The environmental impact of air pollution on the built Heritage of Historic Cairo (Egypt)

Natalia Rovella, Nevin Aly, Valeria Comite, Luciana Randazzo, Paola Fermo, Donatella Barca, Monica Alvarez de Buergo, Mauro Francesco La Russa

PII: S0048-9697(20)36435-4

DOI: https://doi.org/10.1016/j.scitotenv.2020.142905

Reference: STOTEN 142905

To appear in: *Science of the Total Environment*

Received date: 8 July 2020

Revised date: 3 October 2020

Accepted date: 3 October 2020

Please cite this article as: N. Rovella, N. Aly, V. Comite, et al., The environmental impact of air pollution on the built Heritage of Historic Cairo (Egypt), *Science of the Total Environment* (2020), https://doi.org/10.1016/j.scitotenv.2020.142905

The environmental impact of air pollution on the built Heritage of Historic Cairo (Egypt)

Natalia Rovella[a], Nevin Aly[b], Valeria Comite[c]*, Luciana Randazzo[a], Paola Fermo[c], Donatella Barca[a], Monica Alvarez de Buergo[d], Mauro Francesco La Russa[a]

[a] Department of Biology, Ecology and Earth Sciences (DiBEST), University of Calabria, 87036 Arcavacata di Rende, CS, Italy

natalia.rovella@unical.it; luciana.randazzo@unical.it; donatella.barca@unical.it; mlarussa@unical.it

[b] Department of Science and Engineering Mathematics, Faculty of Petroleum and Mining Engineering, Suez University, 43512 Suez, Egypt

Nevin.Aly@suezuniv.edu.eg

[c] Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milan, Italy

valeria.comite@unimi.it; paola.fermo@unimi.it

[d] Geosciences Institute IGEO (CSIC-UCM), Doctor Severo Ochoa 7, 28040 Madrid, Spain

alvarezm@geo.ucm.es

*corresponding author: valeria.comite@unimi.it

Abstract

In the last decades, many researchers investigated the relation between environmental pollution and the degradation phenomena on the built heritage, because of their rapid increase and growing harmfulness. Consequently, the identification of the main pollution sources has become essential to define mitigation actions against degradation and alteration phenomena of the stone materials. In this way, the present paper is focused on the study of the effect of air pollution on archaeological buildings in Historic Cairo. A multi-methodological approach was used to obtain information about the chemical composition of examined black crusts and to clarify their correlation with the air pollution, specifically the heavy metals and the carbonaceous fraction, their main sources, and their impact on the state of conservation of the studied sites. All specimens were characterized by polarized optical microscopy (POM), X-Ray Diffraction (XRD), Electron Probe Micro Analyser coupled with energy dispersive X-ray spectrometry (EPMA-EDS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and Thermo-gravimetric analysis (TGA). The study conducted on heavy metals and carbonaceous fraction showed that the greatest contribution of the accumulation of pollutants is attributable to vehicular traffic and industrial activities, the main polluting sources in Cairo city. Furthermore, the comparison with other studies conducted on the carbonaceous fraction in the black crusts coming from both European and non-European cities, has allowed to discriminate the contribution of the primary and secondary polluting sources. Finally, the correlation of the data obtained on the heavy metals and the carbonaceous fraction allowed to formulate important hypothesis about the processes of sulphation.

Keyword: air pollution; built cultural heritage; black crust; heavy metals; carbonaceous fraction; degradation.

1. Introduction

Cairo is the largest city in Egypt and in Africa; here, the air pollution produced many environmental problems related to aerosol particulate matter and to the high levels mostly of sulphur dioxide and lead. For this reason, it was listed as one of the most polluted cities in the world (Gurjar et al., 2010). The air pollution sources in the city are different and include burning of rubbish, vehicle emissions (~4.5 million cars on the streets of Cairo) and urban industrial activities. The city has 15–20 million inhabitants and is characterized by high congestion due to a population density of 13107/km^2 (Abbass et al., 2020). Furthermore, the lack of rain helps the accumulation of pollutants. Many lead and copper smelters that heavily pollute the city air are unregistered. Pollutants are deposited on the surface of stone materials constituent of the historical buildings. Indeed, those ones suffer serious deterioration phenomena in Cairo as a result of physical-chemical and biological effects (El-Tawab et al., 2012), favouring black crust formation, alveolization, chemical alterations, disaggregation pitting, cracks, erosion (Davidson et al., 2000).

Black crusts are one of the most dangerous degradation products in building stones and are closely connected with environmental pollution, especially the atmospheric one. They are very common on the carbonate substrates as limestones. This lithotype is widely used for the construction of historical monuments in the whole Mediterranean area thanks to its workability, durability and aesthetic features; nevertheless, it is frequently affected by degradation phenomena (Fitzner et al., 2002; La Russa et al., 2013a; Ricca et al., 2019), firstly black crusts.

These degradation layers are formed through sulphation processes of the stone surface where calcium carbonate ($CaCO_3$), which is the main constituent of limestone, is transformed into gypsum $CaSO_4$*$2H_2O$ (Comite et al., 2012, 2020a,b; Rovella et al., 2020). Metals and metal oxides, present in the atmosphere, catalyse the sulphation reaction (Fermo et al., 2020). This process affects mainly stone materials having carbonate nature (for example limestone, marble, lime mortar). In addition, during the crust formation, particulate matter, which contains amorphous carbon and several heavy metals, can be embedded into the gypsum, providing its characteristic black colour (La Russa et al., 2018) and altering the aesthetic appearance of the monuments. For instance, the old structures in Cairo, originally of a whitish colour and some even striped with the “ablaq” style (in some instances it is hard to spot the stripes due to the amount of dust covering the surface) are now completely blackened (Orphy and Hamid, 2004). Moreover, black crusts threaten the conservation of the stone surfaces: hard crusts, usually firmly attached to the stone are very hard to remove and can weaken the surface on which they develop.

For all these reasons the attention of the scientific world is steadily increasing on the effect of air pollution on archaeological buildings in Cairo and, consequently on the relative degradation products (Fitzner et al., 2002).

The present research was conceived in this context and deals with the relation between air pollution and the historical building in Cairo.

The study areas are located in the historic Cairo (Fig. 1S available in *Supplementary material*) and includes the outer walls of Salah El-Din citadel, the Magra El-Oyoun wall, and monuments of the Northern Mamluk cemetery such as the Mosque of the Sultan Faraj ibn Barquq, the Qaitbay Mosque and the tomb of Qansuh Al-Ghuri. They were selected for historical-artistic relevance, location in the urban context characterized by different prevailing pollution sources and building stone materials (i.e., limestone). A complementary analytical approach was applied to achieve some important objectives:

- to characterize the black crusts in terms of minero-petrographic features to evaluate the degradation degree affecting the stone substrates studied;
- to determine the chemical composition of the black crusts in order to establish their correlation with the air pollution, defining the contribution of the heavy metals and the carbonaceous fraction;
- to identify the probable main pollutant sources in the study area

2. Materials and Methods

The limestones used for the construction of the historical stone monuments in Cairo come from local middle and late Eocene outcrops (47.8- 33.9 million years ago) located in Mokattam, Helwan and Giza areas (Aly et al., 2015, 2020). These materials are still being used for stone replacement or rebuilding works in monuments preservation practice as well as for modern buildings.

All the monuments underwent various rebuilding interventions over time and there is not very reliable information about them. Regarding restoration in the modern epoch, it is known that several interventions were carried out in the 19th century, 1990s and early 2000s.

Samples consisting of black crust and stone substrate, were taken from some portions located on vertical surfaces of the selected monuments, seriously affected by degradation phenomena and exposed to high rates of environmental pollution (Table 1).

A complete characterization of stone substrate and black crust associated was carried out, applying different analytical techniques aimed to determining the stationary and mobile combustion sources, major responsible for the blackening and soiling encountered.

Polarized Optical Microscopy (POM) analyses were performed on polished thin sections by using a Zeiss Axiolab associated with AxioCam MR for digital image acquisition. This technique is aimed to characterize both substrate and black crusts and to investigate the substrate/black crust interface determining minero-petrographic features and evaluating the degradation degree of each sample.

X-Ray Diffraction (XRD) analysis was carried out to identify the mineralogical phases constituting the black crusts sampled. Measurements were performed using a Siemens D5000 diffractometer and spectra were taken in the range 5°–65° 2Θ, using a step-size of 0.02° 2Θ and a step-time of 2 s/step. Samples were carefully prepared by separating the limestone substrate from the black crust and pulverized them in an agate mortar.

An Electron Probe Micro Analyser (EPMA) - JEOL - JXA 8230 —coupled with an energy dispersive X-ray spectrometer (EDS) - JEOL EX-94310FaL1Q - Silicon drift type— was used in order to observe the micro-morphology and analyse the composition in terms of major chemical elements. The EDS analyses were carried out according to the following operating conditions: 15 keV HV; 10 nA probe current; 11mm working distance; 40° take off; and 30 seconds live time. Before measuring, samples were graphite (ultra-pure graphite) sputtered to facilitate the electron conductivity by generating a ± 5 nm thick film, applied by Sputter - Carbon Coater QUORUM Q150T-ES, 70 A pulse current and 2.5 sec pulse time).

Chemical analyses of the black crusts, as well as of the substrates, in terms of trace elements were performed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). This method allows to investigate a great number of elements with spot resolutions of about 40–50 μm, also allowing the determination of micrometric compositional variations. The complete procedure is described in Barca et al. (2011).

Thermo-gravimetric analysis (TGA) was employed for the quantification of the carbonaceous fraction (TC total carbon= OC organic carbon + EC elemental carbon), Ox oxalate, CC carbonatic carbon and gypsum, present in the black crusts. It was performed by a Mettler Toledo TGA/DSC 3+, which allows simultaneous TG and DSC (Differential Scanning Calorimetry) analyses. The analyses were conducted in the range 30°- 800°C, increasing temperature with a rate of 20° C/minute. The carbonaceous components were estimated in temperature ranges defined by previously studied standards and using two different atmospheres, i.e. the inert and the oxidizing one. The complete methodology is described in previous works such as La Russa et al. (2017).

3. Results and discussion

3.1. POM Analysis

The main minero-petrographic features of the substrates and black crusts are summarized in Table 1S available in Supplementary material. The substrates are all calcareous rocks and were classified according the criteria of Folk (1959) and Dunham (1962).

The samples 2 (Fig.1a), B and E are biomicrite (Folk, 1959) and wackestone (Dunham, 1962), whereas the samples 3, 12, 14 (Fig.1b), 15 (Fig.1c), H are classified as biomicrite (Folk, 1959) and mudstone (Dunham, 1962). Quartz, iron oxides and macroforaminifera, i.e. nummulites also exceeding 1 mm (Fig.1d) are common in the substrates.

The black crusts are constituted mostly by microcrystalline gypsum, brownish iron oxides and carbonaceous particles. These latter ones are sub-spherical and averagely 40 µm in size (Fig.1b). Generally the crusts are well adherent to the substrates and show commonly very irregular thickness (Fig. 1e); moreover it is possible to distinguish also two layers: one more external and an inner one directly in contact with the substrate (Fig.1b-e) (Table 1S).

3.2 XRD Analysis

The analysis (Table 2S) revealed the presence of gypsum, calcite and secondarily quartz as the main mineralogical species in almost all the crusts examined. Quartz and calcite come from the limestone substrate, while gypsum is the main constituent of the crusts (Barca et al., 2011; Belfiore et al., 2013; La Russa et al., 2013b; Ruffolo et al., 2015). Among the other mineralogical phases, plagioclase, K-feldspar, hematite and clay minerals were identified in subordinate amount.

The crusts include halite, the most common sodium chloride salt in the subsurface water of Egypt and in sea spray coming from the Mediterranean Sea (Aly et al., 2015) and consequently also in Egyptian limestones (Helmi, 1990). The salt is linked to the capillary rise of water from the subsoil and the consequent precipitation of the salt inside the stone (Charola, 2000; Fitzner et al., 2002; Gomez-Heras and Fort, 2007).

3.3 EPMA-EDS Analysis

EPMA-EDS analyses were carried out on the black crusts in order to obtain more detailed morphological information and microchemical data about the major elements constituting the crusts.

In the samples 2 and 3 the crusts show an irregular morphology. Black crusts of samples 12, 14 appear rather compact and adherent to the substrate, especially sample 12 (Fig. 3S a); in this sample gypsum was detected also in substrate, where the crust is thicker and deepens in. The black crust in sample 15 shows a homogeneous morphology (Fig. 3S b). It does not properly adhere to the underlying substrate, due to the presence of numerous fractures, that in some points cross the entire body of the crust. Sample E is rather compact, with a regular external profile and a sharp contact with the substrate (Fig. 3S c). The crust in sample B is more porous with a dendritic morphology. The sample H shows in general an irregular morphology, fractures, and jagged edges. However, it was individuated little portions more homogeneous, compact and adherent to substrate, that were analysed by EDS and then by LA-ICP-MS.

The crusts are constituted mainly by CaO and SO_3 thanks to gypsum-based composition, secondly by SiO_2, and lastly ClO, Al_2O_3, Na_2O, MgO, K_2O, FeO, TiO_2.

3.4 LA-ICP-MS Analysis

Trace elements concentrations were determined by LA-ICP-MS on the black crusts and underlying substrates of all the examined samples. The results obtained for each spot analysis are listed in Table 2S, where average values and corresponding standard deviations are displayed.

Looking at the concentrations of the most significant trace elements (Table 3S), elements like lead (Pb), barium (Ba), vanadium (V), chromium (Cr), cobalt (Co), zinc (Zn) and arsenic (As) have relatively high concentrations, indicating an accumulation of atmospheric pollutants on the gypsum crusts, regardless of the sampling location. The documented high concentrations of lead suggest that this element is still present in the urban environment of Cairo city many years after the ban of leaded gasoline in Egypt (Fujiwara et al., 2011), as it has been also shown by previous studies in other cities around the world (Sanjurjo Sánchez et al., 2011; Török et al., 2011; Graue et al., 2013).

As well known, all these elements can be introduced in the urban environment by a wide range of different anthropogenic processes, mainly mining, smelting, industrial manufacturing, metal processing, etc. (Johnson et al., 2011) but also by domestic and residential activities (heating, vehicles, transport). However, some elements occur naturally in the same urban environment as a result for example of geologic processes (erosion of outcropping bedrocks). The proportion of natural and anthropogenic components may vary widely depending thus on the geology and the industrial history of the urban centre. Our geochemical approach was addressed to define the relation between pollution sources and the degradation state of stone materials; for this purpose, the Enrichment Factor was calculated both for heavy metals, metalloids and Rare Earths Elements (hereafter REE). Enrichment factors calculation is a procedure commonly used in geochemical studies for the determination of the anthropogenic origin of chemical elements. For the purpose of our study, the chemical procedure was followed by normalizing the chemical composition of trace elements in black crusts with respect to those of calcareous substrates on which they grew (Table 4S).

The normalization procedure performed here used Scandium (Sc) as ‘conservative’ element, as it was presumed to have no anthropogenic enrichment or a minor anthropogenic input (Loring, 1991; Gallego et al., 2013). This calculation is carried out by comparing the concentrations of the trace elements with those of the conservative element by following the formula $EF = (M/N)_{sample}/(M/N)_{substrate}$, which is the ratio between the concentrations of the metal (M) and those of the normalizer (N), both for the sample and for substrate samples (Reimann and Caritat, 2000). Figure 2S show EFs for all the examined samples grouped for sampling location criterion. As shown in the Figure 2S, samples 2 and 3 are enriched in Zn, As, Pb, REE (L-REE, light and H-REE, heavy) and Sn, Ba, Pb and HREE, respectively. Similarly, samples 12 and 14 show enrichment in all the LREE and in most metals and metalloids elements. The same enrichment trend (Fig. 2S) is highlighted by the remaining samples (B, E, 15 and H).

Samples B and E reveal enrichments in Co, Mo, Sn, Sb, Ba, Pb, and Sn, Ba, Pb, respectively with associated null or slight enrichment in REE. As regards sample 15, metals and metalloids are similarly enriched as in the previous samples, while the REE show values close to the background. Conversely, sample H shows only a slight enrichment in Sn, Sb and Ba, with no enrichment in REE.

Finally, some heavy metal and metalloids concentrations (V, Cr, Co, Ni, Zn, As, Cd and Pb, Mn and Cu) in the studied black crusts were compared to the corresponding concentrations in road dust samples (after Abdel-Latif and Saleh, 2012), collected across the Cairo city (Fig. 2).

It is worth to note that Zn, Mn and Cu are, together with Fe (not determined in this study), the metals present in the higher concentrations in PM (Atzei et al., 2014). Road dust includes deposits and accumulates on ground surfaces, along roadsides, which is contaminated by heavy metals. It usually does not remain deposited in place for long, but it is easily re-suspended back into the atmosphere, as it was already mentioned. For the purposes of this work, the concentrations of the above-mentioned metals in the <125 μm fraction were considered for the comparison as these sizes are easily resuspended in atmosphere contributing with a significant amount of trace elements in residential, main traffic roads and industrial areas. Metals concentrations in the dust were higher in main traffic roads and industrial areas compared to those of residential areas. Figure 2 shows the box plot diagram, in which minimum, maximum and average values for the selected elements in black crusts samples are reported together with the values corresponding to the metal concentration in the dust collected in Cairo (Abdel-Latif and Saleh, 2012). As can be seen, most of the heavy metal average values in the black crusts fall within the ranges relevant to the dust of the Cairo city. Exceptions in this trend are the value of arsenic (As) and, at lesser extent, the value of cadmium (Cd). In fact, black crusts samples experienced values of these two elements greater than those of dust samples. Both these metals have been widely used in industrial sector, i.e. man-made emissions from metal smelters (iron, steel, copper, lead and zinc production), mining activities, combustion processes (coal and oil) and refuse incineration (stabilizers and pigments in plastics).

Studied black crusts may have accumulated these elements over time being considered as good traps for atmospheric particles, useful for the identification of the particulate matter pollution emission sources in urban areas.

3.5 Carbonaceous fraction

Carbonaceous particles emitted by combustion processes are among the main constituents of aerosol particulate matter (PM) (Bozzetti et al., 2017) and one of the main factors responsible for the blackening of buildings.

The quantification of the carbonaceous species that form the non-carbonatic fraction, i.e. OC (organic carbon) and EC (elemental carbon) in damage layers, are required particularly in urban areas in order to investigate atmospheric deposition processes on building surfaces, to get information on the possible particulate matter sources and to suggest mitigation measurements to fulfil a better conservation of the stone surfaces (Fermo et al., 2015).

While black carbon (also known as elemental carbon, EC) is emitted by combustion processes, such as traffic and biomass burning and is the main responsible for soiling on monuments surfaces (Tidblad et al., 2012), OC has both primary and secondary origin (Bernardoni et al., 2011; Daellenbach et al., 2016). The Mediterranean region is characterized by an intense photochemistry during summer which brings to high concentration, in the aerosol PM, of secondary organic substances (Bozzetti et al., 2017); this phenomenon is particularly favoured in Cairo.

Table 2 shows the values obtained by thermogravimetric analysis and reported as weight percentages (wt.%), highlighting slight differences among the samples.

The greatest variability among samples was found for gypsum (minimum value of 9.7%, maximum value 51.25 %); highest concentrations were obtained for samples 12, 14 and B in accordance with what was observed by XRD analysis.

In general, all the crust samples show higher EC values (wt. %) than OC (Table 2). EC values are also higher than what was generally observed for PM samples in Cairo (Favez et al., 2008; Kanakidou et al., 2011; Lowenthal et al., 2014; Cheng et al., 2016). It is also important to stress out that the carbonaceous substances dominate PM2.5 composition of megacities atmosphere, especially in Cairo (Cheng et al., 2016) with an average annual OC/EC ratio of 2.45 (Lowenthal et al., 2014). This ratio is rather linked to seasonal conditions, with values of 3.45 (autumn season), 2.64 (winter season) and 2.17 for the summer season (Abu-Allaban et al., 2007). The highest levels observed during autumn season have been related to episodes of biomass combustion on the Nile delta (Favez et al., 2008). According to Kanakidou et al. (2011), in Cairo the sources contributing to OC fraction are mainly represented by industry, residential activities, energy production and incinerators, while EC is mainly emitted from mobile sources (diesel traffic) and combustion processes (e.g. domestic heating or industrial activities) (Abu-Allaban et al., 2007; Favez et al., 2008). It is worth to notice that for all the analysed crust samples OC/EC ratio is lower than 1 indicating, with respect to what happens for the aerosol, a more important contribution of EC.

OC and EC values of the crust samples were compared with those obtained for other black crust samples from Cairo taken, in some cases, from the same monuments (Rovella et al., 2020).

Figure 3 shows that, in general, as the sampling height of the crusts decreases, the concentration of EC increases. This confirms that traffic is the main source of this pollutant and is responsible for the emission of particles which mainly affects surfaces at lower heights in direct contact with the road. OC values vary from a minimum of 0.36 to a maximum of 1.88, while EC varies from a minimum of 0.99 to a maximum of 5.95. The clustering based on the relationship between the concentrations of EC and OC and showed in Figure 4a, suggests similar trends for most of the samples even if they come from different areas in Cairo. The only exception is represented by site a) (Fig. 4b) where high EC values are observed for samples 8, 9 and 10 all taken at low heights.

In order to evaluate potential differences on the accumulation of OC and EC in the crusts from Cairo and other polluted cities, a comparisons has been made also with crusts taken from Italian monuments (Fig. 5) such as: Trevi Fountain in Rome (La Russa et al., 2017); several private buildings in Venice (La Russa et al., 2018), Church of Santa Maria delle Grazie in Milan (Comite and Fermo et al., 2018) and the Monza Cathedral located in the homonymous city (Comite et al., 2020c).

Considering all the samples together (Fig. 5a) the presence of two types of samples for which a quite good correlations between OC and EC were observed, has been highlighted. Two averages characteristic OC/EC ratios have been identified: for the first groups OC/EC is around 3,9 (considering the slope of the regression line), while for the second group OC/EC is around 1,9. This allows hypothesizing that for the second group, in which all the Cairo samples fall, the primary sources dominate (higher EC, i.e. traffic contribution) while for the first group a mixed contribution of the sources (primary + secondary) can be suggested. In fact, the city is characterized by high congestion due to, as mention before, a population density of 13107/km^2 and 2.4 million cars (Moustafa et al., 2018) and limited use of public transport (El-Dorghamy et al., 2015) that contribute to the release of black carbon into the air (Mahmoud at al., 2008). Moreover, many vehicles are old, causing a further increase of pollution (Kanakidou et al., 2011). Even in the past, domestic heating or industrial sector introduced significant quantities of black carbon into the air (Abu-Allaban et al., 2007; Favez et al., 2008). For these reasons, the first actions for environmental protection were introduced in the early 1990s and after that, a slight air quality improvement emerged (Kanakidou et al., 2011).

Furthermore, the average OC/EC ratio for all Cairo samples (Fig. 5b) is lower than what observed for the other sites.

3.6 Correlation matrix and general remarks

The correlation between the gypsum content, the carbonaceous fraction and the concentrations of heavy metals can provide further information on the sources of pollutants. Figure 4S shows the correlation matrix between all the experimental variables quantified on the examined samples. Gypsum is positively correlated to different heavy metals, namely Cu, Pb, Sb and Zn, and, to a lesser extent, to the remaining metals and metalloids. This could indicate that probably some elements are closely related to the sulphation processes. In fact, heavy metals have long been considered capable of catalysing these processes (Rodriguez-Navarro and Sebastian, 1996; Wahba and Zaghloul, 2007). A good correlation has been observed between Gy and Cu (0.92). According to Boke et al. (1999), Cu^{+2} ion increases the absorption of SO_2 in the aqueous film present on a carbonate surface. This ion has also been shown to dissipate any gradient of electrical potential allowing hydrogen ions to spread much faster on surfaces (Chang et al., 1981). As a result, an increase in SO_2 uptake is observed which accelerates the sulphation process. Furthermore, Cu has been shown to be released from the exchangeable carbonate phase making this metal potentially available to catalyse surface reactions (McAlister et al., 2008).

From the matrix a very good correlation between Ni and V has been observed indicating the contribution of heavy oil combustions (Bove et al., 2016).

On the contrary, the carbonaceous fraction EC is negatively correlated with gypsum and also with various heavy metals. In fact, the surface of EC particles contains numerous adsorption sites that are capable of enhancing catalytic processes because of their high surface reactivity. As result of its catalytic properties, EC may affect some important chemical reactions involving atmospheric sulphur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3) and other gaseous compounds (Gundel et al., 1989, Böke et al., 1999).

4. Conclusion

The results achieved in this work highlighted the strong correlation between atmospheric pollution and the degradation processes affecting stone materials used in the built cultural heritage of Cairo city. The multi-analytical approach applied, demonstrated how black crusts can be considered such as an efficient “natural passive sampler” of atmospheric pollutants, capable to provide information about atmospheric composition especially in terms of heavy metals and carbonaceous fraction. Precisely:

- the minero petrographic description provided information about the state of conservation of the substrate and the interactions between crust and stone;

- the results about contribution of the heavy metals are consistent with the hypothesis that road dust is an important pollutant source; in fact the black crusts analysed are constituted mainly by heavy metals ascribable most probably to the road dust of Cairo city, with the exception of As and Cd, being widely used in the industrial sector;

- the data on the carbonaceous fraction suggested that the formation of black crusts sampled is influenced by a preeminent action of the primary sources. At the same time, the high EC contents confirmed the contribution of various polluting sources, such as mobile emissions or combustion processes (e.g. domestic heating or industrial activities) in the formation of black crusts. Additionally, EC data underline the clear predominance of pollution produced by vehicles.

This research demonstrated how the contribution of atmospheric pollution is crucial in the evolution of the degradation phenomena, affecting the built cultural heritage in Historic Cairo. Consequently, the reduction of emissions into the atmosphere, adopting for example more eco-sustainable policies, becomes extremely necessary not only for the conservation of cultural heritage but more in general, for the safeguard of the environment and human health.

Acknowledgements

The present research is a part of an Executive program for scientific cooperation between the Italian Republic and the Arab Republic of Egypt, entitled “Characterization of black crusts formed on historical buildings under different levels of ambient air pollution in Cairo and Venice”.

Moreover, it is also part of an international cooperation program funded by CSIC, I-COOP (“Implementation of a reference laboratory for the diagnosis, conservation and restoration of stone-cultural heritage in Egypt”, January 2019 December 2020, Ref. COOPB20379).

Finally, the research was partially funded by the project TOP Heritage (P2018/NMT-4372) of the Community of Madrid. The authors wish to acknowledge professional support of the Interdisciplinary Thematic Platform from CSIC Open Heritage: Research and Society (PTI-PAS).

References

Abbass, R.A., Kumar, P.T., El-Gendy, A., 2020. Car users exposure to particulate matter and gaseous air pollutants in megacity Cairo. Sustain. Cities Soc. 56 (102090), 1-13. https://doi.org/10.1016/j.scs.2020.102090.

Abdel-Latif, N.M., Saleh, I.A., 2012. Heavy Metals Contamination in Roadside Dust along Major

Roads and Correlation with Urbanization Activities in Cairo, Egypt. J. Am. Sci. 8(6), 379-389. ISSN: 1545-1003.

Abu-Allaban, M., Lowenthal, D.H., Gertler, A.W., Labib, M., 2007. Sources of PM10 and PM2.5 in Cairo's ambient air. Environ. Monit. Assess 133, 417–425. https://doi.org/10.1007/s10661-006-9596-8. DOI 10.1007/s10661-008-0526-9.

Aly, N., Hamed, A., Gomez-Heras, M., Alvarez de Buergo, M., 2015. The influence of temperature in a capillary imbibition salt weathering simulation test on Mokkattam limestone. Mater. Construc. 65 (317). https://doi.org/10.3989/mc.2015.00514.

Aly, N., Hamed, A., Abd El-Al, A., 2020. The impact of hydric swelling on the mechanical behavior of Egyptian Helwan Limestone. Period. Polytech. Civ. 64(2), 589-596. https://doi.org/10.3311/PPci.15360.

Atzei, D., Fantauzzi, M., Rossi, A., Fermo, P., Piazzalunga, A., Valli, G., Vecchi, R., 2014. Surface chemical characterization of PM10 samples by XPS. Appl. Surf. Sci. 307, 120-128. https://doi.org/10.1016/j.apsusc.2014.03.178.

Barca, D., Belfiore, C.M., Crisci, G.M., La Russa, M.F., Pezzino, A., Ruffolo, S.A., 2011. A new methodological approach for the chemical characterization of black crusts on building stones: a case study from the Catania city centre (Sicily, Italy). J. Anal. At. Spectrom. 26, 1000–1011. https://doi.org/10.1039/C0JA00226G

Belfiore, C.M., Barca, D., Bonazza, A., Comite, V., La Russa, M.F., Pezzino, A., Ruffolo, S.A., Sabbioni, C., 2013. Application of spectrometric analysis to the identification of pollution sources causing cultural heritage damage. Environ. Sci. Pollut. Res. 20, 8848–59. https://doi.org/10.1007/s11356-013-1810-y.

Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., Fermo P., 2011. PM10 source apportionment in Milan (Italy) using time-resolved data. Sci. Tot. Environ. 409, 4788–4795. https://doi.org/10.1016/j.scitotenv.2011.07.048.

Böke, H., Göktürk, E.H., Caner-Saltık, E.N., Demircia, Ş.,1999. Demirci Effect of airborne particle on SO –calcite reaction. Appl. Surf. Sci. 140 (1-2), 70–82. https://doi.org/10.1016/S0169-4332(98)00468-1.

Bove, M.C., Brotto, P., Calzolai, G., Cassola, F., Cavalli, F., Fermo, P., Hjorth, J., Massabò, D., Nava, S., Piazzalunga, A., Schembari, C., Prati P., 2016. PM10 source apportionment applying PMF and chemical tracer analysis to ship-borne measurements in the Western Mediterranean. Atmos. Environ. 125, 140-151. https://doi.org/10.1016/j.atmosenv.2015.11.009.

Charola, A.E., 2000. Salts in the Deterioration of Porous Materials: An Overview. J. Am. Inst. Conservat. 39(3), 327-343. https://doi.org/10.1179/019713600806113176.

Chang, C.S., Rochelle, G.T., 1981. SO2 absorption into aqueous solutions. AIChE J. 27(2), 292–298.

Cheng, Z., Luo, L., Wang, S., Wang, Y., Sharma, S., Shimadera, H., Wang, X., Bressi, M., De Miranda, R.M., Jiang, J., Zhou, W., Fajardo, O., Yan, N., Hao, J., 2016. Status and characteristics of ambient PM2.5 pollution in global megacities. Environ. Int. 89–90, 212–221. https://doi.org/10.1016/j.envint.2016.02.003.

Comite, V., Barca, D., Belfiore, C.M., Bonazza, A., Crisci, G.M., La Russa, M.F., Pezzino, A., Sabbioni, C., 2012. Potentialities of spectrometric analysis for the evaluation of pollution impact in deteriorating stone heritage materials. In: Rendiconti online della Società Geologica Italiana, 86 Congresso Nazionale della Società Geologica Italiana, Arcavacata di Rende, 18–20 September 2012, Roma, vol. 21, pp. 652–653.

Comite, V., Fermo, P., 2018. The effects of air pollution on cultural heritage: the case study of Santa Maria delle Grazie al Naviglio Grande (Milan). E.P.J. Plus. 133 (12), 556-566. https://doi.org/10.1140/epjp/i2018-12365-6.

Comite, V., Ricca, M., Ruffolo, S.A., Graziano, S.F., Rovella, N., Rispoli, C., Gallo, C., Randazzo, L., Barca, D., Cappelletti, P., La Russa, M.F., 2020a. Multidisciplinary approach to evaluate the geochemical degradation of building stone related to pollution sources in the Historical Centre of Naples (Italy). Int. J. Conserv. Sci. 11(1), 291-304. https://doi.org/10.3390/app10124241.

Comite, V., Pozo-Antonio, J.S., Cardell, C., Rivas, T., Randazzo, L., La Russa, M.F., Fermo, P., 2020b. Environmental impact assessment on the Monza cathedral (Italy): a multi-analytical approach. Int. J. Conserv. Sci. 11(1), 291-304.

Comite, V., Pozo-Antonio, J.S., Cardell, C., Randazzo, L., La Russa, M.F., Fermo, P., 2020c. A multi-analytical approach for the characterization of black crusts on the facade of an historical cathedral. Microchem. J. 158, 105121. https://doi.org/10.1016/j.microc.2020.105121.

Daellenbach, K.R., Bozzetti, C., Křepelová, A., Canonaco, F., Wolf, R., Zotter, P., Fermo, P., Crippa, M., Slowik, J.G., Sosedova, Y., Zhang, Y., Huang, R.J., Poulain, L., Szidat, S., Baltensperger, U., El Haddad, I., Prévôt, A.S.H., 2016. Characterization and source apportionment of organic aerosol using offline aerosol mass spectrometry. Atmos. Meas. Tech. 9(1), 23–39. https://doi.org/10.5194/amt-9-23-2016.

Davidson, C.I., Tang, F., Finger, S., Etyemezian, V., Sherwood, S.I., 2000. Soiling patterns on a tall limestone building: changes over 60 years. Environ. Sci. Technol. 34(4), 560–565. https://doi.org/10.1021/es990520y.

Dunham, R.J., (1962). Classification of carbonate rocks according to depositional textures. Amer. Assoc. Petrol. Geol. Mem. 1, 108-121.

Duquennois, A.N., Newman, P., 2009. Linking the green and brown agendas: A case study on Cairo, Egypt. UN habitat, global report on human settlements. http://www.unhabitat.org/grhs/2009, last accessed: 24 June 2020.

El-Dorghamy, A., Allam, H., Al-Abyad, A., Gasnier, M., 2015. Fuel economy and CO2 emissions of light-duty vehicles in Egypt. Centre for Environment and Development in the Arab Region and Europe (CEDARE). http://web.cedare.org/, last accessed: 20 June 2020.

El-Tawab, N.A., Mahran, A., Badr, I., 2012. Restoration and preservation of the wooden ceiling of Al-Ashraf Qaytbay madressa, Cairo Egypt. EJARS 2(1), 11-28. doi: 10.21608/ejars.2012.7456

Favez, O., Cachiera, H., Sciare, J., Alfaro, S.C., El-Araby, T.M., Harhash, M.A., Abdelwahab, M.M., 2008. Seasonality of major aerosol species and their transformations in Cairo megacity. Atmos. Environ. 42, 1503–1516. https://doi.org/10.1016/j.atmosenv.2007.10.081.

Fermo, P., Turrion, R.G., Rosa, M., Omegna, A., 2015. A new approach to assess the chemical composition of powder deposits damaging the stone surfaces of historical monuments. Environ. Sci. Pollut. Res. 22, 6262-6270. https://doi.org/10.1007/s11356-014-3855-y.

Fermo, P., Comite, V., Ciantelli, C., Sardella, A., Bonazza, A., 2020. A multi-analytical approach to study the chemical composition of total suspended particulate matter (TSP) to assess the impact on urban monumental heritage in Florence. Sci. Total. Environ. 740-140055.

Fitzner, B., Heinrichs, K., La Bouchardiere, D., 2002. Weathering damage on Pharaonic sandstone monuments in Luxor-Egypt. Build Environ 38, 1089-1103. DOI: 10.1016/S0360-1323(03)00086-6.

Folk, R.L., 1959. Practical petrographic classification of limestones. Bull. Amer. Assoc. Petrol.

Geol. 43, 1-38. https://doi.org/10.1306/0BDA5C36-16BD-11D7-8645000102C1865D.

Fujiwara, F., Rebagliati, R.J., Dawidowski, L., Gómez, D., Polla, G., Pereyra, V., Smichowski, P., 2011. Spatial and chemical patterns of size fractionated road dust collected in a megacity. Atmos. Environ. 45, 1497-1505. https://doi.org/10.1016/j.atmosenv.2010.12.053.

Gallego, J.R., Ortiz, J.E., Sierra, C., Torres, T., Llamas, J.F., 2013. Multivariate study of trace element distribution in the geological record of Roñanzas Peat Bog (Asturias, N. Spain). Palaeoenvironmental evolution and human activities over the last 8000 cal yr BP. Sci. Total Environ. 454, 16-29. https://doi.org/10.1016/j.scitotenv.2013.02.083.

Gomez-Heras, M., Fort, R., 2007. Patterns of halite (NaCl) crystallisation in building stone conditioned by laboratory heating regimes. Environ. Geol. 52, 259-267. https://doi.org/10.1007/s00254-006-0538-0.

Graue, B., Siegesmund, S., Oyhantcabal, P., Naumann, R., Licha, T., Simon, K., 2013. The effect of air pollution on stone decay: the decay of the Drachenfels trachyte in industrial, urban, and rural environments—a case study of the Cologne, Altenberg and Xanten cathedrals. Environ. Earth Sci. 69, 1095–1124. https://doi.org/10.1007/s12665-012-2161-6.

Gundel, L.A., Guyot-Sionnest, N.S., Novakov, T., 1989. A study of the interaction of NO_2 with carbon particles. Aerosol Sci. Tech. 10(2), 343-351. https://doi.org/10.1080/02786828908959271.

Gurjar, B.R., Nagpure, A.S., Singh, T.P., Hanson, H., 2010. Air quality in megacities, in: Cleveland, C.J. (Eds.), Encyclopedia of Earth. Environmental Information Coalition, National Council for Science and the Environment. Washington D.C. http://www.eoearth.org/article/Air_quality_in_mega cities.

Helmi, F.M., 1990. Study of salt problem in the sphinx, Giza, Egypt. In: 9th Triennial meeting, ICOM Committee for Conservation, 26-31 August 1990, vol.1, Dresden, Germany. Grimstad, K. (Ed.), ICOM Committee for Conservation, Los Angeles, pp. 326-329.

Johnson, C.C., Demetriades, A., Locutura, J., Ottesen, R.T., 2011. Mapping the Chemical Environment of Urban Areas. Wiley, New York City, United States, ISBN: 978-0-470-74724-7, 640 Pages.

Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E., Dermitzaki, E., Unal, A., Koçak, M., Markakis, K., Melas, D., Kouvarakis, G., Youssef, A.F., Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojie, F., Wittrock, F., von Savigny, C., Burrows, J.P., Ladstaetter-

Weissenmayer, A., Moubasher. H., 2011. Review Megacities as hot spots of air pollution in the East Mediterranean. Atmos. Environ. 45(6), 1223-1235. https://doi.org/10.1016/j.atmosenv.2010.11.048.

La Russa, M.F., Ruffolo, S.A., Belfiore, C.M., Aloise, P., Randazzo, L., Rovella, N., Pezzino, A., Montana, G., 2013a. Study of the effects of salt crystallization on degradation of limestone rocks.

Period. Mineral. 82(1), 113-127. http://dx.doi.org/10.2451/2013PM0007.

La Russa, M.F., Belfiore, C.M., Comite, V., Barca, D., Bonazza, A., Ruffolo, S.A., Crisci, G.M., Pezzino, A., 2013b. Geochemical study of black crusts as a diagnostic tool in cultural heritage. Appl. Phys. A Mater. 113, 1151–62. https://doi.org/10.1007/s00339-013-7912-z.

La Russa, M.F., Fermo, P., Comite, V., Belfiore, C.M., Barca, D., Cerioni, A., De Santis, M., Barbagallo, L.F., Ricca, M., Ruffolo, S. A., 2017. The Oceanus statue of the Fontana di Trevi (Rome): The analysis of black crust as a tool to investigate the urban air pollution and its impact on the stone degradation. Sci. Total. Environ., 593-594, 297-309. https://doi.org/10.1016/j.scitotenv.2017.03.185.

La Russa, M.F., Comite, V., Aly, N., Barca, D., Fermo, P., Rovella, N., Antonelli, F., Tesser, E., Aquino, M., Ruffolo, S.A., 2018. Black crusts on Venetian built heritage, investigation on the impact of pollution sources on their composition. Eur. Phys. J. Plus 133, 370. https://doi.org/10.1140/epjp/i2018-12230-8.

Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments.

ICES J. Mar. Sci. 48(1), 101-115. https://doi.org/10.1093/icesjms/48.1.101.

Lowenthal, D.H., Gertler, A.W., Labib, M.W., 2014. Particulate matter source apportionment in Cairo: recent measurements and comparison with previous studies. Int. J. Environ. Sci. Technol. 11 (3), 657–670. https://doi.org/10.1007/s13762-013-0272-6.

Mahmoud, K.F., Alfaro, S.C., Favez, O., Abdel Wahab, M.M., Sciare, J., 2018. Origin of black carbon concentration peaks in Cairo (Egypt). Atmos. Res. 89 (1-2), 161–169. https://doi.org/10.1016/j.atmosres.2008.01.004.

McAlister, J.J., Smitha, B.J., Tőrők, A., 2008. Transition metals and water-soluble ions in deposits on a building and their potential catalysis of stone decay. Atmos. Environ. 42 (33), 7657–68. https://doi.org/10.1016/j.atmosenv.2008.05.067.

Mostafa, A.N., Zakey, A.S., Monem, A.S., Wahab M.M.A., 2018. Analysis of the surface air quality measurements in the Greater Cairo (Egypt) metropolitan. GJAR, 5(6), 207–214.

Orphy, M., Hamid, A., 2004. Problems Islamic monuments in Cairo face. In: 13th International Brick and Block Masonry Conference Amsterdam, July 4-7, 2004. Martens, D.R.W., Vermeltfoort, A.T. (Eds). Eindhoven: Technische Universiteit Eindhoven.

Reimann, C., Caritat, P., 2000. Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. Environ. Sci. Technol. 34(24), 5084–5091. https://doi.org/10.1021/es001339o.

Ricca, M., Le Pera, E., Licchelli, M., Macchia, A., Malagodi, M., Randazzo, L., Rovella, N., Ruffolo, S.A., Weththimuni, M.L., La Russa, M.F., 2019. The CRATI Project: New Insights on the Consolidation of Salt Weathered Stone and the Case Study of San Domenico Church in Cosenza (South Calabria, Italy). Coatings 9, 330-345. https://doi.org/10.3390/coatings9050330.

Rodriguez-Navarro, C., Sebastian, E., 1996. Role of particulate matter from vehicle exhaust on porous building stones (limestone) sulfation. Sci. Total Environ. 187, 79–91. https://doi.org/10.1016/0048-9697(96)05124-8.

Rovella, N., Aly, N., Comite, V., Ruffolo, S.A., Ricca, M., Fermo, P., Alvarez De Buergo, M., La Russa, M.F., 2020. A Methodological approach to define the state of conservation of the stone materials used in the Cairo historical heritage (Egypt). Archaeol. Anthrop. Sci. in press. https://doi.org/ 10.1007/s12520-020-01126-x.

Ruffolo, S.A., Comite, V., La Russa, M.F., Belfiore, C.M., Barca, D., Bonazza, A., Crisci, G.M., Pezzino, A., Sabbioni, C., 2015. An analysis of the black crusts from the Seville Cathedral: A challenge to deepen the understanding of the relationships among microstructure, microchemical features and pollution sources. Sci. Total Environ. 502, 157-166, https://doi.org/10.1016/j.scitotenv.2014.09.023.

Sanjurjo Sánchez, J., Vidal Romaní, J.R., Alves, C., 2011. Deposition of particles on gypsum-rich coatings of historic buildings in urban and rural environments. Constr. Build. Mater. 25, 813–822. https://doi.org/10.1016/j.conbuildmat.2010.07.001.

Tidblad, J., Kucera, V., Ferm, M., Kreislova, K., Brüggerhoff, S., Doytchinov, S., Screpanti, A., Grøntoft, T., Yates, T., De La Fuente, D., Roots, O., Lombardo, T., Simon, S., Faller, M., Kwiatkowski, L., Kobus, J., Varotsos, C., Tzanis, C., Krage, L., Schreiner, M., Melcher, M., Grancharov, I., Karmanova, N., 2012. Effects of air pollution on materials and cultural heritage: ICP materials celebrates 25 years of research. Int. J. Corros. 1-16. https://doi.org/10.1155/2012/496321.

Török, Á., Licha, T., Simon, K., Siegesmund, S., 2011. Urban and rural limestone weathering; the contribution of dust to black crust formation. Environ. Earth Sci. 63, 675–693. https://doi.org/10.1007/s12665-010-0737-6.

Wahba, M.M., Zaghloul, A.M., 2007. Adsorption characteristic of some heavy metals by some soil minerals. Res. J. Appl. Sci. 3(6), 421 – 426.

Williams, C., 2002. Islamic Monuments in Cairo: The Practical Guide. The American University in Cairo Press, Cairo.

Caption Figures

Fig. 1. Microphotographs obtained by OM observations highlighting the main textural features of the limestones and the overlaying black crusts. The red dashed lines mark the layers of the black crusts and their contact with the substrate. Each image is relative to a different sample at 5X magnification. a) sample 2 (Crossed Polarized Light view - CPL). b) Sample 14 (Plane Polarized Light view – PPL). c) Sample 15 (CPL). d) Sample E (CPL). e) Sample H (CPL).

Fig. 2. Box plot variations of heavy metal concentrations in black crusts samples.

Fig. 3. Graph of the OC and EC concentrations (wt.%) obtained from the analysis of the black crust samples in relation to the sampling height for each site. The monuments of the entire Cairo data set are: a) Al Manial Palace; b) Magra El-Oyoun wall; c) Salah El Din citadel; d) Tower of Bab Al Azab; e) Qaitbay Mosque; f) Sultan Faraj ibn Barquq Mosque (collection of a new sample 15), g) Quansuh Al-Ghury Mausoleum; h) Al Silahdar Mosque.

* after Rovella et al. (2020).

Fig 4. a) EC vs OC binary diagram of the crust samples analysed by the different monuments in Cairo (this work and after Rovella et al., 2020); b) map of the city of Cairo where the different monuments are located.

Fig. 5. a) Binary diagram OC vs EC of the analysed black crusts. b) Histogram of the average

OC/EC ratios of the analyzed black crust from the Cairo city (this work and after Rovella et al., 2020). Literature data used for the comparison refer to the crust samples taken from Cairo after Rovella et al., 2020; from the Trevi Fountain in Rome (La Russa et al., 2017); from several private buildings in Venice (La Russa et al., 2018), from the Church of Santa Maria delle Grazie in Milan (Comite and Fermo, 2018) and from the Cathedral of Monza located in the homonymous city (Comite at al., 2020).

Table 1 Information about samples in terms of position and age of construction (William, 2004). They consist of both black crust and limestone substrate.

Monument	Sample ID	Position	Height of sampling
Salah El Din citadel (1176-1183)	2	Western walls	1 m
	3		1,90 m
Magra El-Oyoun (1193)	12	Western walls	2,5 m
	14		1,3 m
Sultan Faraj ibn Barquq Mosque (1400-1411)	15	Main Facade	2,5 m
Qaitbay Mosque (1472-1474)	B	Main Facade	0,80 m
	E		1,0 m
Qansuh Al-Ghuri Mausoleum (1503-1505)	H	Main Facade	1,8 m

Table 2 OC (Organic Carbon), EC (Elemental Carbon) OX (carbonate Oxalate) CC (Carbonate Carbon) Gy (Gypsum) concentrations (wt%).

Sample	OC	EC	OX	CC	Gy
2	0.87	2.83	0.28	3.70	8.45
3	1.22	1.53	0.14	3.72	22.63
14	0.96	2.40	0.15	3.14	25.55
12	0.75	1.45	0.22	3.01	51.25
15	0.66	1.23	0.11	3.11	15.01
B	0.99	1.48	1.15	4.26	32.98
E	1.36	2.15	0.15	2.75	9.57
H	1.12	1.99	0.09	4.55	9.57

Declaration of competing interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Author contributions

Natalia Rovella, **Writing - Original Draft, Writing - Review & Editing, Validation, Formal analysis, Investigation**
Nevin Aly, **Writing - Review & Editing, Investigation**
Valeria Comite, **Formal analysis, Writing - Original Draft, Investigation, Methodology**
Luciana Randazzo, **Formal analysis, Investigation, Data Curation, Methodology**
Paola Fermo, **Writing - Review & Editing, Data Curation**
Donatella Barca, **Formal analysis, Data Curation,**
Monica Alvarez de Buergo, **Writing - Review & Editing**
Mauro Francesco La Russa, **Supervision, Writing - Review & Editing, Funding acquisition, Project administration**

Graphical abstract

Highlights:

-Black crusts from Cairo have been analyzed by several techniques

-The effect of urban air pollution on the monuments of Cairo have been investigated

- The methodology allowed identification of pollution sources in the black crusts

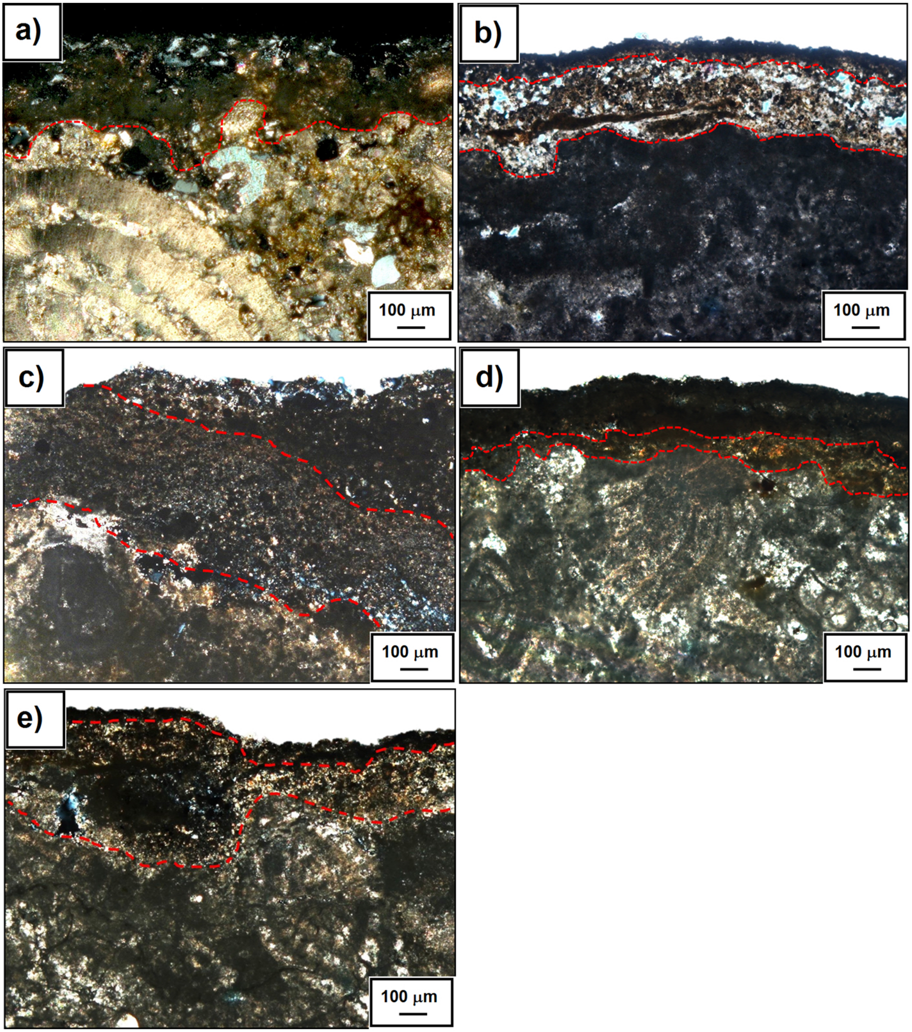


Figure 1

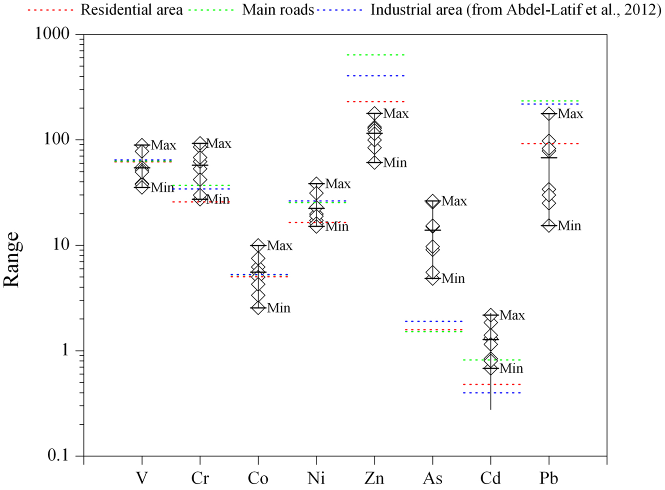
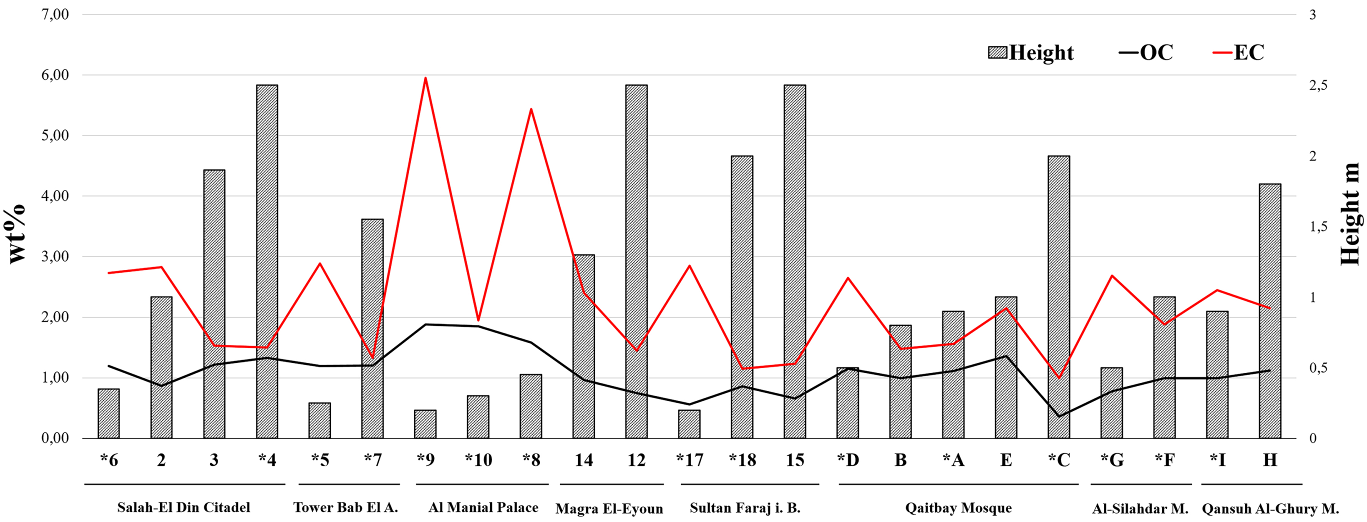

Residential area
Main roads
Industrial area (from Abdel-Latif et al., 2012)
1000
100
10
1
0.1
Range
V
Cr
Co
Ni
Zn
As
Cd
Pb
Max
Min

Figure 2



▨Height
OC
EC
wt%
Height m
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
3
2,5
2
1,5
1
0,5
0
*6
2
3
*4
*5
*7
*9
*10
*8
14
12
*17
*18
15
*D
B
*A
E
*C
*G
*F
*I
H
Salah-El Din Citadel
Tower Bab El A.
Al Manial Palace
Magra El-Eyoun
Sultan Faraj i. B.
Qaitbay Mosque
Al-Silahdar M.
Qansuh Al-Ghury M.

Figure 3

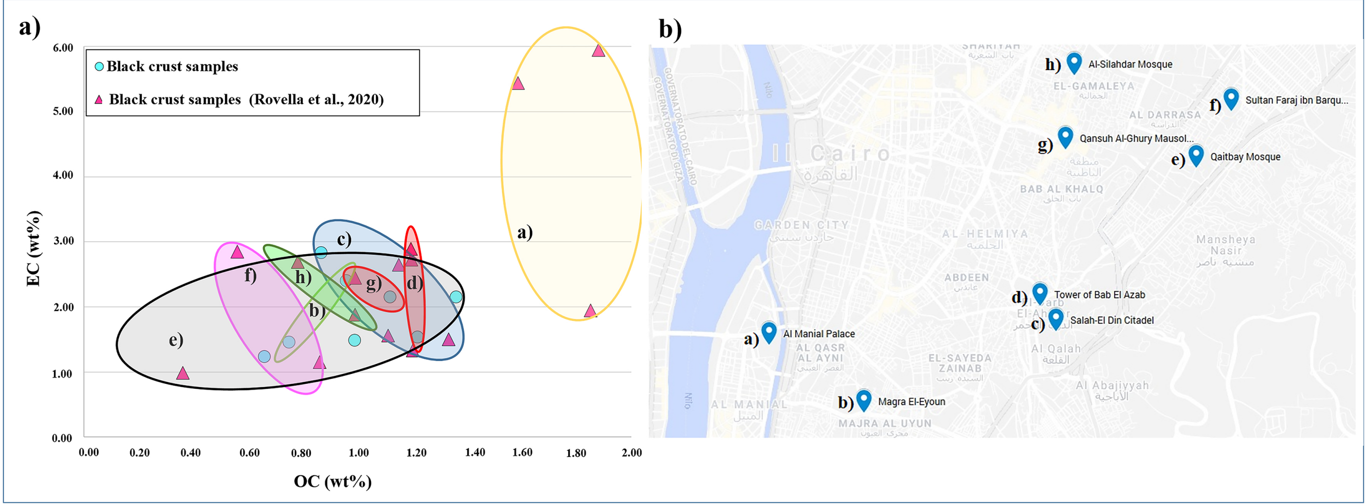

a)
Black crust samples
Black crust samples (Rovella et al., 2020)
EC (wt%)
OC (wt%)
0.00
1.00
2.00
3.00
4.00
5.00
6.00
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
2.00
a)
b)
c)
d)
e)
f)
g)
h)
b)
h) Al-Silahdar Mosque
f) Sultan Faraj ibn Barqu...
g) Qansuh Al-Ghury Mausol...
e) Qaitbay Mosque
d) Tower of Bab El Azab
c) Salah-El Din Citadel
a) Al Manial Palace
b) Magra El-Eyoun
Cairo
GARDEN CITY
AL-HELMIYA
ABDEEN
EL-GAMALEYA
AL DARRASA
BAB AL KHALQ
Mansheya Nasir
EL-SAYEDA ZAINAB
Al Qalah
Al Abajiyyah
AL QASR AL AYNI
AL MANIAL
MAJRA AL UYUN

Figure 4

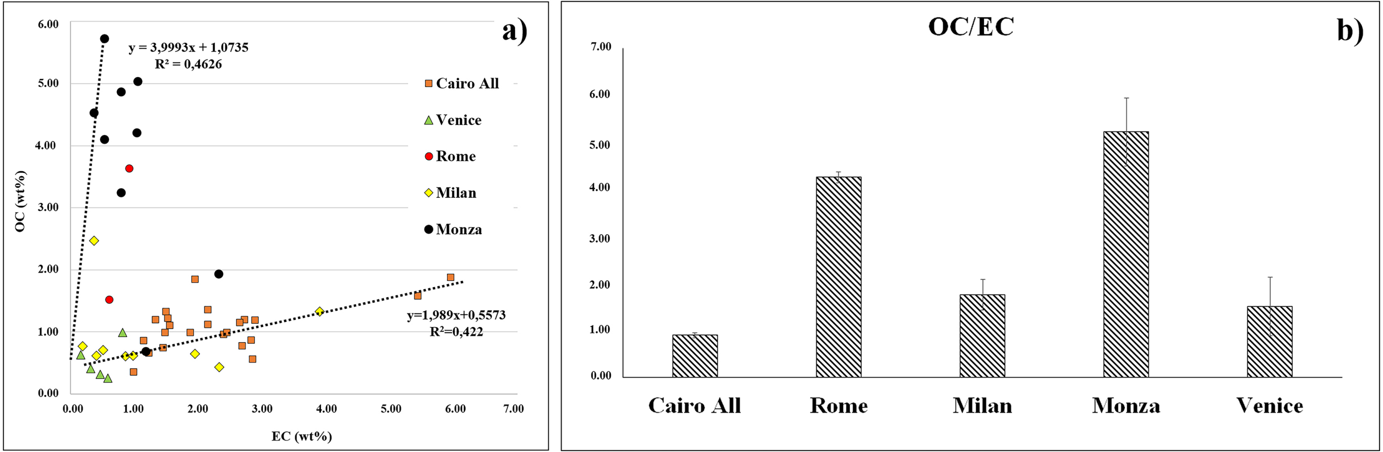

a)
OC (wt%)
EC (wt%)
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
y = 3,9993x + 1,0735
R² = 0,4626
y=1,989x+0,5573
R²=0,422
■ Cairo All
▲ Venice
● Rome
◆ Milan
● Monza
b)
OC/EC
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
Cairo All
Rome
Milan
Monza
Venice

Figure 5