Urban Climate 41 (2022) 101046

Contents lists available at ScienceDirect

Urban Climate

journal homepage: www.elsevier.com/locate/uclim

Effects of atmospheric pollutants on human health and deterioration of medieval historical architecture (North Africa, Tunisia)

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ARTICLE INFO

Keywords:
Medieval architecture
Atmospheric pollutants
Ultrafine particles
Public policy
Human health

ABSTRACT

Air pollution is a factor of concern on a global scale, accelerating the deterioration of historic medieval architecture and having harmful effects on human health. The general objective of this study is to understand the risks of atmospheric contamination that contribute to the degradation of the medieval historical heritage of (1) Bab El Bhar, (2) the Tunis Train Station and (3) the Bardo National Museum, in the City of Tunis, capital of Tunisia, located in North Africa. Sequentially, 64 samples were collected in SMPSs and 64 of dust particles in sites 1, 2 and 3, from 2015 to 2019. Field Emission Scanning Electron Microscopy (FE-SEM) was utilized together with High Resolution Transmission Electron Microscopy (HR-TEM) and the coupled with an Energy Dispersive X-ray (EDS), which allowed a better characterization and identification of NPs in images, using Energy Dispersive X-ray (EDS). The Bab El Bhar SMPS samples yielded a higher proportion of ultrafine and organic particles. Sedimented dusts showed high proportions of organometallic particles (Al, As, Ba, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Se, Si, Sn, Ti, V and Zn). The need to create public policies to protect both human health and physical historic infrastructure is noted, as this study identified dangerous elements harmful to human health in ultrafine particles, easily suspended by the wind and highly corrosive to historical buildings from the medieval period in the air of a busy metropolitan tourist site.

1. Introduction

The largest urban centers in the world have among the highest concentrations of air pollutants. These pollutants include ultra-fine particulate materials, released in most cases by both the industrial sector and in the exhaust of internal combustion motor vehicles. Both of these sources support local socioeconomic activities. The release of air pollutants in areas with greater urban density has been shown to be harmful to the health of the population (Liu et al., 2021; Oliveira et al., 2021a; Ouyang et al., 2021; Petkus et al., 2021;

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https://doi.org/10.1016/j.uclim.2021.101046
Received 27 September 2021; Received in revised form 22 November 2021; Accepted 28 November 2021
Available online 2 December 2021
2212-0955/

Zhou et al., 2021). These atmospheric contaminants vary quantitatively in cities (Ouyang et al., 2021; Petkus et al., 2021). Based on related research, the need to create public policies that can minimize their harmful impacts on the health of the population is evident (Neckel et al., 2020; Ouyang et al., 2021).

Atmospheric contamination is only aggravated by population growth as cities grow larger to accommodate additional inhabitants. According to Petkus et al. (2021), this population growth contributes to higher levels of atmospheric pollution. As cities grow, so does the associated motorized vehicular traffic, thus resulting in more pollutants being generated and released into the local atmosphere (Oliveira et al., 2021a).

Air pollution has been shown to cause several problems in regard to human health. One such issue is the hastening of cognitive aging of the population, through exposure to fine particles ($PM_{2.5}$) and nitrogen dioxide (NO_2). These releases are characteristic of gaseous pollutants pumped into the atmosphere by burning fossil fuels (Liu et al., 2020; Petkus et al., 2021).

The identification of atmospheric air quality levels in cities is of fundamental importance to assess the concentration of these pollutants and their consequences; not only for the population and public health, but also for the preservation of historic buildings located within the city limits (Gallego-Cartagena et al., 2020; Oliveira et al., 2021a). Certain historic buildings, considered World Heritage Sites by the United Nations Educational, Scientific and Cultural Organization (UNESCO), stimulate local economies, as they concentrate touristic activities, which themselves generate an increase in motorized vehicular flow (Saini et al., 2020; Brodny and Tutak, 2021; Oliveira et al., 2021a, 2021b). This increased vehicular use causes a greater release of pollutants into the atmosphere, some of which later accumulates on the surfaces and cracks of the historic buildings the tourists are traveling to view, thus accelerating the process of degradation of these buildings.

These corrosive effects caused by the accumulation of particulates from atmospheric pollution are harmful to historic buildings in that they cause a weakening of the built structure itself, due to the accumulation of nanoparticles (NPs) and ultrafine particles (UFPs) (Korkanç et al., 2019; García-Florentino et al., 2020; Rajput et al., 2020; Samara et al., 2020). Silva et al. (2020a, 2020b), Zahmatkesh et al. (2020) and Oliveira et al. (2021b), have demonstrated that hazardous elements contained within this pollution and concentrated in NPs and UFPs, in addition to affecting historic buildings, can generate risks to the health of the local population, and tourists who visit the historic sites, which boost the city's economic activities.

Howard et al. (2019), Wen et al. (2020) and Wu et al. (2021) have shown that NPs and UFPs present on the surface of historic buildings can contain hazardous elements such as: mercury (Hg), lead (Pb), cadmium (Cd) and arsenic (As). These compounds are found in different phases, organic and non-organic, and can be highly carcinogenic.

A series of studies were carried out in Tunisia's capital city, Tunis by Robe and Carbonnelle (1982) in order to identify the sources of atmospheric pollution there. Their results showed high levels of nitrogen dioxide (NO_2) and carbon dioxide (CO_2) as a result of intense vehicular traffic. Additionally, high concentrations of sulfur dioxide (SO_2) and hydrocarbons were present in the places of greatest industrial activity in the city of Tunis (Robe and Carbonnelle, 1982). Further studies focusing on the same city, carried out by Bettaieb et al. (2020) from 2005 to 2007 again found high levels of NO_2 in the local atmosphere and identified it as the main hazardous element in the atmosphere in the urban area of Tunis. According to Mraihi et al. (2015) the city of Tunis emits large amounts of gases into the atmosphere, in concentrations of SO_2 and CO_2 in the form of NPs and UFPs, due to road traffic concentrated in the urban center. Additionally, high levels of elements hazardous to human health, such as: chromium (Cr), cobalt (Co), zinc (Zn) and lead (Pb) have been found in the Tunis industrial area, followed by the excessive presence of calcium carbonate ($CaCO_3$) derived from cement production (Bayouli et al., 2021).

Barhoumi et al. (2020) conducted a similar study focusing on the coastal Tunisian city of Bizerte. Atmospheric particles (APs) were monitored over a period of one year. Hazardous elements were found in the analyzed APs. Both mercury (Hg) and hazardous elements of organic origin including the presence of 40% dioxin in atmospheric APs. This dioxin was derived from elements such as organochlorine pesticides (OCPs) and organic nitrogen (ON) released by agricultural activities. These emissions then combined with polycyclic aromatic hydrocarbons (PAHs) and organic carbon (OC) released to the atmosphere by motor vehicles. Furthermore, high levels of polychlorinated biphenyls (PCBs) were found as a result of industrial activity (Barhoumi et al., 2020).

This current study is justified as there is no record of the assessment of air pollution levels aimed at the influences on the degradation of UNESCO listed historic structures in the city of Tunis. Effective identification of atmospheric pollutants deposited on the surface of historic buildings have been shown to encourage the formation of public policies with measures aimed at immediate actions for the restoration and preservation of the cultural heritage sites (Morillas et al., 2020; Oliveira et al., 2021a, 2021b).

The city of Tunis in unique in that it is the focus of a collection of scientific studies on air quality (which include PM_{10}, $PM_{2.5}$, PM_1 and nanoparticles). The atmosphere of the city itself is directly influenced by the Mediterranean Sea, North Africa and parts of Europe (Azri et al., 2009; Ellouz et al., 2013; Schembari et al., 2014; Oliveira et al., 2021a). Thus, the risks of atmospheric contamination that contribute to the degradation of the medieval historical heritage of the (1) Bab El Bhar, (2) Tunis Train Station and the (3) Bardo National Museum, in the city of Tunis are wide and varied. This study is of great importance for the preservation of the UNESCO world heritage sites and medieval historic buildings in the city of Tunis.

2. Material and methods

2.1. Study area

The District of Tunis, consists of the metropolitan area composed of Tunis, Ariana and Bem Arous, located in North Africa, comprising approximately 2.2 million inhabitants. It is characterized as the political and economic center of Tunisia, with a national population of 11,950,477 inhabitants (Larbi and Leitmann, 1994; Tunisia Population, 2021). The city of Tunis (Fig. 1) has an estimated

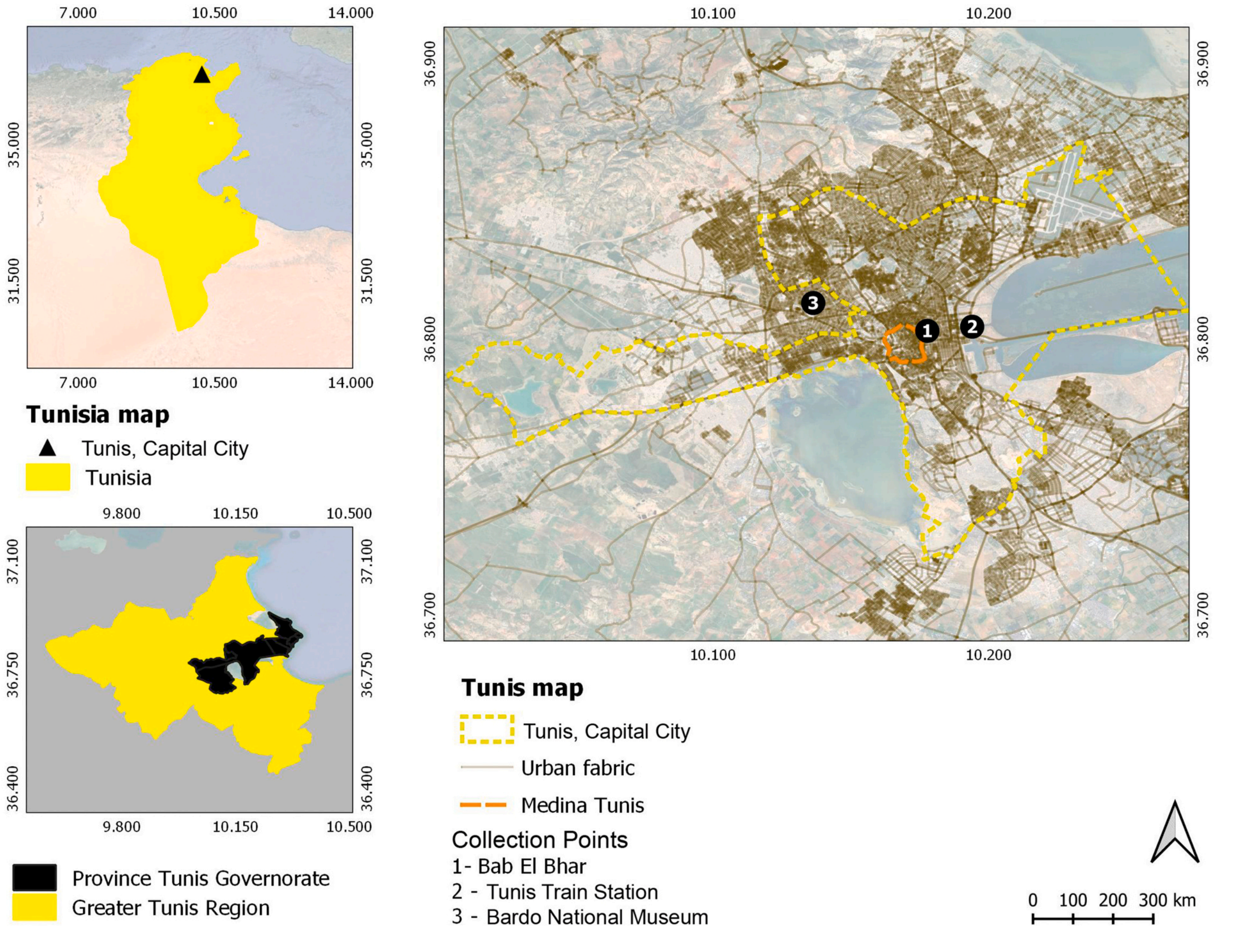

Fig. 1. Location of the Tunisia region, Capital Tunis in North Africa. Source: Adapted from Tunisia Population (2021).

2021population of 693,210 (Tunisia Population, 2021).

Prior to the COVID-19 pandemic, Tunisia welcomed 9 million tourists in 2019. Tourism was concentrated mainly around the architectural buildings that make up the medieval city of Tunis, which arose and grew under ancient Ottoman reign during the 16th and 17th centuries, by Berberes, known as the first inhabitants of the Tunisian region (Findlay and Paddison, 1986; Saidi et al., 2021; Salyer et al., 2021; Tunisia Population, 2021). The medieval city of Tunis had its walls demolished in 1860 under French occupation (Findlay and Paddison, 1986), however; alleyways and historic structures from the medieval city remain and were declared a UNESCO World Heritage Site in 1979 (Mahroug and Belakehal, 2016).

The total urbanized area of the city of Tunis increased from an initial 40 km^2 in 1956, to 105 km^2 in 1975, to approximately 200 km^2 in the 1990s. This expansion transformed Tunis from a colonial city to a large metropolis connected with the financial flows of international capitalism (Stambouli, 1996). The northern region, where the capital Tunis is located, is characterized by a very heterogeneous relief composed of the Medjerda river plain and the Kroumirie mountains (Feki et al., 2016). The northern region has a Mediterranean climate with a humid atmosphere, in which the climate is characterized as humid temperate, with cumulative average annual precipitation ranging from 400 mm to 1500 mm (Feki et al., 2016; Azzolin et al., 2021; Nizar et al., 2021).

The economic growth of the Tunis metropolitan region has brought about congestion and the consequent environmental problems related to transport and its related CO_2 emissions (Euchi and Kallel, 2021). To understand the risks of atmospheric contamination to the world heritage sites located in the city of Tunis, three historic buildings listed as UNESCO World Heritage Sites were evaluated. Each site receives a high number of tourists annually. The three sites chosen were: 1) Bab El Bhar in the city center; 2) the Tunis Train Station also in the central area; and 3) the Bardo National Museum (Fig. 1) which, despite being in the metropolitan region, does not have the same incidence of vehicular traffic or trains circulating in the nearby area as sites 1 and 2. According to Morillas et al. (2020) and Oliveira et al. (2021a, 2021b) studies involving historic buildings in relation to the consequences of air pollution should be evaluated and monitored in places with intense movement of people, thus aiming to understand the real modality of the health of the local population and tourists who visit these medieval buildings.

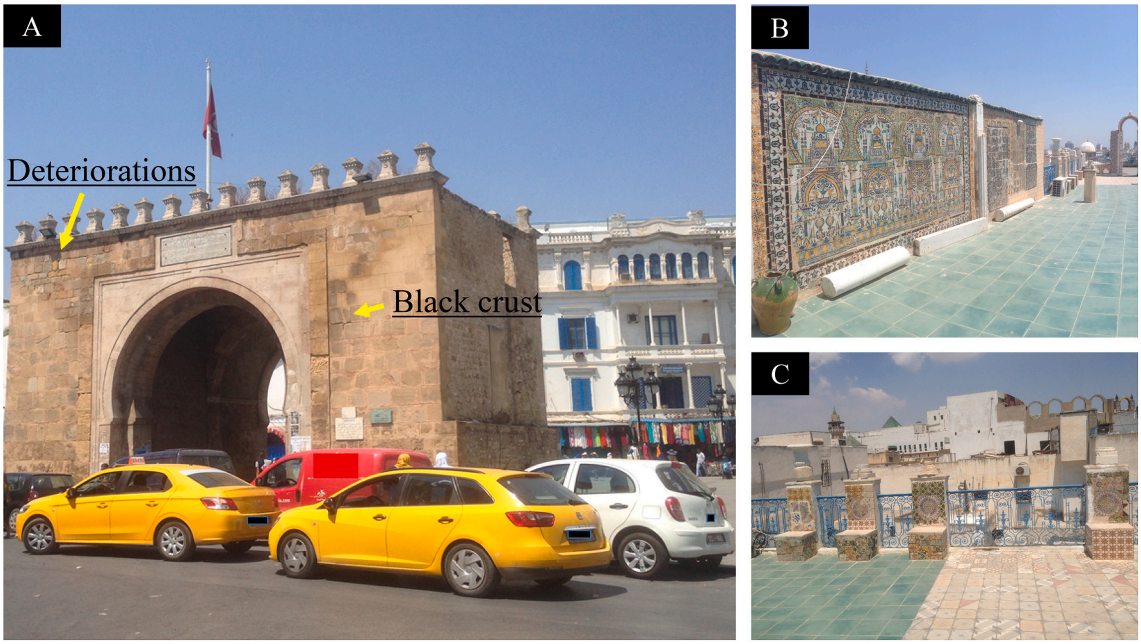

Fig. 2. Representation of the vehicular traffic of old buses and cars around the medieval building of Bab El Bhar (A), with the representation of the roof of the building of Bab El Bhar and its medieval tiles (B and C).

Fig. 3. Tunis train station – (A) train platform, (B and C) PVC coating at the station.

2.2. Analysis methodology in relation to collected points (1, 2 and 3)

The three points analyzed in the city of Tunis consist of (1) Bab El Bhar, (2) the Tunis Train Station and (3) the Bardo National Museum. The Bab El Bhar collection point was the site with the greatest vehicular traffic of old motorized buses and cars of the three sites sampled, highlighted in Fig. 2 A). The use of diesel cars and buses more than 3 decades old is common in the city of Tunis. This helps to understand why Bab El Bhar was the study area with the highest amount of organic particles detected, despite the large amount of minerals such as quartz and some clays being abundant in this medieval Bab El Bhar building. The roof of Bab El Bhar is

Fig. 4. Entrance door to the Bardo National Museum.

Fig. 5. Attemtped terrorist act on a work of art in the Bardo National Museum.

composed of preserved medieval tiles, over which high numbers of tourists and local residents regularly traverse (Fig. 2 B and C). Thus, our sampling analyzed only loose particles, which were detached from the historic building of Bab El Bhar, thus avoiding further degradation of this historic building. Also, as it is a concentration point of people, favoring the relationship of human exposure in relation to ultrafine particles obtained for the analysis performed (Morillas et al., 2020; Oliveira et al., 2021a, 2021b).

The Tunis Railway Station allows for relatively little air circulation, although the population has free access and can come and go as they please. It is largely constructed from concrete, with a PVC cover. (Fig. 3 (A, B and C)). It is precisely due to this PVC that the degradation that may exist in the structure of the station is not noticed. The vast majority of tourists and local residents use the metro to travel to other urban centers and beaches, such as: Sidi Bou Said, where more metallic particles were detected. Furthermore, the poor condition of the trains is notable, which likely justifies the high proportions of metallic particles derived from the wear of the trains' brakes, in addition to the rails. Lima et al. (2021) highlights that a train station potentiates high harm to human health, by negatively influencing air quality. The collection of particulate materials followed the standards established by Lima et al. (2021), with the use of self-made passive samplers (SMPSs), for collections on the embarkation platform, at a level of 185.6 to 170.7 cm above the ground, which is the average height of the Tunis population that would be directly in contact with these suspended particulates. Sampling was also carried out inside the trains, which move with closed windows. Climate is controlled by mechanical ventilation systems and air conditioning with ambient humidity.

The collection of road dust samples at the Bardo National Museum in the city of Tunis was conducted at the entrance to the museum (Fig. 4). However, the passive fixed sampler was not located at the same site but instead kept at the Le Relais cafe, due to the difficulty of obtaining authorization from the museum to fix the sampler at a height of 185.6 to 170.7 cm high from the floor, in order to sample the air located at the average human height of the resident population. Note that the Arab world was more careful with their mosaics

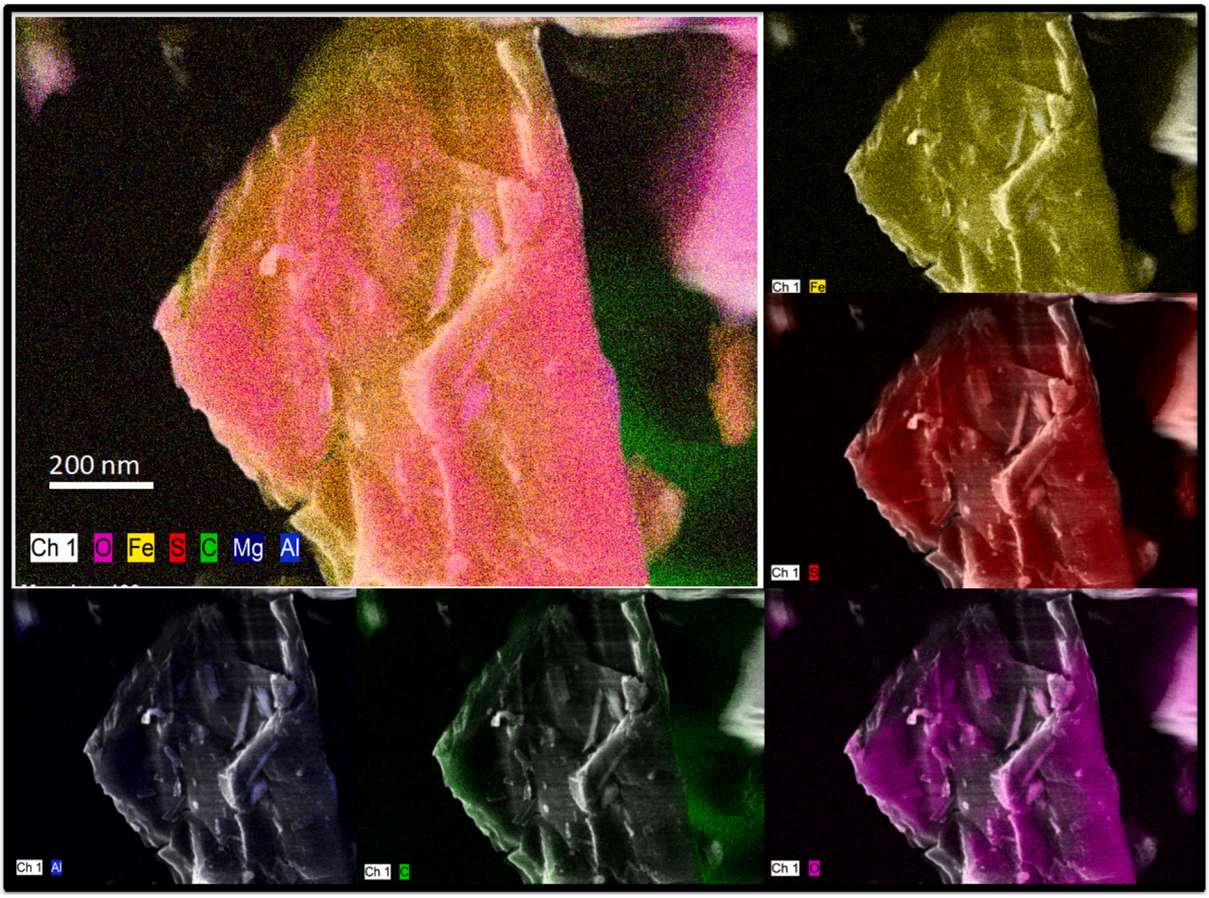

Fig. 6. The mapping of an ultra-fine quartz particle containing several chemical elements present in Bab El Bhar clays.

from the medieval period as the most important objects were displayed in museums and not in the open air. Unlike some Italian historic monuments and mosaics exposed to weathering and pollution for decades, degrading much of the legacy left to them by the Romans (Oliveira et al., 2020). Arab culture cultivated the preservation of historical sites better than the current Romans themselves, as even the monuments in Rome are being degraded by rain, earthquakes and atmospheric contamination (Oliveira et al., 2021a). However, several works were impacted in the Bardo National Museum by terrorist attacks at different times, such as in 2015, when sampling for this project commenced. Even though it is not a result of environmental contamination, Fig. 5 illustrates a terrorist shot that was fired at one of the objects on display at the National Bardo Museum.

A total of 64 samples were collected using self-made passive samplers (SMPSs) in addition to 64 samples of sedimented dust particles in sites 1, 2 and 3, at intervals of every 3 months, over the course of four years, from 2015 to 2019. Sampling methodology was carried out according to Oliveira et al. (2021a) and Trejos et al. (2021). The collected material was stored in a sterilized glass test tube to avoid changes in the results of the samples, which were transported in a sealed Styrofoam box for laboratory analysis, which allowed for greater reliability of the results of this study (Oliveira et al., 2021a, 2021b; Trejos et al., 2021). The laboratory analyses used electron microscopy to understand the type of morphology of the collected material, determining the chemical composition of the elements collected at Bab El Bhar, the Tunis Train Station and the Bardo National Museum, together with the identification of UFPs and NPs. Particles of 0.1 and 10 μm were considered in the analysis, using FE-SEM and HR-TEM (Oliveira et al., 2021a, 2021b). This allowed us to analyze the NPs at 100 nm, applying the technique of high-resolution imaging of the type of structure of the elements analyzed, consisting of the most modern method of representing NPs by images on a world scale (Ernould et al., 2020; Silva et al., 2021). Obtaining the identification of the elements analyzed in the NPs was used through the analysis technique of Hodoroaba (2020), Oliveira et al. (2021a, 2021b) and Silva et al. (2021), using the Energy Dispersive X-ray (EDS) of microanalysis system, applied to samples collected at Bab El Bhar, train station and Bardo National Museum. It is worth noting that the road dust sampling material obtained all the correct procedures that avoided altering the NPs with external particles present in the environment, when the materials from the collected samples were sedimented (Amato et al., 2009; Silva et al., 2021).

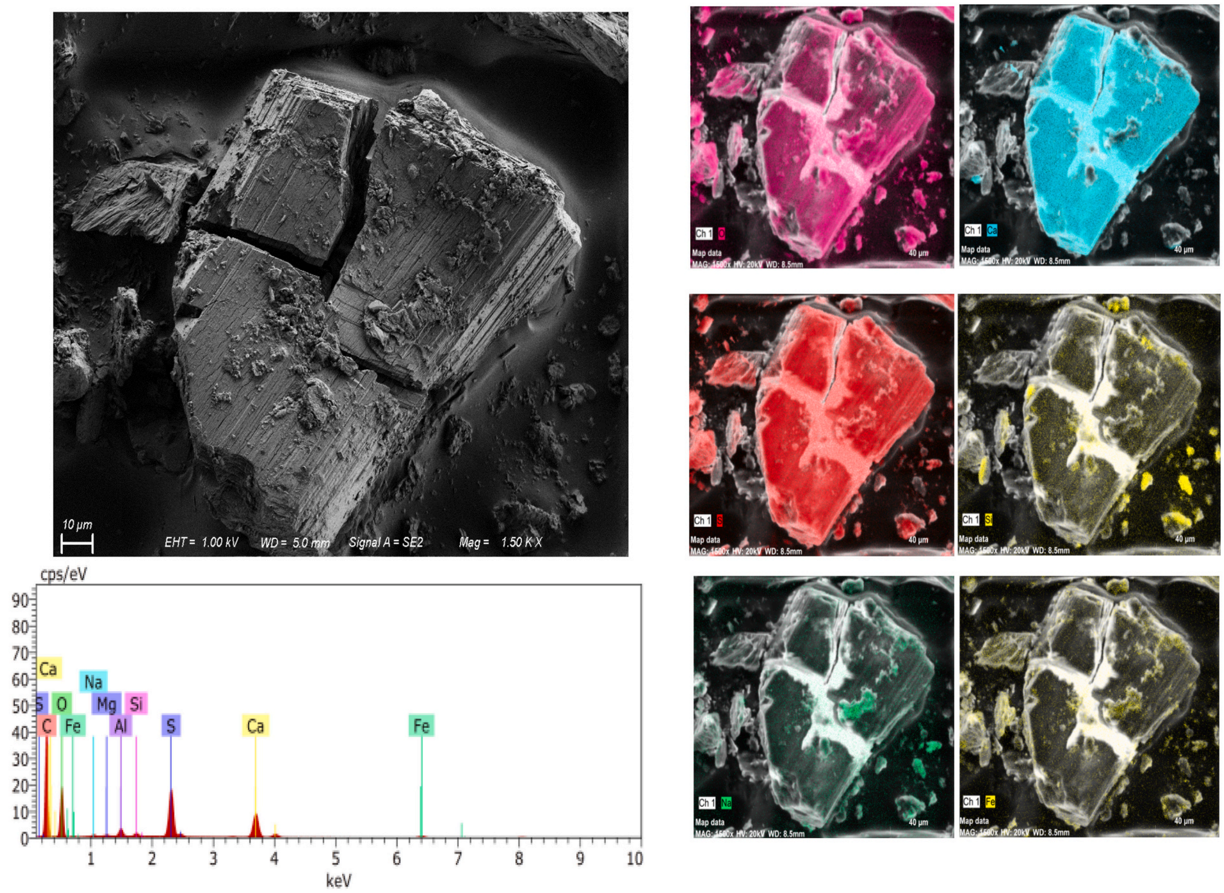

Fig. 7. Occurrence of amorphous phases embedded in plaster was detected at Bab El Bhar.

3. Results and discussion

3.1. Samples taken at Bab El Bhar, the Tunis Train Station and the Bardo National Museum

The Bab El Bhar samples yielded a greater proportion of organic particles when compared to the Tunis Train Station and the Bardo National Museum. Alves et al. (2021) and Gelhardt et al. (2021) highlight the high proportions of organic particles (PM_{10}) in ultrafine particles, which originate from the release of carbon and total solvents released into the atmosphere. These ultrafine particles released into the atmosphere accumulate on the surface of buildings, accelerating the degradation process (Oliveira et al., 2021a, 2021b; Silva et al., 2021).

The analyses carried out at Bab El Bhar revealed an abundance of quartz and some clays, especially in road dust and in the SMPS sampler. This is due to the strong winds that suspend many particles from the soil, causing them to remain suspended in the atmosphere and carrying a large quantity of sediments into the urban area of Tunis. Fig. 6 demonstrates the illustration of the mapping of an ultrafine quartz particle containing several chemical elements present in clays. Also, the presence of iron (Fe) and magnesium (Mg) particles can be noted. According to Gogoi et al. (2019), Morillas et al. (2019) and Neckel et al. (2021) excess Fe contamination in humans can cause impairment of the gastrointestinal tract, cirrhosis of the liver, various cancers, Alzheimer's Disease, and cardiovascular arrhythmia. Mg is an element that is extremely corrosive to historic buildings, as it is a key component of ester solvents and carbonates emitted in ultrafine particles into the atmosphere as a result of vehicular and industrial sector emissions, which are only intensifying on a world scale (Morillas et al., 2019; Palisoc et al., 2021; Prasad et al., 2021; Zhang et al., 2021).

The Bab El Bhar road dust also contained minerals present in the soil. The occurrence of sulfur in mapping coincides with the occurrence of carbon, therefore showing that there are also organic particles associated with ultrafine quartz (Fig. 6). Another mineral widely detected at Bab El Bhar was gypsum. This mineral is derived especially from the normal wear of interior walls, in addition to accelerated wear due to the presence of organic acids from vehicular traffic, which accumulate on concrete that contains calcium oxide (CaO). This last statement is due to the fact that in all gypsum particles the occurrence of amorphous phases embedded in the gypsum was also detected, indicating that they are part of the same formation process. Thus, it is possible to affirm that this process is having an impact on the degradation of the buildings present in Bab El Bhar (Fig. 7). A study on fiber particles in China by Li et al. (2020), found that 80% of ultrafine particles have a length of less than 20 µm, which allows them to re-suspend in air and combine with other

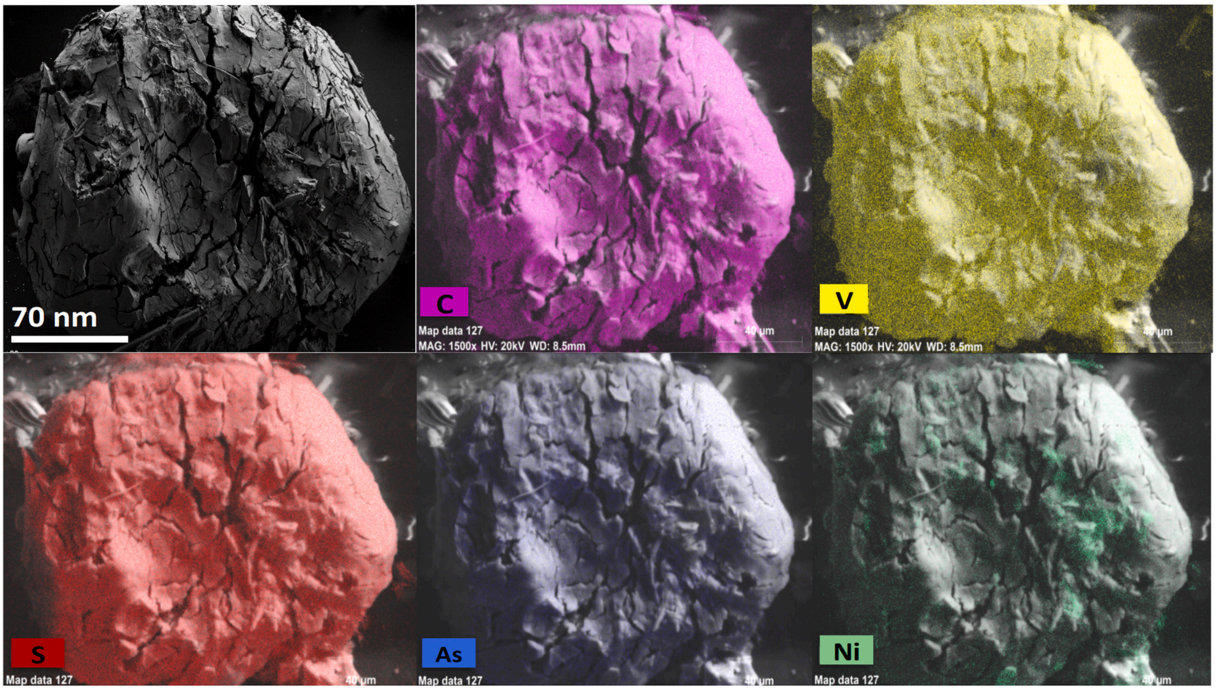

Fig. 8. Hazardous elements detected in Bab El Bhar, such as: arsenic (As), vanadium (V) and nickel (Ni).

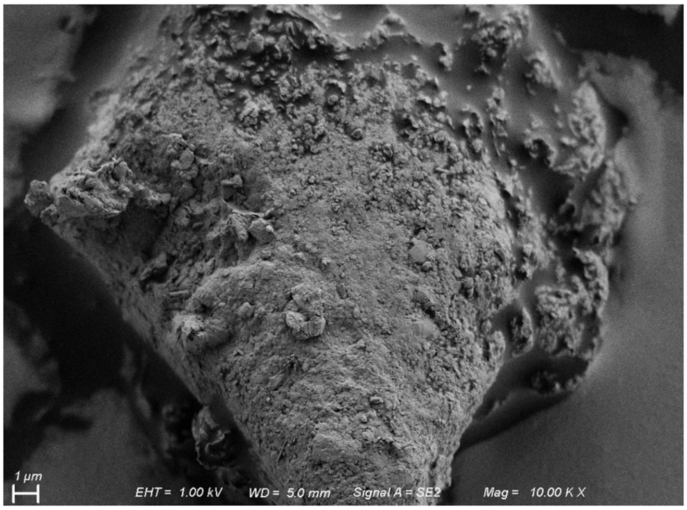

Fig. 9. Hazardous elements identified at the train station in the city of Tunis, such as: Cr, Zn, As, Pb, Se, among others.

particles of greater density.

The most dangerous elements were found among the organic nanoparticles detected at Bab El Bhar. Arsenic (As), vanadium (V) and nickel (Ni) were detected along with sulfur (S) and carbon (C). Only 35% of the NPs detected contained more than 1 dangerous element in their structure. The occurrence of Ni and V is directly associated with the combustion of petroleum derivatives, so it is very likely that it is derived from the exhaust of diesel buses and cars that pass in the vicinity of Bab El Bhar (Fig. 8). Neckel et al. (2021) emphasize that Ni contamination in humans can lead to various cancers. Vanadium is formed by corrosive gases, which, in addition to more easily degrading the historical sites under study, contributes to harmful effects on the population's health. These effects include coughing up mucus and irritation in the pulmonary bronchi (Silva et al., 2021; Wang et al., 2021).

As reported by Lima et al. (2021) in a study of trains in the city of Porto Alegre, Brazil train stations can contain high proportions of ultra-fine and nanometric particles. We found this to be the case in the Train Station samples in the SMP sampler. The main reason for the abundance of such metallic particles is the wear of the brakes and rails of the railway system (Lima et al., 2021). Visual inspection

Table 1
Main hazardous elements detected in nanoparticles in the sampled areas.

Studied Area	Principal Hazardous Elements	Dimensional characteristics	
		Diameter (nm)	Length (μm)
Bab El Bhar (Fig. 6 e 7)	Al, As, Ca, C, Cr, Fe, Mg, Na, Ni, O, Pb, S, Si, Se, V, Zn	63 ± 3	200 ± 8
Tunis Train Station	Al, As, Ba, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Se, Si, Sn, Ti, V, Zn	92 ± 4	200 ± 8
Bardo National Museum	Al, K, Mg, Na, Ni, Si, P, V	73 ± 2	200 ± 8

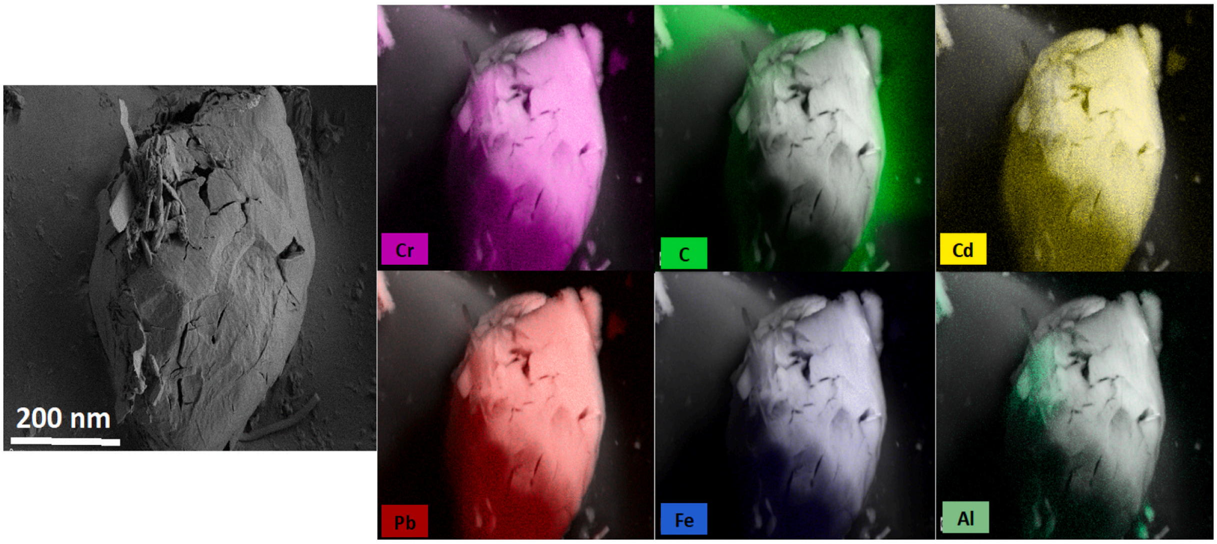

Fig. 10. Toxic elements of Cd, Pb and Cr and not-so-concerning elements (Al, Si, and Fe) identified at the train station in the city of Tunis.

Fig. 11. Spherical organic particles with sizes of approximately 1 μm were detected in this area of the Bardo National Museum in Tunis.

by the sampling team determined that maintenance is clearly rare in this part of the city of Tunis. Of the samples, 128 angular particles were found in road dust and 205 angular particles in SMPS samples. In both collection procedures, the particles contained amorphous manometric materials agglomerated on them. The chemical composition of such agglomerates was extremely diverse, however they always contained dangerous elements, such as: Cr, Zn, As, Pb, Se, among others (Fig. 9) (Table 1).

At the train station in the city of Tunis, about 95% of particles smaller than 500 nm were amorphous. Most of the time they contained both toxic elements (Cd, Pb and Cr) and non-toxic elements (Al, Si, and Fe) (Table 1). This supports the conclusion that the formation of such particles is part of a complex system of interaction between elements derived from the wear of the train tracks and

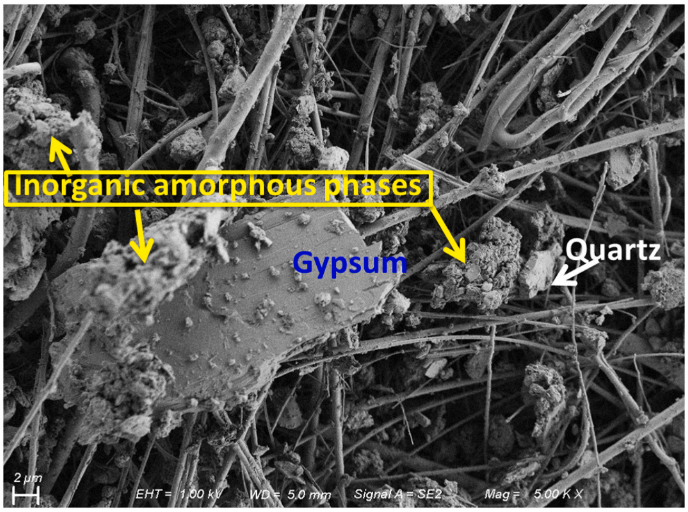

Fig. 12. Main minerals detected in filters obtained from road dust (gypsum, quartz, and some clays) at the Bardo National Museum in Tunis.

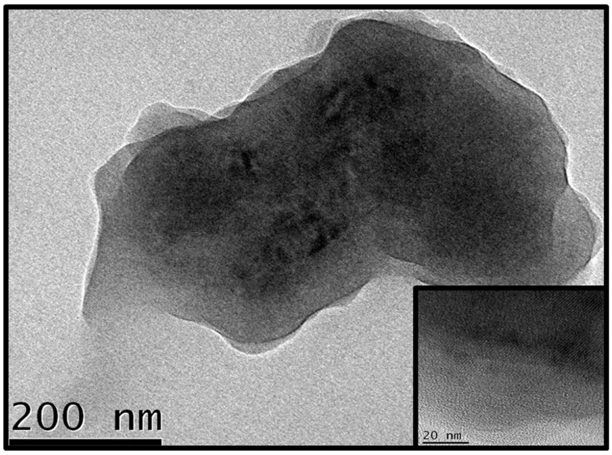

Fig. 13. Presence of amorphous ultrafine particles, containing defined structures of graphenes and fullerenes.

brakes, and is suspended in ultra-fine particles in the train station (Fig. 10).

As described in the Materials and Methods section, the road dust was obtained in front of the main entrance to the Bardo National Museum whereas the SMPS was located in the restaurant attached to an external annex to the Bardo National Museum. With this it was possible to evaluate the sedimented particles, as well as the particles that are found in the surroundings of the museum. Although the Bab El Bhar has greater vehicular traffic, with buses and old diesel cars, only in the area analyzed at the Bardo National Museum were spherical organic particles reported. A possible explanation for this may be that in the Bardo National Museum area there was a greater intensity of winds that may have facilitated the concentration of said particles, so that despite the high proportion of minerals and angular inorganic phases, the formation of carbonaceous spheres was easier due to the difference between the densities of such spheres and minerals (Korkanç et al., 2019; Morillas et al., 2019; Hatđr, 2020; Oliveira et al., 2021a, 2021b; Silva et al., 2021; Zhou et al., 2021).

Many spherical organic particles with sizes of approximately 1 μm were detected in this area of the Bardo National Museum (Fig. 11). It is supposed that the main source of these dangerous elements in the analyzed area of the National Museum of Bardo is the vehicular traffic that generates considerable soot around the museum. After all, elements such as Ni and V that typically derive from the combustion of petroleum derivatives were also detected. Similar microspheres were also detected in road dust in abundance at the Bardo National Museum. These main minerals detected in filters obtained from road dust were gypsum, quartz, and some clays in the area of the Bardo National Museum (Fig. 12). In addition to these inorganic phases, numerous amorphous agglomerations of Al, Si, K, Mg, Na, and P were also detected in the analysis area of the Bardo National Museum (Table 1). Such phases could be deposited on the minerals, or in an isolated way (Fig. 12). Presenting a relationship similar to the studies by Morillas et al. (2019), Oliveira et al. (2021a, 2021b) and Silva et al. (2021), where the largest particles were deposited on minerals and the smaller ones were isolated without contact with minerals.

As many soot particles internally mixed with hazardous elements deposited on road dust filters could not be properly analyzed by FE-SEM, due to their small sizes, it was necessary to use HR-TEM for ultra-fine particles, so that via HR-TEM images reveal lattice fringes (Liu et al., 2017). With this it was possible to detect ultrafine amorphous particles, containing defined structures of graphenes and fullerenes (Fig. 13). Bearing in mind that the better the analyzed particles, the harder they are to be detected, therefore, the use of HR-TEM for ultrafine particles is the most efficient technique for the detection and identification of ultrafine particles on a world scale (Liu et al., 2017; Morillas et al., 2019; Hatđr, 2020; Oliveira et al., 2021a, 2021b; Silva et al., 2021).

4. Conclusion

Although there is regular vehicular traffic in all three study areas of this study, Bab El Bhar, the Tunis Train Station and the Bardo National Museum, not all MSPS samples had a high proportion of organic particles in all size fractions analyzed. The area analyzed at Bab El Bhar was the one with the highest proportion of ultra-fine particles and organic nanometrics, capable of accelerating the corrosion process of this medieval historical building. To mitigate this impact caused by pollution levels, the authors suggest implementing a public policy that prevents the circulation of motor vehicles in this central area of the city. This would contribute to improving the human health of the local residential population and would also ensure better preservation of the area's cultural heritage. The ultra-fine particles detected in this study, which are easily suspended by the wind, are also extremely corrosive to these historical buildings from the medieval period.

Lastly, larger ventilation openings are recommended for the train station, enhancing better air circulation. This would avoid possible risks of contamination by dangerous elements for passengers and tourists, especially for those who depend on the train on a daily basis.

Credit author statement

Luis F.O. Silva and Marcos L. S. Oliveira: Conceptualization, Funding acquisition.
Alcindo Neckel, Celene B. Milanes and Brian W. Bodah: final manuscript writing.
Laércio Stolfo Maculan, Laura P. Cambrussi and Guilherme L. Dotto: review & editing.

Declaration of Competing Interest

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.

Acknowledgements

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication. We also wish to thank the Center for Studies and Research on Urban Mobility (NEPMOUR/IMED). National Council for Scientific and Technological Development (CNPq), Brazil.

References

Alves, C., Evtyugina, M., Vicente, A., Conca, E., Amato, F., 2021. Organic profiles of brake wear particles. Atmos. Res. 255, 105557 https://doi.org/10.1016/j.atmosres.2021.105557.

Amato, F., Pandolfi, M., Viana, M., Querol, X., Alastuey, A., Moreno, T., 2009. Spatial and chemical patterns of PM_{10} in road dust deposited in urban environment. Atmos. Envirom. 43 (9), 1650–1659. https://doi.org/10.1016/j.atmosenv.2008.12.009.

Azri, C., Mabrouk, C., Medhioub, K., 2009. Diurnal evolutions of nitrogen oxides (NOx), ozone (O_3), and PM_{10} particles at a busy traffic cross-road in the city of Tunis. Environ. Prog. Sustain. Energy 28 (1), 143–154. https://doi.org/10.1002/ep.10315.

Azzolin, M., Cattelan, G., Dugaria, S., Minetto, S., Calabrese, L., Col, D.D., 2021. Integrated CO_2 systems for supermarkets: field measurements and assessment for alternative solutions in hot climate. Appl. Therm. Eng. 187, 116560 https://doi.org/10.1016/j.applthermaleng.2021.116560.

Barhoumi, B., Tedetti, M., Heimbürger-Boavida, L.E., Onrubia, J.A.T., Dufour, A., Doan, Q.T., Boutaleb, S., Touil, S., Scippo, M.L., 2020. Chemical composition and in vitro aryl hydrocarbon receptor-mediated activity of atmospheric particulate matter at an urban, agricultural and industrial site in North Africa (Bizerte, Tunisia). Chemosphere 258, 127312. https://doi.org/10.1016/j.chemosphere.2020.127312.

Bayouli, I.T., Bayouli, H.T., Dell'oca, A., Meers, E., Sun, J., 2021. Ecological indicators and bioindicator plant species for biomonitoring industrial pollution: eco-based environmental assessment. Ecol. Indic. 125, 107508 https://doi.org/10.1016/j.ecolind.2021.107508.

Bettaieb, J., Toumi, A., Leffondre, K., Chlif, S., Salah, A.B., 2020. High temperature effect on daily all-cause mortality in Tunis 2005–2007. Rev. Epidemiol. Sante Publique 68 (1), 37–43. https://doi.org/10.1016/j.respe.2019.09.007.

Brodny, J., Tutak, M., 2021. The analysis of similarities between the European Union countries in terms of the level and structure of the emissions of selected gases and air pollutants into the atmosphere. J. Clean. Prod. 279, 123641 https://doi.org/10.1016/j.jclepro.2020.123641.

Ellouz, F., Masmoudi, M., Medhioub, K., 2013. Study of the atmospheric turbidity over northern Tunisia. Renew. Energy 51, 513–517. https://doi.org/10.1016/j.renene.2008.04.035.

Ernould, C., Beausir, B., Fundenberger, J.J., Taupin, V., Bouzy, E., 2020. Characterization at high spatial and angular resolutions of deformed nanostructures by on-axis HR-TKD. Scr. Mater. 185, 30–35. https://doi.org/10.1016/j.scriptamat.2020.04.005.

Euchi, J., Kallel, A., 2021. Internalization of external congestion and CO_2 emissions costs related to road transport: the case of Tunisia. Renew. Sust. Energ. Rev. 142, 110858 https://doi.org/10.1016/j.rser.2021.110858.

Feki, H., Slimani, M., Cudennec, C., 2016. Geostatistically based optimization of a rainfall monitoring network extension: case of the climatically heterogeneous Tunisia. Hydrol. Res. 48 (2), 514–541. https://doi.org/10.2166/nh.2016.256.

Findlay, A.M., Paddison, R., 1986. Planning the Arab city: the cases of Tunis and Rabat. Prog. Plan. 26, 1–82. https://doi.org/10.1016/0305-9006(86)90006-1.

Gallego-Cartagena, E., Morillas, H., Maguregui, M., Patiño-Camelo, K., Marcaida, I., Morgado-Gamero, W., Silva, L.F.O., Madariaga, J.M., 2020. A comprehensive study of biofilms growing on the built heritage of a Caribbean industrial city in correlation with construction materials. Int. Biodeterior. Biodegradation 147, 104874. https://doi.org/10.1016/j.ibiod.2019.104874.

García-Florentino, C., Maguregui, M., Carrero, J.A., Morillas, H., Arana, G., Madariaga, J.M., 2020. Development of a cost effective passive sampler to quantify the particulate matter depositions on building materials over time. J. Clean. Prod. 268, 122134 https://doi.org/10.1016/j.jclepro.2020.122134.

Gelhardt, L., Dittmer, U., Welker, A., 2021. Relationship of particle density and organic content in sieve fractions of road-deposited sediments from varying traffic sites based on a novel data set. Sci. Total Environ. 794, 148812 https://doi.org/10.1016/j.scitotenv.2021.148812.

Gogoi, M., Boruah, P., Sengupta, P., Saikia, L., 2019. Separation of ultrafine chalcogenide particles using Fe_3O_4 magnetic nanoparticles and ligands with metal selectivity. Miner. Eng. 137, 147–156. https://doi.org/10.1016/j.mineng.2019.04.004.

Hatđr, M.E., 2020. Determining the weathering classification of stone cultural heritage via the analytic hierarchy process and fuzzy inference system. J. Cult. Herit. 44, 120–134. https://doi.org/10.1016/j.culher.2020.02.011.

Hodoroaba, V.D., 2020. Energy-dispersive X-ray spectroscopy (EDS). Characteriz. Nanopart. 397-417 https://doi.org/10.1016/b978-0-12-814182-3.00021-3.

Howard, J., Weyhrauch, J., Loriaux, G., Schultz, B., Baskaran, M., 2019. Contributions of artifactual materials to the toxicity of anthropogenic soils and street dusts in a highly urbanized terrain. Environ. Pollut. 255, 113350 https://doi.org/10.1016/j.envpol.2019.113350.

Korkanç, M., Hüseyinca, M.Y., Hatđr, M.E., Tosunlar, M.B., Bozdağ, A., Özen, L., İnce, İ., 2019. Interpreting sulfated crusts on natural building stones using sulfur contour maps and infrared thermography. Environ. Earth Sci. 78 (13), 1–14. https://doi.org/10.1007/s12665-019-8377-y.

Larbi, H., Leitmann, J., 1994. Tunis. Cities 11 (5), 292–296. https://doi.org/10.1016/0264-2751(94)90081-7.

Li, Y., Shao, L., Wang, W., Zhang, M., Feng, X., Li, W., Zhang, D., 2020. Airborne fiber particles: types, size and concentration observed in Beijing. Sci. Total Environ. 705, 135967 https://doi.org/10.1016/j.scitotenv.2019.135967.

Lima, B.D., Teixeira, E.C., Hower, J.C., Civeira, M.S., Ramírez, O., Yang, C.X., Oliveira, M.L.S., Silva, L.F.O., 2021. Metal-enriched nanoparticles and black carbon: a perspective from the Brazil railway system air pollution. Geosci. Front. 12 (3), 101129 https://doi.org/10.1016/j.gsf.2020.12.010.

Liu, L., Kong, S., Zhang, Y., Wang, Y., Xu, L., Yan, Q., Lingaswamy, A.P., Shi, Z., Lv, S., Niu, H., 2017. Morphology, composition, and mixing state of primary particles from combustion sources - crop residue, wood, and solid waste. Sci. Rep. 7 (1), 1–15. https://doi.org/10.1038/s41598-017-05357-2.

Liu, H., Yin, S., Chen, C., Duan, Z., 2020. Data multi-scale decomposition strategies for air pollution forecasting: a comprehensive review. J. Clean. Prod. 277, 124023 https://doi.org/10.1016/j.jclepro.2020.124023.

Liu, G., Xia, X., Zhao, C., Zhang, X., Zhang, W., 2021. Ultrafine Ni nanoparticles anchored on carbon nanofibers as highly efficient bifunctional air electrodes for flexible solid-state zinc-air batteries. J. Colloid Interface Sci. 588, 627–636. https://doi.org/10.1016/j.jcis.2020.11.053.

Mahroug, E., Belakehal, A., 2016. The evolution of heritage atmospheres in the medina of Tunis since the 19th century. In: *Islamic Heritage Architecture And Art* 159. WIT Press, pp. 161–169. https://doi.org/10.2495/iha160141.

Morillas, H., Marcaida, I., Maguregui, M., Upasen, S., Gallego-Cartagena, E., Madariaga, J.M., 2019. Identification of metals and metalloids as hazardous elements in $PM_{2.5}$ and PM_{10} collected in a coastal environment affected by diffuse contamination. J. Clean. Prod. 226, 369–378. https://doi.org/10.1016/j.jclepro.2019.04.063.

Morillas, H., de Mendonça, F.F.F., Derluyn, H., Maguregui, M., Grégoire, D., Madariaga, J.M., 2020. Decay processes in buildings close to the sea induced by marine aerosol: salt depositions inside construction materials. Sci. Total Environ. 721, 1–9. https://doi.org/10.1016/j.scitotenv.2020.137687.

Mraihi, R., Harizi, R., Mraihi, T., Bouzidi, M.T., 2015. Urban air pollution and urban daily mobility in large Tunisia's cities. Renew. Sust. Energ. Rev. 43, 315–320. https://doi.org/10.1016/j.rser.2014.11.022.

Neckel, A., da Silva, J.L., Saraiva, P.P., Kujawa, H.A., Araldi, J., Paladini, E.P., 2020. Estimation of the economic value of urban parks in Brazil, the case of the City of Passo Fundo. J. Clean. Prod. 264, 121369 https://doi.org/10.1016/j.jclepro.2020.121369.

Neckel, A., Korcelski, C., Kujawa, H.A., da Silva, I.S., Prezoto, F., Amorin, A.L.W., Maculan, L.S., Gonçalves, A.C., Bodah, E.T., Bodah, B.W., Dotto, G.L., Silva, L.F.O., 2021. Hazardous elements in the soil of urban cemeteries; constructive solutions aimed at sustainability. Chemosphere 262, 128248. https://doi.org/10.1016/j.chemosphere.2020.128248.

Nizar, O., Jean-Pierre, G., Habib, B., 2021. Significance of 2-methylhopane and 22,29,30 Trisnorhop 17(21)-ene biomarkers in holocene sediments from the Gulf of Tunis - Southern Mediterranean Sea. J. Afr. Earth Sci. 173, 104043 https://doi.org/10.1016/j.jafrearsci.2020.104043.

Oliveira, M.L.S., Tutikian, B.F., Milanes, C., Silva, L.F.O., 2020. Atmospheric contaminations and bad conservation effects in Roman mosaics and mortars of Italica. J. Clean. Prod. 248, 119250 https://doi.org/10.1016/j.jclepro.2019.119250.

Oliveira, M.L.S., Flores, E.M.M., Dotto, G.L., Neckel, A., Silva, L.F.O., 2021a. Nanomineralogy of mortars and ceramics from the forum of Caesar and Nerva (Rome, Italy): the protagonist of black crusts produced on historic buildings. J. Clean. Prod. 278, 123982 https://doi.org/10.1016/j.jclepro.2020.123982.

Oliveira, M.L.S., Neckel, A., Silva, L.F.O., Dotto, G.L., Maculan, L.S., 2021b. Environmental aspects of the depreciation of the culturally significant Wall of Cartagena de Indias – Colombia. Chemosphere 265, 129119. https://doi.org/10.1016/j.chemosphere.2020.129119.

Ouyang, X., Wei, X., Li, Y., Wang, X.C., Klemeš, J.J., 2021. Impacts of urban land morphology on $PM_{2.5}$ concentration in the urban agglomerations of China. J. Environ. Manag. 283, 112000 https://doi.org/10.1016/j.jenvman.2021.112000.

Palisoc, S., Santos, D.J., Natividad, M., 2021. Borohydride-based electrolyte system for magnesium-persulfate (mg||MgS_2O_8) rechargeable battery. Ain Shams Eng. J. 1–10. https://doi.org/10.1016/j.asej.2020.09.032.

Petkus, A.J., Wang, X., Beavers, D.P., Chui, H.C., Espeland, M.A., Gatz, M., Gruenewald, T., Kaufman, J.D., Manson, J.E., Resnick, S.M., 2021. Outdoor air pollution exposure and inter-relation of global cognitive performance and emotional distress in older women. Environ. Pollut. 271, 116282 https://doi.org/10.1016/j.envpol.2020.116282.

Prasad, S.V.S., Prasad, S.B., Verma, K., Mishra, R.K., Kumar, V., Singh, S., 2021. The role and significance of magnesium in modern day research-a review. J. Magnes. Alloys 1-61. https://doi.org/10.1016/j.jma.2021.05.012.

Rajput, V., Minkina, T., Mazarji, M., Shende, S., Sushkova, S., Mandzhieva, S., Burachevskaya, M., Chaplygin, V., Singh, A., Jatav, H., 2020. Accumulation of nanoparticles in the soil-plant systems and their effects on human health. Ann. Agric. Sci. 65 (2), 137–143. https://doi.org/10.1016/j.aoas.2020.08.001.

Robe, M.C., Carbonnelle, J., 1982. Study of atmospheric pollution in an urban zone deprived of measurement systems, for purposes of legislation application to the city of Tunis. Sci. Total Environ. 23, 61–67. https://doi.org/10.1016/0048-9697(82)90122-x.

Saidi, O., Malouche, D., Saksena, P., Arfaoui, L., Talmoudi, K., Hchaichi, A., Bouguerra, H., Romdhane, H.B., Hsairi, M., Ouhichi, R., 2021. Impact of contact tracing, respect of isolation and lockdown in reducing the number of cases infected with COVID-19: case study. Int. J. Infect. Dis. 1-34 https://doi.org/10.1016/j.ijid.2021.02.010.

Saini, A., Harner, T., Chinnadhurai, S., Schuster, J.K., Yates, A., Sweetman, A., Aristizabal-Zuluaga, B.H., Jiménez, B., Manzano, C.A., Gaga, E.O., 2020. GAPS-megacities: a new global platform for investigating persistent organic pollutants and chemicals of emerging concern in urban air. Environ. Pollut. 267, 115416 https://doi.org/10.1016/j.envpol.2020.115416.

Salyer, S.J., Maeda, J., Sembuche, S., Kebede, Y., Tshangela, A., Moussif, M., Ihekweazu, C., Mayet, N., Abate, E., Ouma, A.O., 2021. The first and second waves of the COVID-19 pandemic in Africa: a cross-sectional study. Lancet 397 (10281), 1265–1275. https://doi.org/10.1016/s0140-6736(21)00632-2.

Samara, C., Melfos, V., Kouras, A., Karali, E., Zacharopoulou, G., Kyranoudi, M., Papadopoulou, L., Pavlidou, E., 2020. Morphological and geochemical characterization of the particulate deposits and the black crust from the Triumphal Arch of Galerius in Thessaloniki, Greece: implications for deterioration assessment. Sci. Total Environ. 734, 139455 https://doi.org/10.1016/j.scitotenv.2020.139455.

Schembari, C., Bove, M.C., Cuccia, E., Cavalli, F., Hjorth, J., Massabò, D., Nava, S., Udisti, R., Prati, P., 2014. Source apportionment of PM_{10} in the Western Mediterranean based on observations from a cruise ship. Atmos. Environ. 98, 510–518. https://doi.org/10.1016/j.atmosenv.2014.09.015.

Silva, L.F.O., Pinto, D., Neckel, A., Dotto, G.L., Oliveira, M.L.S., 2020a. The impact of air pollution on the rate of degradation of the fortress of Florianopolis Island, Brazil. Chemosphere 251, 126838. https://doi.org/10.1016/j.chemosphere.2020.126838.

Silva, L.F.O., Pinto, D., Neckel, A., Oliveira, M.L.S., 2020b. An analysis of vehicular exhaust derived nanoparticles and historical Belgium fortress building interfaces. Geosci. Front. 11 (6), 2053–2060. https://doi.org/10.1016/j.gsf.2020.07.003.

Silva, L.F.O., Lozano, L.P., Oliveira, M.L.S., da Boit, K., Gonçalves, J.O., Neckel, A., 2021. Identification of hazardous nanoparticles present in the Caribbean Sea for the allocation of future preservation projects. Mar. Pollut. Bull. 168, 112425 https://doi.org/10.1016/j.marpolbul.2021.112425.

Stambouli, F., 1996. Tunis city in transition. Environ. Urban. 8 (1), 51–63. https://doi.org/10.1177/095624789600800117.

Trejos, E.M., Silva, L.F.O., Hower, J.C., de Flores, E.M.M., González, C.M., Pachón, J.E., Aristizábal, B.H., 2021. Volcanic emissions and atmospheric pollution: a study of nanoparticles. Geosci. Front. 12 (2), 746–755. https://doi.org/10.1016/j.gsf.2020.08.013.

Tunisia Population, 2021. Tunisia Population Estimator. Demographic Data. https://worldpopulationreview.com/countries/tunisia-population (Accessed 4 August 2021).

Wang, J., Zhang, P., Wang, S., Yang, L., Luo, J., Shen, B., 2021. Mechanisms and kinetics of a new cleaner single cyclic roasting-leaching process for the extraction of vanadium from Linz–Donawitz converter slag using $CaCO_3$ and H_2SO_4. Cleaner Eng. Technol. 4, 100204 https://doi.org/10.1016/j.clet.2021.100204.

Wen, Z.Y., Tang, X.F., Wang, T., Gu, X.J., Zhang, W.J., 2020. Detection of chemical compositions of ultrafine nanoparticles by a vacuum ultraviolet photoionization nucleation aerosol mass spectrometer. Chin. J. Anal. Chem. 48 (4), 491–497. https://doi.org/10.1016/s1872-2040(20)60009-3.

Wu, R., Zhao, X., Liu, Y., 2021. Atomic insights of Cu nanoparticles melting and sintering behavior in Cu Cu direct bonding. Mater. Des. 197, 109240 https://doi.org/10.1016/j.matdes.2020.109240.

Zahmatkesh, I., Sheremet, M., Yang, L., Heris, S.Z., Sharifpur, M., Meyer, J.P., Ghalambaz, M., Wongwises, S., Jing, D., Mahian, O., 2020. Effect of nanoparticle shape on the performance of thermal systems utilizing nanofluids: a critical review. J. Mol. Liq. 114430 https://doi.org/10.1016/j.molliq.2020.114430.

Zhang, Z., Xie, Y.H., Huo, X.Y., Chan, S.L.I., Liang, J.M., Luo, Y.F., Mu, D.K.Q., Ju, J., Sun, J., Wang, J., 2021. Microstructure and mechanical properties of ultrafine grained CoCrFeNi and $CoCrFeNiAl_{0.3}$ high entropy alloys reinforced with Cr_2O_3/Al_2O_3 nanoparticles. Mater. Sci. Eng. A 816, 141313. https://doi.org/10.1016/j.msea.2021.141313.

Zhou, J., Wang, C., Song, M., Chen, X., Xia, W., 2021. Simple synthesis of ultrafine amorphous silicon carbide nanoparticles by atmospheric plasmas. Mater. Lett. 299, 130072 https://doi.org/10.1016/j.matlet.2021.130072.