere, improving the quality of the air.

On the other hand, the cooperation of more experts such as restorers, conservators, physicists, chemists, and geologists provides various intervention strategies to mitigate the damage produced by black crusts.

Different cleaning methods have been developed considering the morphology and thickness of the crust, the texture and state of conservation of the stone substrate, and the requirements necessary to preserve the aesthetic and structural integrity of the monument: the treatments should not cause color changes in the original substrate, the loss of material, or secondary products such as salts. Obviously, the cleaning procedure must therefore be gentle, gradual, selective, environmentally friendly, and economically affordable [74].

The physical (e.g., rubbing, abrasives) and chemical (e.g., solvents) methods are considered traditional and to carry some risks such as excessive aggressiveness and the inability to distinguish the crust to be removed from the original substrate. On the other hand, in recent decades new techniques have been experimented such as laser and biological cleaning [75–78].

Laser cleaning is less invasive than the conventional methods, easier to control, and can distinguish the soiling from the substratum; however, the procedure can produce color changes, and there can be problems in distinguishing the crust on polychrome substrates.

Biological cleaning is part of a new philosophy that is spreading in the field of the restoration and conservation of cultural heritage, namely, implementing the use of green products such as essential oils [79] or exploiting natural processes relating, for example, to bacterial metabolic activity.

In this regard, the use of sulfate-reducing bacteria (SRB) was identified for the removal of sulfates (such as black crusts) from stone substrates. The SRB can reduce sulfates to H_2S in anaerobic conditions and dissociate gypsum into Ca^{2+} and SO_4^{2-} ions. Hence, the Ca^{2+} ions react with CO_2 to form new calcite (bio-precipitation), in this way also improving the microstructure of the substrate [76].

Finally, recently, nanoparticles were widely tested for preventive restoration and conservation aims. The most recent studies focused on materials able to inhibit the deposition of pollutants and soiling particles on the monuments and consequently also the inception of degradation processes such as the formation of black crusts. One of the most investigated and applied materials is nanotitanium dioxide coatings because of the self-cleaning and biocidal properties of the titania [80,81].

5. Conclusions

Black crusts are an important degradation form that stone materials suffer in highly polluted urban environments. They have attracted the interest of chemists, physicists, geologists, and conservators, whose efforts have been focused on understanding their structure from the macroscopic to microscopic scale, their composition, their effects on stone materials, and the influence of the environment on their features. Thus, this paper demonstrated the complexity of the topic but also the efficacy of a multidisciplinary approach.

All the information collected has important scientific value and also numerous applicative implications. Complementary analytical techniques have been applied to determine the composition of the crusts. Moreover, the data are useful for stone conservators in the planning of the most suitable strategies to preserve the original substrate and to inhibit the deposition of further pollutants on the surface, as suggested by the different methods of cleaning and conservation reported in this paper, e.g., from the conventional physical and chemical ones to the more advanced laser cleaning and biocleaning.

Furthermore, the results achieved regarding the mechanism of the development of the crusts are socially relevant. They can be important for all the stakeholders involved in the management of built heritage to promote policies aimed at its valorization and, more generally, at environmental safeguarding, e.g., reducing the emission of greenhouse gases produced by anthropic activities. In fact, the development of gradually more detailed studies has allowed us to determine the kind and, above all, the source of particulate matter and organic fraction (e.g., VOC, EC, OC, TC). This could be crucial to support more incisive intervention policies to improve air quality and consequently people's and monuments' health.

In addition, the research outcomes have established some correlations between black crusts and the surrounding air pollution, leading to them being considered as a "record" and also a "passive sampler" of past pollution patterns. However, in this case, there is not yet a well-defined procedure to obtain accurate and unambiguous information. Despite the large literature on this topic, some issues still have to be addressed, as specified below.

One process that is still unclear is the oxidation of sulfur dioxide to sulfur trioxide: Does it take place before the pollution reaches the stone, or is it catalyzed by other pollutants on the surface of the stone? Is the oxidation catalyzed by other air pollutants, such as O_3, NOx, metals, or soot? It has been shown that bacteria could play a role; however, the mechanisms are still not well understood.

Lastly, an important question about the future: what will be the impact of the foreseen pollution patterns on the formation of black crusts and, more generally, on the integrity of stone? If the emissions of SOx, NOx, and particulate matter lower over time, then the formation of black crusts could be a less critical issue in the future. However, an increase in global temperatures and carbon dioxide concentrations in the atmosphere as well as the intensification of extreme meteorological events are expected. Thus, the effects of these new environmental conditions on the conservation of built heritage are not clear.

If the climate changes, it is reasonable that a new equilibrium between materials and the environment will be achieved, so that the paradigm "air pollution—conservation of built heritage" will switch to "climate change—conservation of built heritage".

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