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REVIEW ARTICLE

Impact of air pollution on outdoor cultural heritage objects and decoding the role of particulate matter: a critical review

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Abstract

Atmospheric gases and particulate matter (PM) in contact with the material's surface lead to chemical and physical changes, which in most cases cause degradation of the cultural heritage material. Atmospheric damage and soiling are recognized as two pivotal forms of deterioration of cultural heritage materials caused by air pollution. However, the atmospheric damage effect of PM is rather complicated; its variable composition accelerates the deterioration process. Considering this, one of the important contributions of this work is to review the existing knowledge on PM influence on atmospheric damage, further recognize, and critically evaluate the main gaps in current understanding. The second phenomenon related to cultural heritage material and PM pollution is soiling. Even if soiling was recognized long ago, its definition and knowledge have not changed much for several decades. In the past, it was believed that black carbon (BC) was the primary soiling agent and that the change of the lightness could effectively measure the soiling. With the change of pollution situation, the lightness measurements do not represent the degree of soiling correctly. The additional contribution of this work is thus, the critical evaluation of soiling measurements, and accordingly, due to the change of pollution situation, redefinition of soiling is proposed. Even though numerous studies have treated soiling and atmospheric damage separately, there is an overlap between these two processes. No systematic studies exist on the synergy between soiling and atmospheric damage caused by atmospheric PM.

Keywords Cultural heritage material · Soiling · Atmospheric damage · Particulate matter · Brown carbon

Introduction

Air pollution is the main culprit in heritage decay in minds of many, but it may not seem the most critical in certain circumstances. Weathering of cultural heritage occurs naturally and is often believed to contribute to a sense of age and serenity that is fundamental to how we value our heritage. However, the degradation caused by air pollution is real, measurable, and it adds an extra dimension to the damage, which is often evident. A clear example of this is the influence of acid rains and high concentration of sulfur dioxide (SO_2) upon different materials of cultural heritage objects, especially carbonate stones (gypsum formation and erosion as well as black crust accumulation), which left a mark on cultural heritage worldwide (Bowler and Brimblecombe 2000; Brimblecombe 2003).

In fact, most materials from which heritage is made are prone to atmospheric deterioration. Stone materials (limestone, marble, sandstone, etc.) are prone to surface erosion, loss of details, and blackening. Besides, biological colonization is also a type of stone weathering processes. On the other

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hand, metals typically undergo surface corrosion; oxidation of different metals produces a stable patina layer (oxide layer) over the metal surfaces, which, in some cases, results in pitting and perforation of the material. Timber, as a construction material, most often undergoes biological decay, which is followed by material deterioration and loss of the coating paint. Medieval potash glass is prone to corrosion and loss of details, while modern soda glass typically undergoes blackening while losing its decorative value.

We should keep in mind that cultural heritage material's weathering processes also occur in unpolluted environments (Hechler et al. 1991). Environmental factors (wind, rain, solar radiation, etc.) are unavoidable and not easy to control. They are commonly considered background deterioration, and most frequently, they act in synergy with air pollution. In most cases, these environmental factors are associated with a physical mechanism of damage and can also act in alliance leading to excessive stress to the material surfaces (Price and Doehne 2011; Sabbioni 2003). Not only are physical damages related to environmental factors, but chemical deterioration can also occur due to their involvement. The *karst effect* is a common chemical mechanism of deterioration caused by environmental factors. This is the chemical reaction between water, acidified with carbon dioxide (CO_2) or some organic acids and calcite ($CaCO_3$), which leads to the calcium bicarbonate ($Ca(HCO_3)_2$) formation being about 100-times more soluble than $CaCO_3$ and thus results in faster material loss (Cardell-Fernández et al. 2002).

Although material degradation can be physical, chemical, biological, or a combination thereof, in this paper, we focus on the impacts of air pollution, which are mainly associated with chemical aggression. In general, any reactive air pollutant that surrounds cultural heritage can chemically attack the materials the object is made of. In most cases, meteorological conditions only accelerate the chemical damage caused; for example, a chemical reaction occurring at the surface of a monument is typically accelerated by higher temperature or light (usually termed as thermal or photochemical damage), which is well known for timber and marble (Watt et al. 2009). Chemical damage often results in the dissolution of surface details and alteration of material's surface topography.

The vital role of air pollution in chemical deterioration of materials was recognized after adopting the convention on long-range transboundary air pollution (CLRTAP) within the United Nations Economic Commission for Europe (UN ECE) in 1979. Driven by the raised awareness of different material's vulnerability to air pollution in the mid-1980s, a sequence of International Cooperative Programs (ICP) was launched to assess the impact of various air pollutants on the essential parts of the ecosystem. Among others, alteration of cultural heritage materials due to air pollution was recognized as detrimental, and as a result, a program called ICP-Materials was launched in 1985 to fill some of the main gaps in knowledge in this field. Within the program, a vast network for monitoring air pollution trends and the influence of air pollution on cultural heritage was developed (Chico et al. 2017).

In the frame of ICP-Materials, it was thought that gaseous pollutants were the only causative agents of atmospheric damage, which was thought to be a consequence of a chemical attack of these pollutants (Di Turo et al. 2016; Tidblad et al. 1999). Later, however, it has been shown that particulate matter (PM) plays a critical role in the processes of atmospheric damage (Ferm et al. 2006). Atmospheric damage is here considered the term in a broader sense, which includes corrosion of metal materials and the deterioration of stone, glass, and mortar material; it may proceed through physical, chemical, and biological processes. However, metal corrosion and the decay processes of stones happen via different mechanisms.

Although PM's role in material deterioration has been known for a long time, it is still most often classified as physical (visual) damage to the material only. The term *soiling* is most commonly used to describe the impact of PM on building material and is defined as the physical effect of the darkening of exposed surfaces, which is a consequence of PM deposition containing specific soiling agents, e.g., black carbon (BC).

In the most recent review paper about the impact of air pollution on cultural heritage material by Vidal et al. (2019), it has been recognized that atmospheric damage and soiling are primary forms of material degradation caused by air pollution. However, in most research works to date (Cole 2000; Creighton et al. 1990; Ferm et al. 2006; Ionescu et al. 2006; Knotkov 1993; Schreiner and Melcher 2004; Toprak et al. 1997), these two processes are strictly treated separately, albeit, from the earlier works from the field (Crnković et al. 1994; Gauri 1980; Macchiarola et al. 1999; MariC 1938), it is clear that they overlap. The most evident and generally accepted example, where these processes overlap and combine, is the formation of *black crust*. Nevertheless, there are many other synergies between atmospheric damage and soiling, which have not been researched or well understood and should be investigated in the future. Namely, from the perspective of harm caused by air pollution, atmospheric damage, soiling, and a combination of both are equally important.

Air pollution and its effect on cultural heritage objects

Unlike the environmental factors, which impact on building material is usually hard to quantify and predict, air pollution is measurable, and it has been shown to correlate well with material damage (Brimblecombe 2013). Moreover, not only is atmospheric pollution considered an accelerating factor in the decay of cultural heritage objects (Aulinas et al. 2009; Chapoulie et al. 2008; Varotsos et al. 2009), but it has also been recognized that by the end of the previous millennium, the vast majority of cultural heritage monuments (e.g., monuments, groups of buildings and sites) had been significantly damaged because of predominant anthropogenic environmental influences (Siegesmund et al. 2008; Winkler 1966). Modern society development and rapid growth of population are the leading causes of this (Brimblecombe 2003).

In general, the substances which pollute the atmosphere are either gases or dispersed fine solid or deliquescent particles (aerosols), which are always in coexistence with each other (Metaxa 2011). The major gas-phase pollutants, which are present in the atmosphere in trace amounts and profoundly influence air quality, are sulfur-containing compounds (Sulfur dioxide, SO_2; sulfuric acid, H_2SO_4; dimethyl sulfide, CH_3SCH_3; and carbonyl sulfide, OCS), nitrogen-containing compounds (nitrous oxide, N_2O; nitrogen oxides, NO_x; ammonia, NH_3; and amines, RNH_2), carbon-containing gases (carbon dioxide, CO_2; carbon monoxide, CO; methane, CH_4; volatile organic compounds, VOC), halogen-containing compounds (methyl chloride, CH_3Cl; methyl bromide, CH_3Br), and the tropospheric ozone (Seinfeld and Pandis 2016). Among gaseous pollutants, SO_2, NO_x, and O_3 are the most critical, seriously affecting material damage on cultural heritage worldwide. Even more critical, in a sense of material deterioration, are secondary products produced from these gases, such as H_2SO_4 and HNO_3 (Watt et al. 2009). Nevertheless, these gases are also responsible for PM formation through different secondary (photo)chemical reactions. Each gas represents a potential precursor for (secondary) PM formation. More details about chemistry, physics, and sources of these pollutants can be found elsewhere (Finlayson-Pitts and Pitts Jr 1999, Hobbs 2000; Holloway and Wayne 2015; Seinfeld and Pandis 2016; Watt et al. 2009). Here, only trends and the role of these gaseous compounds in material deterioration will be briefly discussed. The focus is on the most critical pollutants (i.e., SO_2, NO_X, O_3, and PM) that cause acidification, and therefore damage to materials.

Several international exposure programs were launched all over the world in the mid-1980s, the general aim of which was to collect environmental and material corrosion data and map the atmospheric corrosivity (Knotkov 1993; Mariaca and Morcillo 1998; Tidblad et al. 1999). These programs (Table 1) all showed high deterioration rates in several urban and industrial locations due to the predominant SO_2 pollution at that time. It is essential to point out that in the past, also some shorter exposure pilot programs were launched; one of the successful pilot programs was NATO/CCMS (Zallmanzig 1985). However, these short pilot programs were less comprehensive in terms of duration and data collection than the international programs shown in Table 1 and did not bring any considerable advances in the field to warrant more attention.

In 1987, the ISO CORRAG program was launched to provide metal corrosion and environmental data supported by ISO/TC 156 testing method. ISO CORRAG program included 53 sites in 14 countries, mostly located in Argentina, Canada, Japan, New Zealand, USA, and Europe (only a few sites are mentioned) (Knotkov 1993). On the other side, the MICAT program's goal was to map the atmospheric corrosivity of metal materials in 12 Ibero-American countries, including Spain and Portugal (Mariaca and Morcillo 1998). Nevertheless, the shortcomings of the ISO CORRAG and the MICAT programs were the lack of data on gases other than SO_2 and wet deposition. Namely, the main concern at that time was SO_2 and related acid rain phenomena, and accordingly, it was thought that SO_2 was the primary atmospheric pollutant (Yocom 1979). Their shortcomings were later supplemented with the ICP-Materials program, aiming to investigate the effect of acid rain deposition on material surfaces. Still, there was a lack of data on the dry deposition of Cl^-, HNO_3, and PM, which are needed to provide the whole picture of a complex pollution situation. Within the European Commission 5th Framework Program (FP5), the *Multi-Assess* (Kucera 2005) project was later funded, which was performed at the ICP-Materials test sites with an emphasis on multi-pollution. In fact, the program represents

Table 1 The leading international exposure programs launched in the mid-1980s with the resulting main references

Program	SO_2	NO_2	O_3	HNO_3	Cl	PM	Main references
ISOCORRAG	X				X		(Dean 1987), (Strekalov & Panchenko 1996), (Knotkov 1993), (Schroeder 1999)
MICAT	X				X		(Morcillo 1995), (Mariaca & Morcillo 1998), (Rodríguez 1999), (Morcillo et al. 2012)
ICP-Materials	X	X	X				(Tidblad et al. 2001, 1991, 1993, 1995), (Tidblad and Leygraf 1995), (Kucera and Fitz 1995), (Reisener et al. 1995), (Zakipour et al. 1997), (Krätschmer et al. 2002)
Multi-Assess	X	X	X	X		X	(Ferm et al. 2004), (Watt et al. 2004), (Tidblad 2004), (O Hanlon et al. 2004), (Henriksen 2004), (Ferm et al. 2005), (Samie et al. 2005), Samie et al. (2006), (Samie et al. 2007a, b), (Ionescu et al. 2006), (Watt et al. 2008), (Melcher et al. 2008), (Kreislova et al. 2009), (Screpanti & De Marco 2009)

the prolonged hand of the ICP-Materials, whereas the measurements of HNO_3 and PM were added. Therefore, from today's perspective, the *Multi-Assess* project is by far the most suitable for investigating multi-pollutant effects on cultural heritage objects in non-marine environments.

During the 35 years of ICP-Materials, it has been noticed that the average pollutant levels and the atmospheric damage intensity of different materials have changed (Tidblad et al. 2017, 2012). The trends for different gases, however, are divergent. The concentration of O_3 increased during the 1990s and remained relatively constant afterward. On the other hand, SO_2 and NO_2 levels were decreasing during the entire period and continue to decline (Aas et al. 2019).

Main pollutants affecting the deterioration of cultural heritage material

Within ICP-Materials, it was perceived that the atmospheric damage of materials was decreasing during the investigated period, which was mainly attributed to the decreasing SO_2 concentrations (Tidblad et al. 2017, 2012). The role of SO_2 was specially recognized in the corrosion of metals (Tanaka et al. 2016) and stone surface deterioration (Siegesmund et al. 2007). Combustion of solid fossil fuels and other materials, that contain sulfur, releases SO_2 into the atmosphere, where it gradually converts to SO_3 and, in the presence of water, further to H_2SO_4. SO_2 itself represents the leading acidifying agent of the atmosphere, and in fact, the corrosion/oxidation of metals is well known to be favored in acidic medium (Svensson and Johansson 1993; Tanaka et al. 2016; Tidblad et al. 1991; Xiang et al. 2011). The formed H_2SO_4 (homogeneously in the aqueous phase or heterogeneously at the stone surface by dry deposition of SO_2) (Cardell-Fernández et al. 2002) is also very harmful to stone surfaces, particularly for carbonate stones. It initiates the gypsum crust formation (Camuffo et al. 1983; Crnković et al. 1994; Sabbioni et al. 2000), which may cause stone degradation and soiling by the formation of *black crust*. Luckily, the overall emissions of SO_2 have been decreased by up to 74% since 1970 (Fig. 1) (NAEI 2017).

The main reason is the reduction in commercial, residential, and industrial emissions, fuel use changes, and the increasing use of abatement equipment (Watt et al. 2009). Hence, nowadays, in several countries, SO_2 does not represent a severe threat to cultural heritage objects anymore. Of course, this is not true for regions and countries where air pollution is not tackled adequately (Aas et al. 2019).

Meanwhile, the apparent mono-pollution situation has changed to multi pollution (Kucera 2005; Kucera et al. 2007). Currently, NO is the most significant reactive gas emitted into the atmosphere in substantial amounts (NAEI 2017; Watt et al. 2009) (Fig. 2). Even though NO is relatively harmless to cultural heritage material, in the atmosphere, it is readily oxidized by ozone, which is the immediate source of most atmospheric NO_2. The formed NO_2 reacts further, producing, among others, HNO_3 and particulate nitrate, which are the most stable species formed from NO_x (Seinfeld and Pandis 2016; Watt et al. 2009).

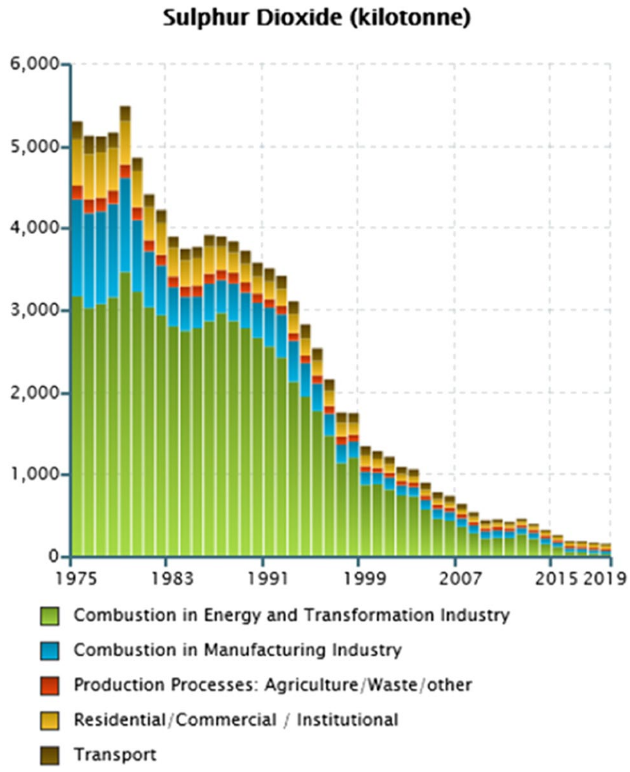

Fig. 1 Emission summary data for SO_2 (in kiloton) from 1975 to 2019 (NAEI 2017)

Besides contributing to acidification and eutrophication, gaseous HNO_3 causes deterioration of many materials. There are only a few reports on HNO_3 measurements in the urban air in Europe and elsewhere (Eleftheriadis et al. 1998; Erduran and Tuncel 2001; Fox et al. 1988; Piringer et al. 1997; Tanner et al. 1998; Tidblad et al. 2012). HNO_3 is thus potentially one of the most challenging pollutants to analyze and in most cases, its concentration is only estimated by the equation developed by Kucera et al. (2007) within the Multi-Asses project.

Within the *Multi-Assess* project, Ferm et al. (2005, 2004, 2006) and Samie et al. (2005, 2006, 2007a, b) extensively studied its impact on different metals (copper, zinc, and carbon steel), whereas the influence of HNO_3 on stone materials has been less investigated. However, in the literature, some evidences on HNO_3 causing deterioration of stone material can be found (Haneef et al. 1992; Kirkitsos and Sikiotis 1995, 1996; Roots 2008; Sikiotis and Kirkitsos 1995). Although air pollution caused by O_3 is at the highest level

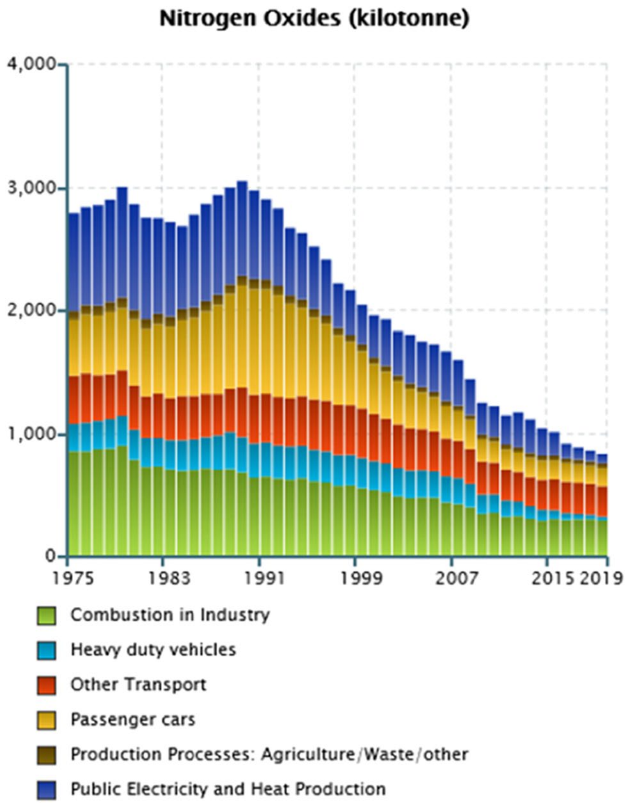

Fig. 2 Emission summary data for NO_x (in kiloton) from 1975 to 2019 (NAEI 2017)

nowadays (Fig. 3), the least is known about its influence on cultural heritage materials (Screpanti and De Marco 2009).

Tropospheric O_3 is a secondary pollutant formed in the atmosphere due to the sequence of reactions, involving two significant groups of precursors: VOCs and NO_x. The formation of O_3 is initiated by the reaction of hydroxyl radicals (OH●) and organic molecules, and NO_x catalyzes the subsequent transformation in a complex cascade of free-radical reactions; more about the chemistry and formation of tropospheric O_3 can be found elsewhere (Seinfeld and Pandis 2016). Only a few reports on the O_3 influence on cultural heritage can be found in the literature, reporting solely on the cumulative damage, without considering any detailed mechanisms of O_3 action (Huang et al. 2019; Manual 2008; Screpanti and De Marco 2009). Nevertheless, it has been recognized that O_3 has a direct effect on degradation of natural rubber, plastic, textiles, paint, and surface coatings (Coyle et al. 2002; Lee et al. 1985). In general, O_3 is easily decomposed (when exposed to solar irradiation) to dioxygen and singlet atomic oxygen, which is a highly oxidizing agent and has a large corrosive effect on different metals (Svensson and Johansson 1993; Tidblad and Leygraf 1995; Weissenrieder et al. 2004). Moreover, Screpanti and De Marco (2009) reported that the role of O_3 is even more important in atmospheric damage when acting in synergy with other pollutants, such as NO_2 and SO_2.

Because of the recognized increasing importance of PM pollution and insufficient knowledge about its interactions with different environmental compartments, atmospheric PM deserves a special attention also in the frame of cultural heritage preservation. A general overview of atmospheric PM is out of the scope of this work; however, here, only the leading ideas about their sources, formation, composition, and sink will be presented. More specific details can be found in classical atmospheric chemistry and physics textbooks (Andreae & Crutzen 1997; Hobbs 2000; Holloway and Wayne 2015; Seinfeld and Pandis 2016).

In ambient air, PM mostly includes both phase states, solid and liquid phases depending on ambient conditions (especially RH). In general, PM represents a wide range of chemically and physically diverse substances that can be distinguished by their origin, size, formation mechanism, chemical identity, atmospheric behavior, and measurement methods (Seinfeld and Pandis 2016; Watt et al. 2009). Although atmospheric PM is present in low concentrations in ambient air, its number and mass concentration, size distribution, physical properties, and chemical composition are of immense importance. In terms of its influence on cultural heritage objects, especially on stony, metal, and glassy ones, the most important are the size and chemical composition (Chatoutsidou and Lazaridis 2019; Kucera and Fitz 1995). Depending on the size, atmospheric PM can be removed from and potentially deposited on the cultural heritage objects by diverse deposition mechanisms. Moreover, depending on the size, the chemical composition of PM will be different influencing the interaction with the substrate where they will deposit (Finlayson-Pitts and Pitts Jr 1999, Seinfeld and Pandis 2016).

Roughly, atmospheric PM with a diameter of less than 2.5 µm is known as fine particles ($PM_{2.5}$), while those with diameters greater than 2.5 µm are referred to as coarse particles Among others, PM size is the most influential parameter for the determination of its aerodynamic properties, including sedimentation, diffusion, interception, and impaction (Hinds 1999).

The quantity of PM in the air is frequently monitored and expressed in terms of number or mass concentrations. Depending on the urban or remote site typology, PM can reach number concentrations of 10^6–10^7 cm^{-3} or 5–100 cm^{-3}, respectively (Laakso et al. 2003; Schneider et al. 2015; Wu et al. 2008). The air quality management usually takes PM mass concentration as the most important air quality indicator. Since the World Health Organization (WHO) recognized PM as the most dangerous substance to human health, its limit values are nowadays set in different national and international standards; e.g., the Directive 2008/50/EC of the European Parliament defines

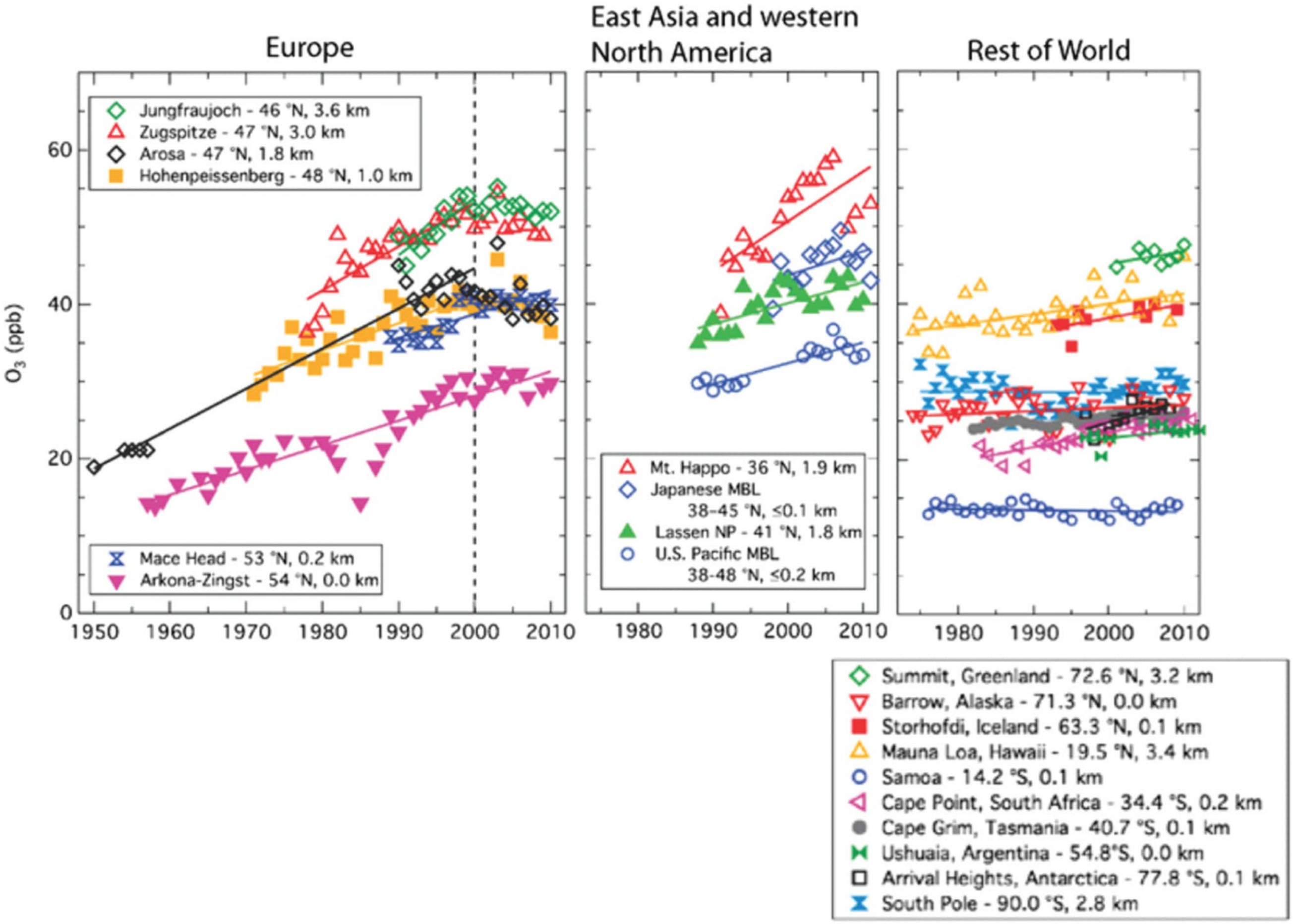

Fig. 3 Global distribution and trends of tropospheric ozone (Cooper et al. 2014)

limit average annual concentrations of $PM_{2.5}$ and PM_{10} at 25 and 40 µg m^{-3} (PM_{10} particles ≤ 10 µm, $PM_{2.5}$ particles ≤ 2.5 µm) (European Parliament 2008). Despite of a strong tendency toward lowering the allowed levels of PM pollution, in some parts of the world, especially in China and India, its concentrations still largely exceed the limit values and reach up to 1000 µg m^{-3} (Agarwal et al. 2020; Yang et al. 2018). Note that these orientation values are also important from the perspective of cultural heritage preservation.

The concentration, chemical composition, and size distribution of atmospheric particles are temporally and spatially highly variable (Finlayson-Pitts and Pitts Jr 1999). Depending on the size and site typology (urban, rural, remote, marine), they can contain sulfate, ammonium, nitrate, chloride, sodium, trace metals, carbonaceous material, crustal elements, and water. The carbonaceous fraction is composed of minor elemental (EC) and major organic carbon fractions (OC). The mixture of EC and OC containing small amounts of other elements such as oxygen, nitrogen and hydrogen is frequently called soot (Chang et al. 1982). Besides, soot contains different polycyclic aromatic hydrocarbons (Szatyłowicz and Skoczko 2019) as well as toxic heavy metals, including vanadium (V), nickel (Ni), iron (Fe), and barium (Ba) (Corbin et al. 2018). EC or black carbon (BC) (depending on the measuring technique) is emitted directly into the atmosphere, predominantly from combustion sources. These particles are in the range of 20–30 nm (Seinfeld and Pandis 2016). In contrast to the inorganic compounds, which are in principle well characterized, the OC fraction of atmospheric aerosol is very poorly understood; thus, only about 10–40% of the atmospheric organic aerosol (OA) is characterized on the molecular level (Andreae and Crutzen 1997; Noziere et al. 2015; Pöschl 2005). However, it is believed that OA is hazardous to human health and climate even when present in low concentrations (Pöschl 2002). Besides, many OC compounds are reactive and can cause damage after PM deposition (Sabbioni et al. 2003). It has been recognized that the colored OC, which is known as atmospheric brown carbon (BrC), plays an important role in many atmospheric processes (Andreae and Gelencsér 2006; Chen and Bond 2010; Laskin et al. 2015; Sun et al. 2007).

Among others, BrC interferes with BC determination and thus influences the definition and measurements of soiling.

There are many motivations to study atmospheric PM; however, most often, its influence on construction and heritage materials falls out of the scope of this studies. Although the potential role of PM in atmospheric damage was recognized a long time ago, its influence on material degradation has been only qualitatively explained throughout individual studies until the *Multi-Assess* project (see Table 2). Already in the early 1980s, the first evidence of the damage to material caused by PM was reported; however, those observations were related to specific situations where PM coexisted with acidic gases, such as SO_2, SO_3, and NO_x (Environmental Protection Agency 1982). Although these early observations showed that atmospheric damage caused by SO_2 and moisture increased in the presence of PM (Lee et al. 1985), the scientific community could not confirm this hypothesis until very recently (Ferm et al. 2006; Kucera et al. 2005).

Critical and intriguing role of PM in cultural heritage preservation has been recognized and, for the first time, systematically studied within the European FP5 program, which supported the *Multi-Assess project* (Kucera 2005). Ferm et al. (2006) designed passive PM collectors and found that the mass of deposited PM mainly belonged to the coarse particle mode. As the passively collected PM correlated very well with PM_{10}, it allowed them for the simultaneous determination of the deposition velocity. Because of the high content of anions and cations (almost 25% of the deposited mass), they speculated on the PM involvement in metal corrosion. Kucera (2005) on the other hand did not observe any direct effect of PM organics (mainly carboxylic acids, such as formic and acetic acids) on material corrosion; they concluded that OC could be adsorbed on the material surface affecting the ability to moisten the surface and, consequently, influence wet films' thickness and continuity. With this, PM became indirectly critical for the deterioration of different metal materials. Moreover, Ionescu et al. (2006) and Melcher et al. (2008) studied glass weathering due to air pollution. They showed that a high degree of glass weathering was due to PM deliquescent constituents. However, the main part of deposited PM was of unknown chemical composition and further studies are required. Tzanis et al. (2009) studied the influence of PM on atmospheric damage in Athens and their results revealed that different ions were deposited on different heights of the building facades. More recently, Di Turo et al. (2016) have shown with the random forests analysis (RFA) that PM_{10} contributes significantly to the surface recession and mass loss of stone and other metal materials. Soling is another more known phenomenon related to material damage caused by PM. Although it is a generally accepted phenomenon, it is not clear how different PM components participate in this process. Although soling can potentially occur on any material (Grossi et al. 2003; Mansfield 1989; Martin and Souprounovich 1986), it exerts the most severe damage to the stone and glass surfaces (Kucera 2005; Yocom and Kawecki 1986). In the beginning, it was thought that BC was the main soiling agent (Del Monte et al. 1981), which followed from the fact that soiled surfaces were black. With the change of the pollution situation, however, the composition of atmospheric PM has also changed. Recently, the organic fraction of atmospheric PM has become more important in comparison to the past (Jacobson et al. 2000; Timonen et al. 2008), and accordingly, Bonazza et al. (2005) believe that soiling due to OC will likely prevail in the next future. Moreover, the deposited OC would, among others, also create conditions for higher biological activity (Bonazza et al. 2007). Already in 1993, Saiz-Jimenez (1993) demonstrated that air composition in the selected area governed the composition of PM deposited on cultural heritage. Today, it is well known that a specific group of organic compounds present in atmospheric PM can absorb light in a particular wavelength range (near UV and visible part of the spectrum), producing brown-yellowish color to the viewer (Laskin et al. 2015). If these compounds deposit on a particular surface, they can change its color, contributing to the material's soiling. However, this

Table 2 A summary of individual studies and studies within ICP-Material that reported the atmospheric damage of various metals

Metal	References (ICP-Materials)	References (individual studies)
Cast iron	(Tidblad and Kucera 2003)	(Weissenrieder et al. 2004), (Xia and Chunchun 2006), (Kusmierek and Chrzescijanska 2015)
Carbon steel	(Kucera and Fitz 1995) Samie, (Samie et al. 2007a), (Ivaskova et al. 2015),	(Xiao et al. 2008),(Castaño et al. 2010) (Yu et al. 2016), (Tanaka et al. 2016)
Zinc	(Knotkova et al. 2005), (Samie et al. 2007a)	(Svensson and Johansson 1993), (Odnevall Wallinder et al. 2001), (Kusmierek and Chrzescijanska 2015)
Copper and bronze	(Tidblad et al. 1991), (Reisener et al. 1995), (Krätschmer et al. 2002), (Samie et al. 2005, 2006, 2007b), (Knotkova & Kreislova 2007),	(Fonseca et al. 2004), (Mendoza et al. 2004), (Lin & Frankel 2013), (Yu et al. 2020), (Titakis and Vassiliou 2020)
Aluminum	(Tidblad & Kucera 2003), (Kreislova et al. 2013), (Kreislova & Knotkova 2017)	(Vilche et al. 1995), (Oh et al. 1999), (Wang et al. 2007), (Sun et al. 2009), (Birbilis and Hinton 2011)

phenomenon would change the perception, definition, and monitoring of soiling. Therefore, despite the circumstantial evidence, the specific role of PM in the soiling process is still ill-defined. Clearly, more research is needed in this field with the emphasis on the contribution of organic matter. Soiling and atmospheric damage can obviously appear in synergy. As noted, the formation of *black crust* is a clear example where soiling and atmospheric damage overlaps. In areas protected from rain, the formed gypsum surfaces made of $CaSO_4 \cdot 2H_2O$ on carbonate stone are stable and are acting as an additional passive collector for different kinds of PM, compromising the monument's decorative function (Grossi et al. 2006). Nevertheless, the gypsum crust present on different mortar material is unstable and can undergo to secondary reaction forming ettringite and thaumasite (Blanco-Varela et al. 2001; Sabbioni et al. 2001). Another example, where soiling and atmospheric damage interact, is the cementation process. Namely, Ca^{2+} may leach from the deposited PM and recrystallize and so may cement the entire deposit and form an additional surface with convenient properties for PM collection. Similar features are also found for iron oxides, silicon dioxide, and clay minerals (Borggaard 1983; Chen et al. 2017; Palomino et al. 2008).

Atmospheric damage of cultural heritage objects

To avoid the confusion between metal corrosion and deterioration of stone, wood, and glass material, it is essential to make a clear distinction between them. The term corrosion is, in most cases, related to metal materials. It is a very well-known phenomenon, dangerous for cultural heritage material integrity, relatively fast process, and consequently connected with high conservation and restauration costs. Most metals are easily oxidized under the atmospheric influence; they tend to lose electrons to oxygen in the air. As oxygen is reduced, it forms a metal-oxide on the material surface. Such a patterned oxide layer is a corrosion layer, and in the field of cultural heritage, it is called a patina layer (FitzGerald et al. 2006). The corrosion layer is not always ruinous. It can also sometimes be protective (passive layer) — Noble patina, but in most cases, the concentration of pollutants and the acid rain lead to the formation of an non-protective layer (active, so-called vile patina) (Chiavari et al. 2007). Corrosion of metals is an electrochemical process for which the presence of electrolytes is needed. In a polar solvent (such as water), anions and cations are dissociated, producing an electrically conducting solution, which means that water or humidity are always required for the metal corrosion. The wetness of a metal surface is a consequence of condensed humidity. Different substances responsible for corrosion are dissolved in the liquid layer on the metal surface, where with time a layer of corrosion products is formed, hindering ion transport and reducing corrosion rate. Corrosion products that are formed at the surface are mainly oxides, hydroxides, and oxyhydroxides. With exposure, corrosion products are enriched with atmospheric sulfate, nitrate, and chloride species (Brimblecombe 2003; Leygraf et al. 2016; Watt et al. 2009). The corrosion of different metals in cultural heritage was comprehensively studied and very well documented, either within international exposure programs or within isolated individual studies (see Table 2).

Atmospheric damage of heritage materials is a complex process and it does not include only the corrosion of metal materials, but also stone, wood, and glass materials. The mechanism of stone and glass material deterioration differs from metals' electrochemical oxidation. The mechanism of stone material deterioration is somewhat complex and includes other compounds than oxygen itself. Some authors (Patil et al. 2021) pointed out that the main parameters responsible for the chemical weathering of stones are water, CO_2, and oxygen. CO_2 in combination with water produces weak carbon acid, which can be harmful to certain minerals from which the stone is composed. The composition of building stones plays a crucial role in determining the deterioration mechanism. Silicate stones will undergo different mechanisms of deterioration in comparison to carbonate stones. It is known that olivine, a mineral present in silicate stones, after oxidation releases free ions and silicic acid, which violates the structure of the stone. Pyroxene, another group of minerals present in silicate stone, forms cleavage cracks and some non-crystalline materials during the atmospheric damage process (Wilson 2004). Under certain atmospheric conditions, pyroxene minerals can be transformed into chlorite minerals, during which hematite is formed due to the weathering and dehydration reaction of free iron oxides and/or oxyhydroxides (Boudeulle & Muller 1988), which consequently cause degradation of the stone. The degradation mechanisms of silicate stones can be highly complex depending on the composition of the stone and the surrounding atmosphere. Generally, the degradation of silicates (including glass) can be a consequence of several related mechanisms such as hydration, hydrolysis of the ionic-covalent network, and exchange between alkali or alkaline-earth ions and protons in solution (Bunker 1994; Casey et al. 1990). On the other hand, carbonate stones (mainly composed of calcite or dolomite minerals) are sensitive to dissolution reactions. The solubility of carbonate minerals increases with the decreasing silica content and increasing calcium and magnesium content. The solubility of carbonate minerals also increases with decreasing pH (Siegesmund and Snethlage 2011). Most of the reaction products of carbonate mineral dissolution reaction are different soluble salts that either crystallize within the stonework, resulting in physical damage or are washed away, resulting in a loss of material (Massey 1999). The formation of calcium sulfate is an important exception; however, the gypsum crust is the major product of carbonate stone dissolution and is a ubiquitous compound found in building and heritage materials. Therefore, atmospheric damage can be defined as a complex process that takes place at a rate dependent on environmental factors, such as temperature, relative humidity (RH), and precipitation, which are decisive for the time of wetness, and on the content of air pollutants (Kucera & Fitz 1995). Atmospheric damage implies the interaction (mostly chemical) between the components of polluted air and the material substrate, where the composition of the substrate is vital for defining the deterioration mechanism. (Christodoulakis et al. 2017). The complexity of atmospheric damage arises partially due to many phases and different components involved in this process; in any case, water is required for atmospheric damage to occur. Water can be adsorbed as a thin layer on the metal surface, or it can also be absorbed in a more or less porous stone material or on already existing corrosion products. As mentioned earlier, the process of atmospheric damage is dependent on several parameters, and usually, they act together in various combinations. Apropos this, the combinations of these parameters can differently influence the corrosion processes. For example, the combination of SO_2 with NO_x/O_3 and temperature/RH or the combination of HNO_3 with temperature/RH influences the deterioration process differently as the combination of PM, including NaCl with temperature/RH (Watt et al. 2009). Therefore, the comprehension of the influence of SO_2, NO_x, O_3, HNO_3, and PM with the combination of environmental factors is essential, particularly for mega-cities with unique historical monuments being exposed to multi pollution (Cartalis and Varotsos 1994; Varotsos et al. 2009).

Atmospheric damage of cultural heritage material can also occur through biological activity. Different stone materials can support large and diverse communities of microorganisms that colonize both the stone surface and the porous interior. It has been recognized that the microbial processes are implicated in the deterioration of the stone (Diakumaku et al. 1995; Ding et al. 2021; Gorbushina 2007; McNamara and Mitchell 2005; Shilova et al. 2022). The degradation process of cultural heritage material induced by biological activity proceeds primally through the formation and growth of biofilms, which are complex communities of microorganisms attached to a surface. The biofilm formation starts with the initial adhesion of microorganisms to a surface. The interaction between microorganisms and carbonate stone is complex (McNamara and Mitchell 2005; Papida et al. 2000).

In some cases, the presence of microbial growth on stone can be only an aesthetic issue since visible growth of pigmented microorganisms can alter the appearance of buildings and statues. However, it has been noticed that in many cases, microorganisms are one of the main causes of stone deterioration (Warscheid and Braams 2000). It has been speculated that the microbial biodeterioration of stone occurs through organic and inorganic acids produced as metabolic by-products (Sand and Bock 1991). For example, it is known that the most predominant acid produced by lichens and its excretion is oxalic acid. Oxalic acid leads to the formation of calcium oxalate crystals through the chemical reaction of the acid with calcareous stones (Monte 2003). The formation of calcium oxalate crust is an important mechanism of stone material degradation and deserves special attention. Besides the metabolic acids, it has been shown that biofilm can increase the dissolution rate of $CaCO_3$ (Perry IV et al. 2004). Cultural-based studies have identified a few groups of cultured bacteria (Videla et al. 2001), among others also sulfur-oxidizing bacteria (McNamara and Mitchell 2005); they can produce H_2SO_4 that further reacts with the limestone forming gypsum crust, and resulting in stone deterioration. However, the biological degradation of cultural heritage material is a complex field, and it is not in the scope of this review; herein, only the basic ideas about biological degradation are given.

Role of main gas pollutants in atmospheric damage

The influence of gaseous pollutants on cultural heritage material, especially their impact on metal corrosion, was extensively studied within the ICP-Materials (see Table 2). Only the influence of the leading gases (SO_2, NO_x, and O_3) and their acids will be briefly reviewed for stone material; while more attention will be given to the atmospheric damage caused by atmospheric PM.

Building stone material containing a high amount of $CaCO_3$, such as marbles, limestones, sandstones, and mortars are most sensitive to SO_2 (Camuffo et al. 1983; Crnković et al. 1994; Fitzner and Heinrichs 2001; MariC 1938). The emitted SO_2 is readily oxidized in the atmosphere to H_2SO_4, which is, after wet deposition, accumulated at the stone surface. H_2SO_4 can also be formed on the stone surface via a heterogeneous reaction between SO_2 and the stone itself at high RH and in the presence of oxidant (e.g., H_2O_2, O_3) and a catalyst (Fe_2O_3 or even NO_2) (Rosvall et al. 1986). Either formed at the surface or wet deposited on the stone, H_2SO_4 reacts with $CaCO_3$ from the stone and forms calcium sulfate-gypsum ($CaSO_4 \cdot 2H_2O$). Such reactions can induce micro-cracks inside the stone structure, leading to deterioration (Crnković et al. 1994; MariC 1938). Even though gypsum is relatively insoluble in water, it is much more soluble than $CaCO_3$, which is entirely insoluble. Since the formed gypsum layers are fragile when exposed to rain, they can be washed out, causing severe loss in surface details and further declining (Yocom 1979). Depending on the immediate environment of the stone surface, the formed gypsum can also be accumulated, forming *black crust* in combination with PM deposition. The formation of *black* *crust* depends thus mostly on the position of the exposed area (Calparsoro et al. 2017; Grossi et al. 2006). Sabbioni et al. (2000) recognized that gypsum crust could be accumulated in areas soaked by rain but protected from intensive washout. The gypsum crust formation is one form of calcareous stone damage. The mineral dissolution reaction, which is the major mechanism of calcareous stone deterioration gains in importance with increasing acidity. Acid deposition refers to both wet and dry deposition of gaseous and particulate pollutants into water films on mineral surfaces. The atmospheric chemistry of SO_2 and NO_x, which are oxidized to sulfate and nitrate through gas and aqueous-phase processes, influences significantly the atmospheric acidity (Siegesmund and Snethlage 2011). Most of the reaction products of acid deposition are substantially more soluble than the respective parent minerals. The acid dissolution reaction causes serious loss of cohesion if acid attacks and the dissolution occur at grain contacts. Soluble sulfates and nitrates salts are the major reaction products of the mineral dissolution reaction. Even if SO_2 emissions have been significantly reduced in many parts of the world, in the past decades, high stone degradation rates are still reported. The surface of calcareous stone may have been altered permanently in unwashed walls by past exposure to high pollutant levels. The present high rate of degradation indicates a memory effect of the previous pollution situation (Rosvall et al. 1986).

The main sources of NO_x are road traffic and energy production (power plants), and it is thought that near the source, NO_x is a primary pollutant. Nevertheless, the role of NO_x in causing damage to stone materials has not been well documented (Arroyave and Morcillo 1995). Livingston (1985) postulated that NO_x species have little effect on carbonate stone. Haneef et al. (1992) concluded that dry deposition of NO and NO_2 has a minimal effect on stone degradation. In contrast to this, Johansson et al. (1988) reported that NO_2 promotes SO_2 deposition and acts as a catalyst for its oxidation, contributing significantly to the degradation of marble stone. Additionally, Van Grieken et al. (1998) showed that the reaction between nitrate and $CaCO_3$ is not thermodynamically favorable. Likewise, the presence of $Ca(NO_3)$ on a calcareous stone is difficult to prove due to its high solubility in water. Nonetheless, Sikiotis and Kirkitsos (1995) compared the damage effects of NO_2 and SO_2 on Pentelic marble and concluded that the corrosion rates are comparable. Amoroso and Fassina (1983) pointed out that the most significant NO_x role is possibly in the catalytic oxidation of SO_2.

In addition to its role in atmospheric damage, NO_x also represents a precursor for HNO_3 formation. The contribution of HNO_3 in atmospheric damage processes has so far received a little or no attention. Within the *Multi-Assess* project, Ferm et al. (2006, 2005, 2004; see also Tzanis et al. 2009) and Samie et al. (2005, 2006, 2007a, b) started a systematic investigation of the influence of HNO_3 on atmospheric damage. Interestingly, the results indicated that the damage effect of HNO_3 by far exceeds that of SO_2, by a factor between 2 and 20 depending on the material. The concentration of HNO_3 is generally lower than that of SO_2. Yet, due to the aggressiveness of HNO_3 compared to SO_2, the effects of SO_2 and HNO_3 can thus be comparable in the present multi-pollutant situation. HNO_3 is a strong acid, and its salts are very hygroscopic, which in contact with cultural heritage materials can lead to enhanced deterioration. A high sticking coefficient of HNO_3 is the main drawback when designing an atmospheric damage experiment, especially in terms of controlling and monitoring the actual HNO_3 concentration in the exposure chamber and the deposited amount on a sample (Samie et al. 2005). Samie et al. (2005) showed that even a small change in RH significantly influences the adsorbed HNO_3 concentration. Although HNO_3 has high affinity to most construction materials, no commercial online HNO_3 analyzers exist, and accordingly, HNO_3 concentrations are not routinely monitored (Samie et al. 2005). Therefore, as a part of the *Multi-Assess* project, a passive sampler for gas-phase HNO_3 has been developed (Ferm et al. 2004), validated, and placed over all ICP-Materials measuring sites.

Despite its importance in atmospheric damage, there is still a lack of knowledge on the influence of HNO_3 on other building materials, such as stone, mortars, and glass. Nevertheless, a few groups have investigated the impact of HNO_3 on calcareous stone material (Haneef et al. 1992; Kirkitsos and Sikiotis 1995, 1996; Sikiotis and Kirkitsos 1995); the common conclusion was that HNO_3 reacts with $CaCO_3$ forming calcium nitrate ($Ca(NO_3)_2$). As other nitrate salts, it is easily water-soluble and is washed away from the stone, meaning that precipitation, therefore, causes deterioration. Fenter et al. (1995) confirmed that calcite is an excellent sink for HNO_3. The reaction proceeds by absorption of the gas on the surface and is highly dependent on the presence of water. They showed that CO_2 and water are the products of a reaction with a delay in the desorption process.

The pronounced increase in tropospheric O_3 concentration is a consequence of a change in the pollution situation resulting from the increase in VOC and NO_x concentration. O_3 can reach extreme values in urban environments (Tidblad and Leygraf 1995). Huang et al. (2019) noticed that the atmospheric damage effect in the Guangdong province (China) is a consequence of the synergistic action of SO_2 and O_3. The synergy does include not only the ability of O_3 to oxidize SO_2, but also the ability to form oxides, hydroxides, or other oxygen-containing reaction products with a small amount of SO_2. As already noted, O_3 plays an essential role in the formation of HNO_3; therefore, O_3 can influence the atmospheric damage indirectly by producing different reactive species, which can be more aggressive to the cultural heritage material (stone and metal) than O_3 itself. Laboratory studies of the O_3 influence on atmospheric damage are relatively rare. Svensson and Johansson (1993) showed that O_3 oxidizes SO_2 much more efficiently than NO_2 and therefore had considerably higher impact on atmospheric damage, than synergy of NO_2 and SO_2. Besides, they found that the effect of O_3 alone is negligible. However, in the literature, it is most often recognized that the role of O_3 is more emphasized when acting together with other gas pollutants. Following this, Screpanti and De Marco (2009) reported that a high concentration of O_3, which is in synergistic action with other pollutants, leads to atmospheric damage exceeding the tolerable thresholds for cultural heritage buildings.

Pollutants present in the atmosphere influence different materials in synergy with each other and in complex combination with environmental factors. The synergistic effect of a mixture of pollutants has been categorically demonstrated in laboratory studies (Svensson & Johansson 1993; Tidblad and Leygraf 1995).

Role of PM on atmospheric damage

In the past, until the *Multi-Assess* project (see Table 1), it had been given far less attention to the role of PM in the atmospheric damage process than to the gaseous pollutants. Nevertheless, Kucera and Fitz (1995) have recognized that with decreasing SO_2 concentration, PM relative importance increases. During the US-Dutch International Symposium on Aerosols (Lee et al. 1985), Van Aalst (1986) suggested that PM might have more complex effects on material damage apart from soiling. Lipfert et al. (1985) proposed that the deposition of acidic PM, (e.g., H_2SO_4 in PM liquid layer or ammonium bisulfate (NH_4HSO_4) particles) can result in a direct surface attack on the metal material, inducing corrosion. They also recognized that the deposition of salts, such as NaCl or $(NH_4)_2SO_4$, can increase the time of wetness and thus increase the effective deposition of SO_2, and consequently increasing the corrosion. Ten years later, Sabbioni et al. (1996) showed that PM influence the deterioration of stone material (marble, Travertine, and Trani stone) due to the acidity and catalytic characteristics of carbonaceous particles in the formation of H_2SO_4 and HNO_3.

The *Multi-Assess* project is the first project, where on the basis of a combination of laboratory measurements and modeling analysis, the role of PM in the atmospheric damage processes was disclosed. The short-term goal of the accelerated laboratory tests was to identify the specific atmospheric damage effects of PM. From the long-term atmospheric damage rate, it would be unimaginable to distinguish the PM influence only due to its complexity and due to the combination with all other factors in the multi-pollutant situation. Therefore, laboratory studies are an essential tool for studying fundamental relationships between correlated variables. In the frame of *Multi-Asses* project, Kucera (2005) tested the influence of different PM on carbon steel, zinc, copper, and medieval glass. PM included, among others, inert particles such as fused, crushed alumina Al_2O_3, separated diatomaceous earth SiO_2, and real dust particles. To explore the influence of the chemical composition of PM on the building material, Kucera (2005) fused Al_2O_3 and SiO_2 particles with ammonium nitrate (NH_4NO_3), sodium sulfate (Na_2SO_4), and sodium chloride (NaCl). In addition, they also tested the influence of pure $(NH_4)_2SO_4$ with different size distributions. The tested materials encompassed various metals (carbon steel, zinc, and copper) and glass. They found out that the aqueous fraction of PM represented almost 50% of the overall PM weight at RH 70–80%. Consequently, the adsorbed water may have contributed to the dissolution of water-soluble PM components. Kucera (2005) observed that the chloride had a higher atmospheric damage potential than dust particles to metal material. Chloride ions are chiefly corrosive for metal material (the critical RH for Cl^- is 75%), especially when combined with the higher temperature. Following this, the authors detected a very high corrosion rate of metal material in the presence of chloride. They further assumed that other salts, such as NH_4NO_3, $(NH_4)_2SO_4$, and NH_4HSO_4, can also be important for atmospheric damage due to their hygroscopic properties. The approach proposed by Kucera (2005) demonstrated that, from all metals, carbon steel is the most sensitive material to corrosion caused by PM. Importantly, they showed that copper and zinc also undergo corrosion induced by PM, but at a lower rate (Tidblad et al. 2017, 2012). Within the Multi-Assess project, Tzanis et al. (2011) exposed different structural materials (metals, glass stone, and concrete) to air pollution at different heights at a station in Athens. The highest rate of atmospheric damage (weight loss/change of material) was recorded for unalloyed carbon steel at the height of 18 m, while the lowest was at 6 m. For zinc and copper, the atmospheric damage was almost constant with the height and about four times lower than for steel. Bronze was the only material that showed increased mass during the exposure to air pollution. The authors concluded that copper and bronze have almost the same atmospheric damage rate and are less sensitive to air pollution. Chemical analysis of the deposited mass showed that sulfate dominated the other substances. For the medieval glass material, they showed that the leaching depth of K and Ca increases with increasing exposure height. For all stone samples exposed at an unsheltered position, a significant surface recession was noticed. Such long-term exposure studies are useful for determination of the rate of atmospheric damage; however, it is difficult to discriminate between the influence of gas pollutants and the PM with such experiments. Wallinder et al. (2014) showed that the high amount of chloride deposited with PM increased the corrosion rate on bronze. The authors recognize the formation of a two-layered patina.

The inner layer comprises Cu_2O, whereas the outer layer consists of $Cu_2(OH)_3$. They additionally detected SnO_2 as a minor constituent in the patina layers. With time, the outer layer patina becomes more strongly bound to the underlying oxide, which causes a decrease in corrosion rate. However, the authors also observed flaking of the adhering outer layer. They attributed this phenomenon to the formation of CuCl, which can be transformed to $Cu_2(OH)_3Cl$ due to the reaction with moisture and oxygen, causing physical stress inside the patina layer. A high amount of chloride in PM is mostly attributed to the influence of marine environment. Since the marine aerosol study is a complex field, marine aerosols' influence upon atmospheric damage needs to be reviewed separately. Button and Simm (1985) speculated that atmospheric PM could cause stainless steel corrosion. In particular, saline particles of ammonium sulfate or sodium chloride, inert siliceous particles, and carbonaceous deposits influence corrosion pitting and rusting of stainless steel. Another key outcome, as a result of the *Multi-Assess* project, is the finding that the particle size also affects the atmospheric damage rate. Chen et al. (2005) showed that smaller particles cause higher atmospheric damage rates than larger particles at an equal mass of deposition. The authors also noted that smaller particles (< 10 µm) are more evenly distributed than larger particles (< 100 µm). In an independent study, Li and Hihara (2014) and Risteen et al. (2014) recognized that the size and distribution of PM can influence the initiation and propagation of the corrosion process of carbon steel and iron in a more complex way. Azmat et al. (2011) showed that in the presence of PM, zinc corrosion occurs by disrupting protective oxide films and subsequently establishing electrochemical cells, whereby new oxide layers are formed, which may be dissolved again by typical acidic PM. Lobnig et al. (1994) demonstrated that copper reacts with $(NH_4)SO_4$ particles only if the critical RH is exceeded. In this case, the authors noticed that copper corroded heavily, which led to the formation of a thick Cu_2O layer.

Despite a detailed approach proposed in the *Multi-Asses* project by Kucera (2005) and Chen et al. (2005) (and other individual studies), they all consider only the PM's inorganic fraction without taking into account the organic fraction. Thus, the future investigations of atmospheric damage on different materials should definitely include the influence of organic matter. Although it is known that different organic compounds can act as efficient inhibitors for metal corrosion (Abd El-Maksoud 2008; Bhosle and Wagh 1992), some organic compounds promote the metal corrosion process. Korshin et al. (2000) demonstrated that natural organic matter affects the rate of metal leaching from the surface of leaded brass and the morphology of lead-containing corrosion products. In the absence of natural organic matter, thin hexagonal plates of hydrocerussite ($Pb_3(OH)_2(CO_3)_2$) accumulated on the corroding lead. Notably, in the presence of organic matter, the authors noticed that the growth of the crystals of hydrocerussite was inhibited, and the formation of amorphous hydrated surface film was promoted. This resulted in an increase in short- and long-term lead leaching. Gjertsen et al. (2021) investigated the influence of organic acids (formic, acetic acid) on the corrosion of carbon steel at different pH. They showed that in the presence of organic acids and lower pH, the corrosion rate of carbon steel increases. However, the pH was not the most critical factor; the type of acid species involved and the concentration of undissociated acid in the solution considerably influenced the corrosion rates. Amri et al. (2011) and Kahyarian et al. (2017) anticipated that acetic acid acts as a local reservoir of protons near the corroding metal surface rather than participating electroactive in the cathodic part of the corrosion process. Johnson and Leygraf (2006b) investigated the influence of acetic acid and acetaldehyde on the corrosion of zinc surfaces. Independent of the RH, acetic acid and acetaldehyde form zinc oxide and zinc acetate as a reaction product on the zinc surface. The authors concluded that the kinetics of zinc-acetate formation is faster than zinc oxide formation during exposure to acetic acid compared to acetaldehyde. They also proposed a reaction mechanism that includes several steps in both acetic acid and acetaldehyde. The reaction begins with the adsorption of acetate species on the surface, followed by ligand exchange between acetate and surface hydroxyl groups. The acetate species coordinates with zinc to form a surface zinc-acetate ligand, which induces the dissolution of zinc and precipitation of zinc acetate. Johnson and Leygraf (2006a) studied the influence of formic acid on zinc corrosion. They demonstrated that the major corrosion product was zinc format. Formic acid does not undergo to physisorption or solvation on the surface as in the case of acetic acid. In the case of formic acid, the water adlayer plays an important role, and the authors found that at higher RH, the corrosion rate was higher. It was also shown that the formation of zinc carboxylate was faster in the presence of formic acid than acetic acid. However, similar carboxylate induced dissolution mechanisms were proposed for both acids. It is important to note that formic, acetic, oxalic, and many other carboxylic acids were determined in the atmospheric PM (Kitanovski et al. 2011); however, their exact role in atmospheric damage of other materials (bronze, glass, carbonate, and silicate stone) is still unknown and needs to be investigated in the future studies. In addition, other different organic compounds present in atmospheric PM can be adsorbed at the material surface and affect the atmospheric damage indirectly by increasing the ability to wet the surface by increasing the hygroscopicity (Marsh et al. 2017).

Nowadays it is known that atmospheric damage of stone materials induced by PM can proceed via two mechanisms, i.e., (i) crystallization of salts from solution and (ii) hydration of salts that can exist in more than one hydration state (Watt et al. 2008). The crystallization process inside pores of stone material can cause stress, which is sufficient to overcome the stone tensile strength (Casati et al. 2015; Price and Doehne 2011). If the migration of water (containing salts) to the surface of stone is slower than the drying rate, then the solute crystallizes within the pores, at varying depths, causing crumbling and powdering of the material (Van Grieken et al. 1998). One should also consider that the composition of PM is highly complex and not completely revealed and as such can induce different processes causing material degradation. Therefore, future investigations should focus on the composition of PM in connection with atmospheric damage. More recently, Fermo et al. (2018) have compared solid deposits on the facade of the Milano cathedral (Italy) with the air monitoring data; they did not find any direct correlation between the atmospheric gaseous precursors and the related ions in the solid deposit. In contrast to this, Török et al. (2011) compared the content of polyaromatic hydrocarbons (PAH) in ambient PM and in the crust of historical buildings; they recognized the important role of PM in accumulating PAH. Additionally, Di Turo et al. (2016) identified the atmospheric PM as the factor most responsible for outdoor material recession.

Nevertheless, very little can be found on what occurs after the PM is deposited. In fact, no studies exist on the chemical effect of the most common organic PM on the cultural heritage material degradation. Accordingly, more research about the chemistry (e.g., heterogeneous reactions) between the deposit and substrate, and the deposit and surrounding polluted atmosphere is needed.

Dose–response functions for atmospheric damage

Another significant contribution of the *Multi-Assess* project is the development of dose–response functions (DRFs) for material deterioration, where the new multi-pollution situation is considered and included in the function. In terms of air pollution, DRF is defined as a relationship between the material deterioration and concentration of pollutants combined with other environmental factors (Christodoulakis et al. 2017). The DRF links the dose of pollution, measured in ambient concentration and deposition, to the rate of material deterioration. DRF is useful due to predictive abilities and in general, it plays an essential role in different domains of science and engineering (Bhaskar et al. 2004; Ninic and Stark 2007). DRF for material deterioration caused by air pollution has been known for a long time. In the past, it considered only the prevailing SO_2, and many different DRFs for this specific situation can be found in the literature (Watt et al. 2009). As the pollution situation has changed, the need for new functions arose. To quantify this in the form of DRF, a multi-pollutant exposure program was initiated within ICP-Materials (Kucera et al. 2007). The program took place from 1997 to 2001 and included carbon steel, zinc, copper, bronze, and limestone throughout 1, 2, and 4 years. The data collected within the multi-pollutant exposure program were supplemented with the data on HNO_3 and PM, which were obtained during the *Multi-Assess* project. Such data allowed Kucera et al. (2007) to develop a DRF, including both the effect of time and the new parameters of HNO_3 and PM. Besides, in the statistical analysis for the DRF development, Kucera et al. (2007) included additional parameters, such as time, the concentration of gaseous pollutants, temperature, RH, amount of precipitation, pH of precipitation (Watt et al. 2009), and the total amount of deposited PM. Table 3 shows the developed DRFs valid for the multi-pollution situation for carbon steel, zinc, copper, cast bronze, and Portland limestone.

A more in-depth explanation of the corrosion DRF and how it is derived can be found elsewhere (Kucera 2005; Kucera et al. 2007; Watt et al. 2009). From Table 3, it can be seen that Kucera et al. (2007) considered SO_2 in the DRF for almost all materials. Although the SO_2 concentrations have been significantly reduced, it is still essential and as such comprised in the multi-pollution DRF. HNO_3 as a parameter of the multi-pollutant DRF is essential for zinc and limestone, whereas PM_{10} was incorporated in the carbon steel, cast bronze, and limestone DRFs. The deeper meaning of DRFs is to use it for mapping areas of increased risk of corrosion, and such maps are a powerful tool to show the effect of pollution on cultural heritage objects. More about the methodology of mapping of critical areas can be found elsewhere (De la Fuente et al. 2013; Manual 2008; Svuom et al. 2007). Likewise, the DRF can also estimate the corrosion costs and also tolerable levels of pollution (Kucera 2005).

The newly developed multi-pollutant DRF indeed includes the effect of PM, but only for carbon steel, cast bronze, and limestone. More long-term exposure and laboratory studies are needed to determine the effect of PM upon other materials. Such results for different materials should then be used as input data for developing a more robust DRF where PM will be included. However, in future investigations, more attention should be given to PM-specific compounds, potentially harmful to cultural heritage material. In addition, more field data on the organic part of PM are needed, especially more studies on the interactions are needed for known OC components, to thoroughly understand the role of PM in the atmospheric damage process. Different carboxylic acids are a good example of organic compounds present in atmospheric PM, which can be potentially harmful to different metals, but are not yet included in any DRF.

Table 3 Dose–response functions (DRFs) developed within the *Multi-Assess* project and temperature functions for unsheltered materials (Kucera et al. 2007; Watt et al. 2009)

Material	Dose–response-function Temperature function
Carbon steel	$\mathrm{ML} = 29.1 + \mathrm{t}^{0.6}\{21.7 + 1.39\left[\mathrm{SO_2}\right]^{0.6}\mathrm{Rh_{60}}\mathrm{e}^{\mathbf{f(T)}} + 1.29\mathrm{Rain}\left[\mathrm{H^+}\right] + 0.593\mathrm{PM_{10}}\}$ (1) $\mathrm{f(T)} = 0.15(\mathrm{T} - 10)\mathrm{whenT} < 10°C, -0.054(\mathrm{T} - 10)\mathrm{otherwise}$
Zinc	$\mathrm{ML} = 1.82 + \mathrm{t}\{1.71 + 0.471[\mathrm{SO_2}]^{0.22}\mathrm{e}^{0.018\mathrm{Rh}+\mathrm{f(T)}} + 0.041\mathrm{Rain}\left[\mathrm{H^+}\right] + 1.37\mathrm{HNO_3}\}$ (2) $\mathrm{f(T)} = 0.062(\mathrm{T} - 10)\mathrm{whenT} < 10°\mathrm{C}, -0.021(\mathrm{T} - 10)\mathrm{otherwise}$
Copper	$\mathrm{ML} = 3.21 + \mathrm{t}\{1.09 + 0.00201[\mathrm{SO_2}]^{0.4}\left[\mathrm{O_3}\right]Rh_{60}e^{\mathrm{f(T)}} + 0.00878\mathrm{Rain}\left[\mathrm{H^+}\right]\}$ (3) $f(T) = 0.083(T - 10)whenT < 10°C, -0.032(T - 10)otherwise$
Cast bronze	$\mathrm{ML} = 1.33 + \mathrm{t}\{0.00876\left[\mathrm{SO_2}\right]\mathrm{Rh_{60}} \cdot e^{\mathrm{f(T)}} + 0.0409\mathrm{Rain}\left[\mathrm{H^+}\right] + 0.0380\mathrm{PM_{10}}\}$ (4) $\mathrm{f(T)} = 0.060(\mathrm{T} - 11)\mathrm{whenT} < 11°\mathrm{C}, -0.067(\mathrm{T} - 11)\mathrm{otherwise}$
Portland limestone	$\mathrm{R} = 3.1 + \mathrm{t}\{0.85 + 0.0059\left[\mathrm{SO_2}\right]\mathrm{RH_{60}} + 0.054\mathrm{Rain}[\mathrm{H^+}] + 0.078\left[\mathrm{HNO_3}\right]\mathrm{Rh_{60}} + 0.0258\mathrm{PM_{10}}\}$ (5)

ML, mass loss [g m^{-2}].

R, surface recession, [µm].

t, exposure time [years].

Rh_{60}, relative humidity – 60, when Rh > 60, 0 otherwise [%].

T, temperature (annual average) [°C].

$[SO_2]$, sulfur dioxide concentration (annual average), [µg m^{-3}].

$[O_3]$, ozone concentration (annual average), [µg m^{-3}].

Rain, amount of precipitation (annual average), [m $year^{-1}$].

$[H^+]$, hydrogen ion concentration [mg L^{-1}].

$[HNO_3]$, nitric acid concentration (annual average), [µg m^{-3}].

PM_{10}, particulate matter concentration (annual average), [µg m^{-3}].

Soiling

Measurement of soiling

To quantitatively describe the degree of soiling, different methods based on various parameters can be used (see Table 4). Because no unique way for direct analysis of soiling is available today, the measurement of soiling comprises at least two parameters obtained by two different methods. In the next section, different approaches of soiling measurements as well as the main gaps will be presented.

Mass-based methods

According to Terrat and Joumard (1990), two types of mass-based methods exist; (a) classical deposit plate and (b) simple plate method. The deposit plate method is standardized according to standard NF × 43.007. Schultz (1983) used stainless steel plates (50 × 100 mm) coated with an adhesive layer of methylpolysiloxane to collect PM. Particles collected on the surface are removed utilizing dichloromethane (DCM) and weighted. The results are then expressed in g m^{-2} $month^{-1}$. The main disadvantage of the classical deposit plate method, recognized by Terrat and Joumard (1990), is that particles cannot bounce back to the environment, as it occurs with any other surfaces exposed to the environment. They further concluded that the use of DCM for removing PM leads to the dissolution of the coating layer, which is not considered during weighing. Because of these drawbacks, the same authors (Terrat and Joumard 1990) suggested the simple plate method. This method consists of exposing low anodized aluminum plates in a sampler holder in the vicinity of the objects of interest. They proposed to use clean and dry plates weighed in the laboratory on a balance of 0.1 mg precision before exposure. Even if more PM can be captured with the deposit plate method, Terrat and Joumard (1990) prefer the simple plate method because it reflects the actual conditions and it is very easily used. Nowadays, in the field of cultural heritage, the simple plate method is mostly used for passive particle collection, with some modifications concerning the material and the shape of the deposition plate (Figgis et al. 2016; Kucera 2005).

Within the *Multi-Assess* project, Ferm et al. (2004, 2006) developed a passive collector for PM that uses small surrogate surfaces. The net particle deposition is similar to the deposition on the material of cultural heritage objects. In principle, the passive collectors for PM work in the same way as the simple plate method. The main difference between the two is in the nature of the material on which the particles are collected. Kucera (2005) and Tzanis et al. (2009) later reported that such small passive collectors are ideal for sampling around cultural heritage objects, because

Table 4 Overview of the methods used in soiling measurements

Method	Advantages	Shortcomings	Reference
Mass-based methods:			
Classical deposited plates	-More PM can be captured, especially at the beginning of sampling	-Particles do not bounce back to the environment as it occurs in reality -Use of DCM leads to the dissolution of all organic components, which is not considered during weighing	(Schultz 1983), (Nazaroff and Cass 1987), (Maro et al. 2014)
Simple plate	-Reflects the actual condition in regard to particle bouncing -Easy to use	-Metal deposition surface is not relevant for all cultural heritage materials -Metal deposition surface is not inert	(Terrat and Joumard 1990), (Pesava et al. 1999)
Passive PM collector	-Surrogate surfaces (Teflon) are inert -net particles deposition is similar to Deposition on different materials of cultural heritage -Small Teflon filters can be easily and accurately weighted	-Teflon filters need to be spattered for SEM analysis	(Ferm 2004; Ferm et al. 2004, 2006), (Tzanis et al. 2009), (Watt et al. 2008, 2004), (Kucera 2005)
Optical methods:			
Transmission	-Mass of the deposited particles can be determined without weighting	-Limited to materials that are transparent -depends on the thickens of the deposit (saturation phenomena)	(Pedace and Sansone 1972), (Ionescu et al. 2006), (Lombardo et al. 2005)
Reflectance	-Can be used for any kind of material -does not depend on the deposit thickens - Small mass of deposited PM can be determined	-Follows only the change in color without telling from where the color is coming (deposit or substrate)	(Chudnovsky and Ben-Dor 2009), (Watt et al. 2008, 2004), (Figgis et al. 2016; Haynie and Lemmons 1990), (Terrat and Joumard 1990), (Hamilton and Mansfield 1993)
Rephotography and image processing	-It captures only the color, which does not necessarily correlate with the soiling	-Captures the environmental impact of rain washing and possibly pollution on spatially disparate locations	(Thornbush 2014a, 2010, 2014b; Thornbush and Viles 2004)

the sampling is silent, it does not need electricity, can be used for long-term integrative sampling, and can be performed discretely. On the other hand, Klimm et al. (2014) and Al-Hasan and Ghoneim (2005) used the same methodology for photovoltaic cell soiling and recognized that small surrogate surfaces (filters, deposition plates) could be easily and accurately weighed before and after soiling and then returned to the field again. Based on preliminary results, Ferm (2004, 2004) tested five different materials (Teflon, glass stainless steel, glass fiber, aluminum oxide, and polycarbonate) and two different surrogate surface shapes (cylindrically or flat) during the *Multi-Assess* project. The authors determined that Teflon surrogate surface (flat or cylindrical) is the most appropriate material for passive sampling of PM in terms of soiling.

Nonetheless, characterizing the soiling only by the mass reflects the quantity of accumulated PM, which can be useful for studying the physics of soiling. However, the entire accumulated PM does not necessarily produce the soiling effect. Soiling effect depends firstly on the size of the particles and on the composition and color of the particles. Al-Hasan and Ghoneim (2005) and Molki (2010) pointed out that a newly-deposited PM may settle on the existing particles and may increase the PM mass but not the soiling effect, which can introduce uncertainties in the measurement. It is also important to recognize that PM with the same mass and the same size does not necessarily produce soiling effects equally. Therefore, depending on the chemical composition of PM, the soiling effect can be different. It is well known that some compounds have a large absorption cross section, which means that even if they are present in a low quantity in PM, they absorb light more effectively and consequently produce the soiling effect more pronounced. One group of such typical compounds are nitroaromatic compounds (NAC); they are major constituents of BrC, which is an important constituent of atmospheric PM (Laskin et al. 2015).

Nevertheless, Haynie (1985; see also Haynie and Lemmons 1990) and Creighton et al. (1990) claimed that soiling can also be quantified by surface coverage and the percentage of the surface covered by PM can be calculated from the size distribution of the deposited PM. They demonstrated that the size distribution can be obtained by SEM (scanning electron microscopy) analysis of the surrogate surfaces. It can be noted that the surface coverage method faces the same problem as the mass-based method. PM can contain different substances with different absorption cross section (Andreae and Gelencsér 2006), meaning that the same surface coverage can produce a different degree of soiling effect, depending on the chemical composition.

Consequently, by obtaining only one parameter (mass or surface coverage), the soiling effect cannot be accurately described. It is crucial to recognize the importance of the chemical composition of the deposited PM, which reflects the pollution situation, and it should be included as a vital parameter to exactly describe soiling.

Measurement of soiling: reflectance and transmittance methods

In general, two optical methods can be used for soiling measurements (i) light transmission and (ii) light reflectance measurements.

Transmission measurement According to Terrat and Joumard (1990), light transmission is limited to materials that transmit light, such as glass and various fiber filters. They investigated light transmission of a soiled Tergal cloth and concluded that the soiling particles deposited on a Tergal cloth follow a law similar to the Beer-Lambert law. They also demonstrated that the mass of soiling particles could be determined with the light transmission method. Pedace and Sansone (1972) proposed that low quantities of particle deposits can be measured by this method. Terrat and Joumard (1990) pointed out that the main drawback of the method, besides being suitable for only certain kinds of material, is the limitation due to the saturation phenomenon, which occurs with higher PM deposition level. Today, the transmission method is mostly used for quantifying soiling on glass materials via *haze* measurements.

Reflectance measurement Numerous studies report the change in reflectance factor as an index of soiling without emphasizing the change in reflectance spectrum. In contrast, other studies report only the luminance (only the L axis of the *CIE* lab coordinate system — International Commission on illumination — Commission Internationnale d'Eclairage) under the term "reflectance." Therefore, it is important to precisely define the terms concerning reflection measurement. Reflection refers to the phenomenon when a part of radiation is returned after rebounding off of a specific material surface. The reflected radiation can be regular, called specular reflection, when the law of geometric optics is followed; or diffuse reflection, when a particular part of the reflected radiation is regular, and a part of it is diffused (Fig. 4).

Depending on the material, not all the incident radiation is reflected; the *reflectance* is the ratio of the reflected radiant flux to the incident flux (Fig. 5), measured in watts (W) and usually denoted by the Greek letter ρ. It is essential to distinguish between the reflectance and reflectance factor; *the reflectance factor* (R) is defined as the radiant flux ratio reflected in the direction delimited by a given cone to the reflected radiant flux reflected in the same direction by a perfect reflecting diffuser identically irradiated. The reflectance factor can only be useful if the irradiation angular

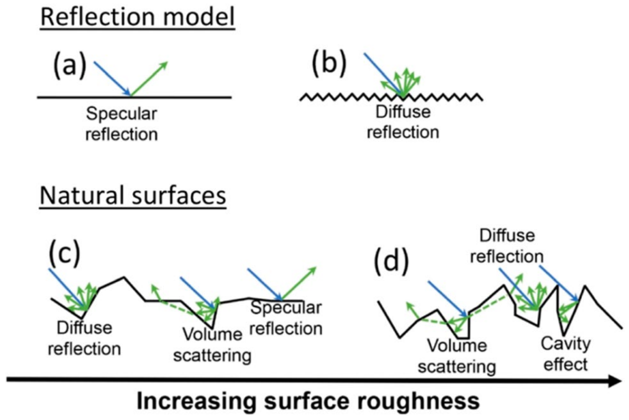

Fig. 4 Interaction of light with a smooth surface (**a**) that displays specular reflection and a rough surface (**b**) that displays diffuse reflection. Natural surfaces are more irregular and increasing the roughness decreases specular reflection (**c**) and promotes diffuse reflection (**d**) (Rost et al. 2018)

distribution and observation cone are defined. With this in mind, results from different instruments can be compared.

Besides the reflectance or reflectance factor, which is always connected to a particular wavelength, it is imperative to report the used measuring geometry. However, the fundamental understanding of the nature of reflectance is not in the scope of this paper, but more detailed information about the notation of the used geometry can be found elsewhere (Illumination 1998, Schanda 2007).

Considering the soiling measurement of cultural heritage materials and today's pollution situation, it would be more appropriate to report the overall color change (ΔE) and the accompany vectors, which represents total color change of a specific surface in comparison to the surface starting point (blank). In a recently published review paper, Vidal et al. (2019) recognized the importance of documenting the overall color change or change in the chroma (ΔC). The ΔE is defined within *CIE*'s color space, and it represents the Euclidean distances in this color space. Because of the change of the pollution situation, the perception of soiling in the future will not be "white" or "black" like it was in the past, and the representation of soiling in the color space would give additional information about the soiled layer's nature. In the literature, such representation of soling is relatively rare. Therefore, the measurements and representation of reflectance in the way described herein, combined with the measurements of mass and surface coverage, should be used as the primary input parameters for developing a prediction tool for soiling, keeping in mind that the chemical composition also plays a crucial role in these processes.

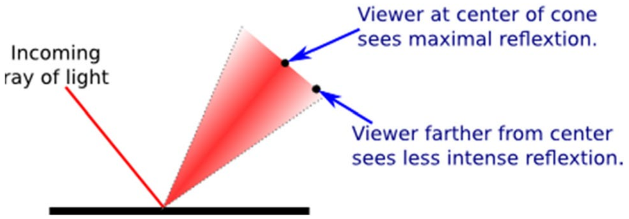

Fig. 5 Principle of reflectance factor

Moreover, Chudnovsky and Ben-Dor (2009) demonstrated a good example of using reflectance spectroscopy as a suitable tool for monitoring PM deposition. They showed that reflectance spectral measurement combined with multivariate calibration analyses enables the detection of small amounts of deposited PM. The authors also indicated that the chemical nature of sample influences the absorption signals; therefore, the reflectance spectral measurement has a potential not only to quantify, but also to define the composition of PM.

Soiling of cultural heritage material

Soiling of different building materials was recognized in the late 1950s of the twentieth century by Carey (1959), and since then, it has occupied the scientific attention. Even if the first systematic long-term exposure study of soiling started within the *Multi-Assess* project (O Hanlon et al. 2004), (Ferm et al. 2004), several independent studies contributed significantly to the understanding of soiling processes (see Table 5). Hancock et al. (1976) showed that when dark PM covers 0.2% of the white surface, the human eye can detect the difference between the soiled and unsoiled areas. To expand the understanding of soiling, a definition of soiling based on public opinion was suggested. Therefore, together with Grossi and Brimblecombe (2004), they used these postulates from Carey (1959) and Hancock et al. (1976) to establish the esthetic thresholds that could define levels, at which building appearance becomes publicly unacceptable. Hence, within the EU 5FP CARAMEL project, the authors established the tolerable level of soiling as 35% loss in reflectance before taking any action. However, they concluded that when the loss of reflectance is greater than 35%, it triggers a significant adverse public reaction. In line with this, the same authors defined the tolerable maintenance cycles and for the case of cultural heritage objects, they found a period of 10–15 years to be appropriate.

Roth and Anaya (1980) showed that the deposition, accumulation, and loss in reflectance due to the deposited PM is a complex function of exposure conditions. Their results indicated that small particles adhere strongly to the surface and are less easily removed by the natural cleaning processes.

Table 5 Overview of the main articles which contributed to the understanding of soiling

Individual studies of soiling	Soiling studies within the ICP-materials
(Pedace and Sansone 1972), (Beloin and Haynie 1975), (Yocom 1979), (Roth and Anaya 1980), (Haynie 1986, 1985), (Lee et al. 1985), (Yocom and Kawecki 1986), (Lanting et al. 1986), (Mansfield 1989), (Creighton et al. 1990), (Haynie and Lemmons 1990), (Hamilton and Mansfield 1993), (Saiz-Jimenez 1993), (Brimblecombe 1996), (Pio et al. 1998) (Grossi et al. 2003, 2006; Grossi and Brimblecombe 2004), (Brimblecombe 1996, 2003, 2013; Brimblecombe and Grossi 2005; Brimblecombe et al. 2007, 2009)	(O Hanlon et al. 2004), (Watt et al. 2004), (Lombardo et al. 2005), (Watt et al. 2008, 2004), (Melcher et al. 2008), (Tzanis et al. 2009), (Verney-Carron et al. 2012)

The authors also noticed that a larger number of small particles increased the reflectance loss. The deposition mechanism responsible for particulate accumulation depends upon the particle size and orientation of the deposition surface. However, regardless of the orientation, particles smaller than 100 nm are accumulated by convective diffusion on all surfaces. The majority of such small particles are water-soluble; in the presence of condensed moisture or high humidity, they can be dissolved and subsequently recrystallize into larger individual particles or onto existing PM. Contrary to this finding, Haynie and Lemmons (1990) deduced that coarse mode particles contribute more to the soiling of both horizontal and vertical surfaces. The authors also demonstrated that rain interacts with the deposited particles contributing to soiling by dissolving or disaggregating particles and leaving a stain. Yocom and Kawecki (1986) postulated that soiling happens within different mechanisms, which comprise several steps or sometimes equilibrium states. According to them, PM can be deposited on the surface by different mechanisms, such as gravitational settling, impaction, interception, diffusion, and thermophoresis. If particles have an electrical charge, also, electrophoresis may contribute significantly. These mechanisms can differ depending on the physical and chemical properties of particles, surface characteristics, local meteorology, and rainwater pathway after it hits the building surface. In the classical textbook for atmospheric aerosols physics by Hinds (1999), it can be found that the deposition mechanism consists of two steps: transport and the interaction with the surface.

Nevertheless, Corn (1976) showed earlier that the relative strength of PM deposition on a surface and loss of reflectance depend preferably on the particle size distribution and the particles' color relative to the color of the deposition surface. He also demonstrated that the interaction between the PM and the surface is, in principle, adhesion and it depends on the particle size; smaller particles adhere stronger to surfaces than larges particles, which is in accordance with the study of Roth and Anaya (1980). According to Hinds (1999), adhesion depends on the roughness of the surface; surfaces that produce more asperities with the particles are more effective in soiling. Besides, particles with a liquid layer adhere more easily to the surface.

Yocom and Kawecki (1986) suggested that the relative surface coverage can approximate the soiling potential of PM. Consequently, they defined the soiling potential of PM as the area that a given quantity of PM could cover if evenly distributed over a surface. So, the authors concluded that the PM size distribution expressed with the surface area mode gives a preliminary estimation of the size of particles that are most potent for soiling. However, Van Aalst (1986) and Haynie (1986) reported that the soiling and deposition of PM depend not only on the size, but also on the deposition velocity. The deposition velocity varies with particle size, and the actual soiling of a surface will not necessarily agree exactly with the soiling potential. Moreover, PM with a diameter of less than the wavelength of visible light may not influence the soling (by surface area coverage) to the same degree as larger PM (Bohren and Huffman 2008).

Although soiling by itself, according to Newby et al. (1991), does not cause direct material damage, the increased frequency of cleaning, washing, or repainting of soiled surfaces could become a considerable economic cost and can reduce the soiled material useful life, besides also damaging the heritage object's original surface. So far, soiling has been discussed only in terms of its physical nature, and unfortunately, there is a lack of literature concerning the chemistry of soiling. Therefore, for a better understanding of soiling, there is an urgent need to investigate soiling more holistically. Future research in this field could focus more on the chemistry of soiling and finding connections or overlaps between soiling and material deterioration. The existing definition of soiling considers only the deposition of PM without considering chemical interaction with the substrate and/or the reactive gases which coexist with PM.

As a vital part of atmospheric OC, primary BrC or BrC formed at the surface through numerous reactions, together with other components of OC, will shape the future definition of soiling, which will also account for a changed status of atmospheric pollution. Soiling, as a complex process resulting from the deposition of different types of particles and their shapes, requires a limitation on the definition of what soiling is. There is an urgent need to redefine the soiling and correlate soling with specific soiling agents and recent finding in the field of atmospheric chemistry. In the past, it was thought that BC is the primary soiling agent. Still, by changing the pollution situation, many other species can cause soiling, particularly different groups of organic compounds, such as BrC. As soiling is a visual damage, it depends on human perception, which is hard to measure accurately (Brimblecombe et al. 2007; Grossi and Brimblecombe 2004).

As previously stated, in most recent studies, the trends and levels of soling are investigated by measuring the loss of reflectance of white surfaces or loss of transmission through a glass (Vidal et al. 2019). According to the redefinition of soiling, there is a demand for new methodologies to measure the rate of soiling. Within these new methodologies, various parameters should be measured to describe soiling and to understand the processes behind. It is essential to include all possible species that can potentially contribute to the soiling phenomena. Thus, it is crucial not only to identify components contributing to the soiling by pure chemical analysis, but also to clarify the accompanying mechanisms.

Models for soiling

In the past century, different soiling models were developed to predict the soiling rate and estimate the risk of soling to valuable cultural heritage material. The soiling model can be useful in policy terms only if it is based on physical laws, permitting soling rates to be described considering the atmospheric pollutant concentrations, and give the model a more fundamental significance with application beyond the location which provides the original data. It is noteworthy that statistical models exist, which can predict the soiling well enough for specific conditions. In 1975, Beloin and Haynie (1975) conducted the first extensive study to develop a predictive tool for soiling. As a result, they developed an empirical model describing the loss of reflectance (Eq. (1)):

$$100{-}\mathrm{R} = \mathrm{B} \cdot \sqrt{\mathrm{C}_{\mathrm{TSP}} \cdot \mathrm{t}} + \mathrm{A} \tag{6}$$

where $100-R$ ($R_0=100$) represents the relative change in reflectance, C_{TSP} the concentration of total suspended particles in µg m^{-3}, and t the exposure period in days. The values A and B stand for the intercept and slope, and they are the result of linear regression analysis. The equation was tested for different materials, and it was shown that concrete, limestone, and window glass had a low correlation. Murray et al. (1985) used the same equation to study the soiling of acrylic emulsion paint. The experimentally measured loss of reflectance from this study agreed satisfactorily with the soiling function prediction.

Mansfield (1989) used an empirical second-order exponential model:

$$\mathrm{y} = \mathrm{e}^{(\mathrm{a}+\mathrm{bx})} \tag{7}$$

$$b = -k\left[year^{-1}\right], x = t[year]$$

where y ($\mathrm{y}=100-R$) represents the reflectance change and e^{a} the intercept, and b the slope, i.e., the soiling rate. Generally, the model has two variables, where $R_0=100$ was treated as one of the data points rather than a fixed point through which the curve must pass. The model showed a satisfying correlation for wood and ceramic material. In the same study, the author (Mansfield 1989) also used a reciprocal model to fit the experimental data points:

$$\frac{1}{y} = a' + b'x \tag{8}$$

$$\mathrm{b}' = -\mathrm{k}\left[year^{-1}\right], \mathrm{x}{=}\mathrm{t}[year]$$

where y again represents the reflectance change, a’ the intercept, and b’ the slope (soiling rate). The reciprocal model follows the experimental data very well for wood and ceramic material. Other empirical models based on the same principle can be found elsewhere (Vidal et al. 2019).

However, these empirical models were limited to specific material and particular atmospheric conditions, without considering the physical laws responsible for soiling rate; therefore, they can be used only under certain circumstances. Empirical models are commonly obtained from analysis of experimental data, and such models fit the data very well, but the reason why they do it cannot be explained by theory. The most frequent disadvantage of empirical models is that experimental data are always needed, and the models are applicable only for the modeled experiments under particular operating conditions. Although empirical models can give reliable results when obtained from a substantial amount of test data, the predicting performance of such models tends to be less accurate as the operating conditions move away from the test conditions of which the empirical model is based. To fill up the gap in knowledge between the experimental data and the predictions, Haynie (1986) and Lanting et al. (1986) in the mid-1980s developed independently theoretical models for soiling rate. It is valuable to note that the derivation of the theoretical models is hard to find in a digital form; therefore, it would be helpful to have the equations in one place to critically evaluate them. Lanting et al. (1986) proposed two theories based on different physical principles, which gave similar values for reflectance change with time, when appropriate input data were used. It should be highlighted that both Lanting’s theories assumed that only BC contributes to soiling.

All approaches are based on the assumption that the change of reflectance occur when a percentage of white surface is covered by PM (Beloin and Haynie 1975; Haynie 1986, 1985; Lanting et al. 1986; Watt et al. 2009), where the rate, at which mass deposits to uncovered surface ($v_{d(u.s)}$) and the rate, at which mass is removed from the same surface ($v_{\mathrm{r(u.s)}}$), can be expressed as:

$$\mathrm{v_{d(u.s)} = A{\cdot}C{\cdot}V_d} \tag{9}$$

$$\mathrm{v_{r(u.s)} = A{\cdot}Y} \tag{10}$$

where A is the uncovered surface area on which PM can be deposited, C is the concentration of the PM in the ambient air (μg m^{-3}), V_{d} is the deposition velocity of PM (cm s^{-1}), and Y represents the rate at which particles are removed from the surface (cm s^{-1}).

Linking these two equations leads to:

$$\mathrm{A = A_0{\cdot}e^{(-kt)}} \tag{11}$$

k represents the soling rate and A_0 is the total area of surface.

If the loss in reflectance is connected to the area covered by PM, then it can be written as:

$$\mathrm{R = R_0\left(\frac{A}{A_0}\right) + R_p(A_c)} \tag{12}$$

where R, reflectance of the soiled surface (%); R_0, initial reflectance from the uncovered surface (%); R_{p}, reflectance from particles on covered surface (%); A, uncovered surface area; A_{C}, covered surface area fraction ($A_{\mathrm{c}} = A_0 - A/A_0$), and A_0, total surface area.

Embedding Eq. (6) in Eq. (7) and approximating that the reflectance from the particles is 0 give:

$$\mathrm{R = R_0{\cdot}e^{-kt}} \tag{13}$$

Equation (8) represents the increasing exponential decay function, which means that the surface coverage exponentially increases over time, which has been most frequently used in soiling studies.

For spherical particles and situation where no removal process occurs, Lanting et al. (1986) expressed the unit cross-sectional area of the particle deposition per unit of the surface as:

$$\mathrm{k = \frac{3 \cdot C \cdot V_d}{4 \cdot \rho \cdot r}}[year^{-1}] \tag{14}$$

where k is the fraction of area covered by particles per unit of time ($year^{-1}$), representing the soiling rate; C, PM concentration (μg m^{-3}); V_{d}, deposition velocity (cm s^{-1}); ρ, density of the particles (g cm^{-3}); r, radius of the projected area of the particles (μm). Detail derivation of the soiling rate (k) can be found elsewhere (Lanting et al. 1986; Mansfield 1989). Similar fundamental principles were used by Harker (1982) to derive the exponential relationship between the change of reflectance and the area coverage by PM.

The second theory of soiling rate (k) that Lanting et al. (1986) proposed is based on the specific absorptivity of BC. Therefore, he expressed the soling rate k as:

$$\mathrm{k = 2MAC{\cdot}C \cdot v_d}[year^{-1}] \tag{15}$$

where MAC represents the mass absorption coefficient and it is given in the units of area per mass, C is the concentration of PM (μg m^{-3}), and v_{d} is the deposition velocity (cm s^{-1}). In the absorption-based theory, Lanting et al. (1986) postulated that the loss of reflectance is proportional to the thickness of the deposit; therefore, on the smooth surface, the reflected light makes a double pass through the particles in the reflection process, so factor 2 is used in Eq. (10).

Haynie (1986) derived the soling rate on the same fundamental principle as the first model of Lanting et al. (1986). He started from the hypothesis that the change in reflectance is directly related to the surface coverage. Instead of assuming that only BC is responsible for soiling, he believed that all deposited PM contributed to the soiling and that difference in contribution depends only on the size of the PM and deposition velocity, but not on the composition and related optical properties. In contrast to Lanting et al. (1986), who used single value input parameters, Haynie (1986) included the size spectrum of PM and evaluated the soling constant (k) as:

$$\mathrm{k = \sum\nolimits_i \frac{3c_iu_i}{4r_i\rho_i}} \tag{16}$$

where c, mass concentration of PM; u, deposition velocity; r, effective particle radius; ρ, effective particles density; i indicates the specific size range of particles. If the particle density is independent of the particle size, then the density should not have an influence on analyzing the soiling constant of different size particles. Therefore, to predict the soiling constant (k), he only mathematically described the concentration (c_{i}) and the deposition velocity (u_{i}) as the only two complex particle size-dependent functions. More about the derivation of these two functions can be found elsewhere (Haynie 1986).

Both theories (Haynie 1986), (Lanting et al. 1986) can be used for calculation of the soiling rate (k) for different assumed PM and BC concentrations. Using Haynie and Lanting's theories, Mansfield (1989) calculated the soiling rates for different concentrations of PM and BC and concluded that the theory of Lanting et al. (1986) gives higher soiling rates ($k \approx 0.095 \times$ [BC]) than the one of Haynie (1986) ($k \approx 0.0085 \times$ [TSP]). Anyhow, one should keep in mind that PM deposition from the air to different building material is a phenomenon that is managed by complex mechanisms; thus, the predictive tools must simplify the situation. Hamilton and Mansfield (1993) carried out the systematic research on the influence of PM on soiling at different positions, sheltered and unsheltered. In their study, the two theories nicely predict the results for the sheltered position (road tunnels) but underestimate the soling rate in the ambient atmosphere (unsheltered position). Nevertheless, the theories of Haynie (1986) and Lanting et al. (1986) do not include complex meteorological conditions, such as rainfall. In general, rainfall may act as a cleaning agent, but it can also produce the redistribution of material with a consequent increase in soiling. The role of rainfall in soiling is not clear; thus, further studies are required, preferably under controlled laboratory conditions.

It is important to underline that the soiling of glass cannot be measured by loss of reflectance; instead, other optical properties appropriate to transparent material can be measured. As mentioned previously, haze factor is certainly one of them. Lombardo et al. (2005) showed that the haze can be mathematically described by the Hill equation, which is an S-shaped curve. Equation (17) represents the general form of the Hill's equation, and it allows the variation of a measured parameter $Y(t)$ with time (t) to be expressed as:

$$\mathrm{Y(t) = B + K[1 + (M \cdot t^{-1})^{H}]^{-1}} \tag{17}$$

where B (Bottom) is the level of response in the absence of dose, and in most cases, it is considered to be zero; K (Span) is top–bottom, where the top is the value of the soiling parameter corresponding to the maximum curve asymptote, or the level of response produced after infinite soiling; M (Half-life) is the time when the response is halfway between the top and bottom corresponding to the curve inflection; H (Hill slope) is the maximum slope of the dose–response curve at the time M, and it is used as a measure of the evolution rate.

Considering theoretical models, their major shortcoming is that they are artificially oversimplifications. Nonetheless, they allow exploring the particular relationship between two variables, and they can be beneficial since they rely on physical principles (conservation of mass, momentum, and energy). However, the information obtained by the theoretical models is most often incomplete but still offering a platform for reliable prediction. The main drawback of the soiling rate theories (Haynie and Lanting theoretical models) is that they include either BC or the entire PM without considering any meteorological conditions. With the knowledge of today's state of atmospheric pollution, it is evident that other potential soiling agents exist besides BC. One of the most concerning soiling agents can be the BrC. Considering the total PM as a soiling agent is only partially correct, as noted in the previous chapter. Regarding the meteorological conditions with today's numerical mathematics development, it could be relatively complex, but necessary to include them in the models; more efforts should be made in this direction in future studies. Interestingly, complex theoretical models were developed based on fluid mechanics for indoor soiling in museums (Grau-Bové et al. 2019; Grau-Bové and Strlič 2013; Lai and Nazaroff 2000; Nazaroff 2004; Nazaroff and Cass 1989). Indoor soiling is a relatively simple system, and it deserves to be reviewed independently. However, the basic ideas could be used for redefining the outdoor soiling (Watt et al. 2009).

When considering which model should be used for the soiling prediction, one should keep in mind that the soiling process is a long-term process. Empirical models are highly sensitive to extrapolation because they are derived on a certain set of experiments. Therefore, using empirical models derived from 5 years of exposure to predict soiling for 10 years would be unprecise and could lead to wrong conclusions. Accordingly, the empirical models should be used to predict soiling for a shorter time and specific environmental conditions for which the empirical data exist. In the case of Haynie and Lanting's theoretical models, it has been shown that both models can predict the soiling rate reliable. However, these models were derived under certain assumptions (BC and the entire PM are considered main soiling agents), which were valid in the past. With the change of the pollution situation and the rise of new soiling agents, the models need to be further improved by incorporating the new multipollutant situation aimed at obtaining reliable and precise predictions.

Dose–response function for soiling

The reviewed soiling models have another actual application; they allow the development of DRF for soiling. The DRF for soiling can be used for different purposes; it can predict soiling trends with time or map the spatial variations in soiling and serve to establish an air-quality standard based on soiling (Watt et al. 2009). Therefore, based on soiling theories, Watt et al. (2008) quantified the relationship between soiling and ambient PM_{10}:

$$\mathrm{k} = \lambda \mathrm{C}_{\mathrm{PM}_{10}} \tag{18}$$

where the proportional constant λ represents the dose–response constant. Substituting Eq. (13) into Eq. (8), Watt et al. (2008) obtained the general form of the DRF:

$$R = R_0 e^{\left(-\lambda C_{PM_{10}}\right) \cdot t} \tag{19}$$

The general DRF for soiling can be used to derive the specific DRF for a particular material. For this purpose, in the framework of *Multi-Assess* project, Watt et al. (2008) conducted a series of experiments in different sites in Europe to test the theoretical relationship (Eq. (19)) against experimental data for different materials. The regression analysis of the experimental data against the physical model established the DRF for different materials.

Figure 6 shows the application of non-linear regression analysis of the general soiling Eq. (13) to the selected experimental data obtained by Watt et al. (2008) at two sites, London and Krakow. White-painted steel and white plastic are shown only as examples of the full data set, which can be found elsewhere (Kucera 2005; Watt et al. 2008). The calculated soiling rate constant *k* (Fig. 6 and Eq. (13)) for individual material and the measured concentration of PM_{10} at each site allowed to investigate their interrelationship through the Eq. (14) (Watt et al. 2008).

As stated by Eq. (13), the relationship between the soiling rate constant *k* and the PM_{10} concentration should be linear if the resuspension rate is negligible. The authors (Watt et al. 2008) further showed that the employed linear regression analysis in Fig. 7 allows the determination of the soiling constant *k* for white painted steel and white plastic related to the PM_{10} concentration, which gives the DRF for the specific material (Table 6).

In the frame of the *Multi-Assess* project, Watt et al. (2008) and Kucera (2005) applied the same methodology to other materials to obtain particular DRF for each material (Table 6). They used materials like white plastic and polycarbonate membrane as surrogate materials, where the net deposition of PM should be the same as on real cultural heritage objects. However, Fig. 7 shows some clear outliers related to the characteristics of the sampling site (Watt et al. 2008).

It can be noticed that the DRFs differ only by the number in the exponent, which represents the dose–response constant. Importantly, *λ* depends on the deposition velocity, which is specific for each material. According to Haynie and Lanting (Haynie 1986; Lanting et al. 1986), the deposited particle size and *MAC* also influence the *λ* value.

As described at the beginning of this chapter, the DRF for soiling can be used for three applications:

(i) Change of soiling through the time can be calculated by substituting appropriate values of time *t* into the DRF given in Table 6. One should be aware that particular uncertainty exists in extrapolating beyond the time frame used to develop the model. This uncertainty will be reduced only when a database covering a considerably longer time frame becomes available as in the case of DRF for corrosion (Table 3) (Kucera 2005; Watt et al. 2008).

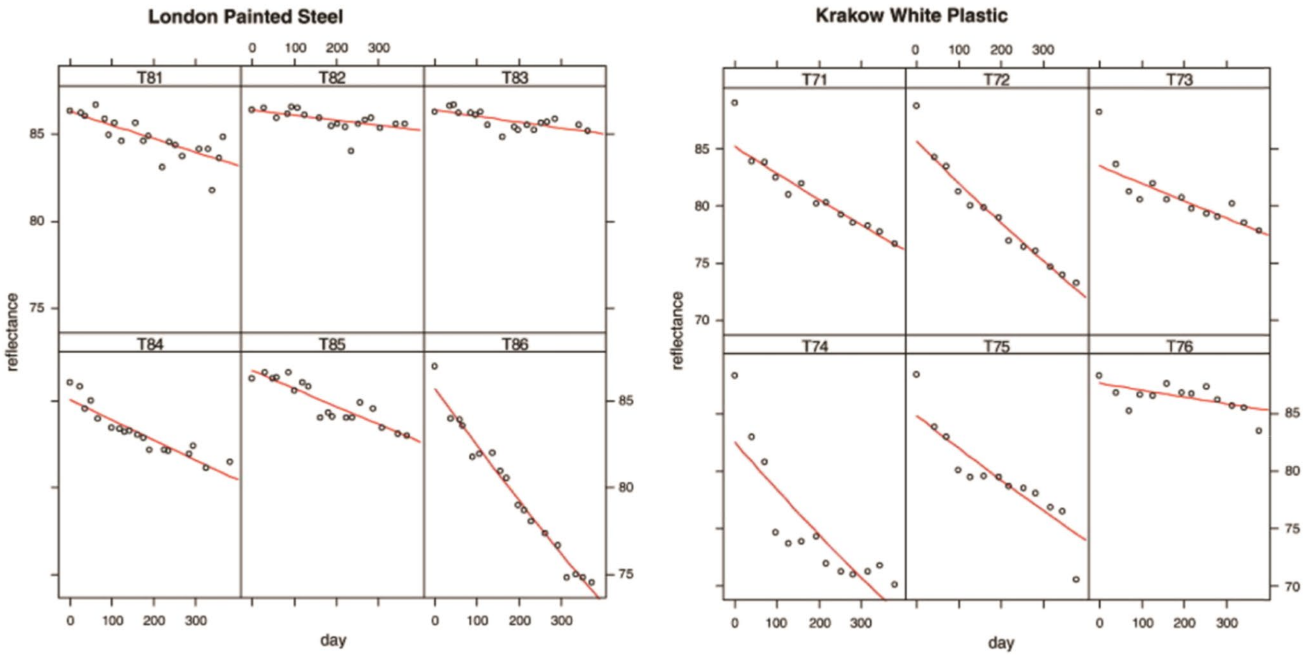

Fig. 6 Measurement of reflectance loss for two materials (white painted steel and white plastic) at two different sites (London and Krakow) (Watt et al. 2008)

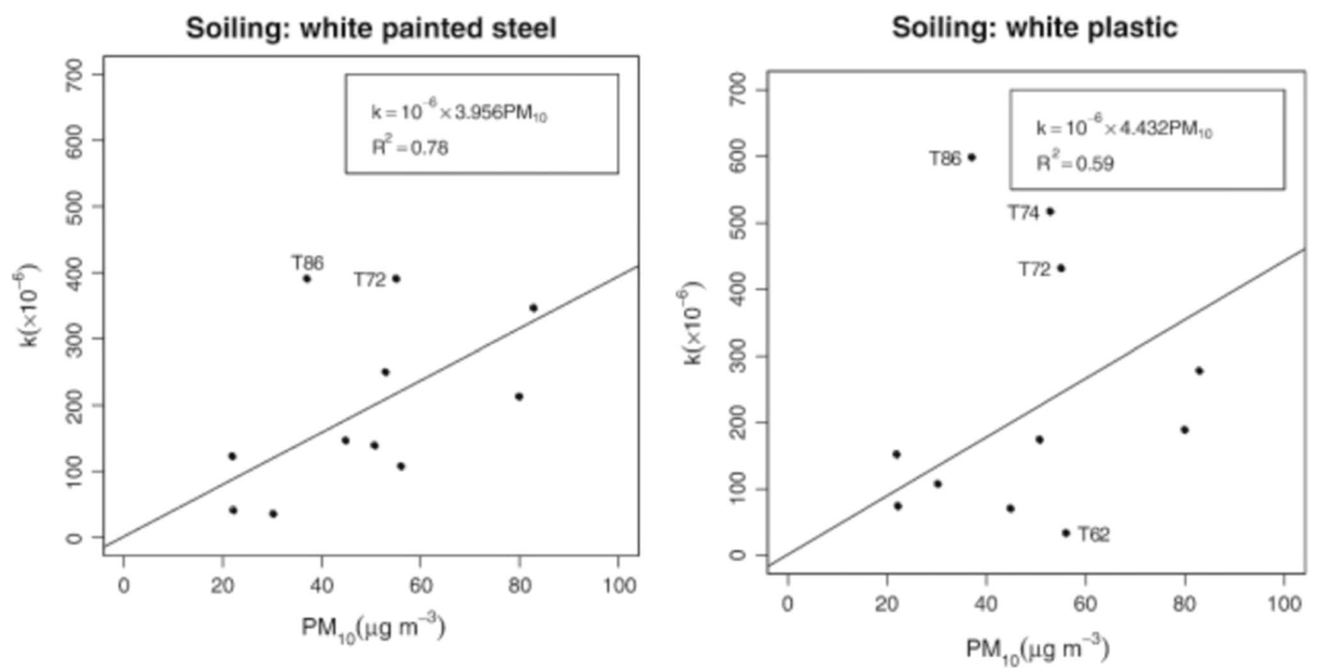

Fig. 7 Relationship between the soiling rate constant *k* (Eq. (18)) and the ambient concentration of PM_{10} (Watt et al. 2008)

Table 6 Dose–response function (DRF) for soiling of different materials

Material	DRF	
Painted steel	$\Delta R = R_0[1 - e^{\left(-C_{PM_{10}} \cdot t \cdot 3.96 \cdot 10^{-6}\right)}]$	(20)
White plastic	$\Delta R = R_0[1 - e^{\left(-C_{PM_{10}} \cdot t \cdot 4.43 \cdot 10^{-6}\right)}]$	(21)
Polycarbonate membrane	$\Delta R = R_0[1 - e^{\left(-C_{PM_{10}} \cdot t \cdot 3.47 \cdot 10^{-6}\right)}]$	(22)
Limestone	$\Delta R = R_0[1 - e^{\left(-C_{PM_{10}} \cdot t \cdot 6.5 \cdot 10^{-6}\right)}]$	(23)

(ii) To display the predicted soiling rate specific for a certain region and particular material, the DRF can be combined with pollution maps to produce maps showing the soiling rate distribution. As in the *CULT-STRAT* (De la Fuente et al. 2013) project, a similar procedure can be applied to make such “risk maps” for soiling.

(iii) To predict a 1-year loss in reflectance for a specific material and particular concentration of ambient PM_{10}. With the knowledge of the tolerable level and tolerable period, the predicted loss in reflectance could be used to establish the air quality standards based on the material soiling. Therefore, via combing the tolerable level and tolerable period with the predicted loss in reflectance, the maximum/minimum ambient air quality, to which the buildings can be exposed before the level of soling becomes unacceptable, can be estimated (Watt et al. 2008, 2009).

Overlaps between soiling and atmospheric damage

The differentiation between atmospheric damage and soling is, to a certain extent, artificial. However, in the literature, many different terminologies can be found to describe the soiling and atmospheric damage; thus, to study these areas systematically, it is necessary to define the terms rigorously. Nevertheless, there is a compelling requisite for searching the new overlaps between soiling and atmospheric damage, which would help to better understand the air pollution impact on cultural heritage material. Besides the *black crust* formation, it can be expected that many other processes occur on the surface of cultural heritage materials representing the overlaps between soiling and atmospheric damage.

Indeed, Van Grieken et al. (2000) suggested that PM can transport harmful substances to the vicinity of the surface, where they can react with the surface, causing a change in the substrate or change in the PM chemical composition, which result in the change of color. It should be highlighted that discoloration/coloration of the material is not the same as the soiling of material. Fitzner and Heinrichs (2001) noticed that different kind of materials can change color due to the chemical weathering of minerals inside the material (e.g., oxidation or reduction of iron and manganese compounds). It is also essential to keep in mind that all deposited PM not necessarily produces visual damage immediately after deposition; something similar to the "memory effect" (dynamic effect) can be expected. Namely, Kucera et al. (2004) showed that the secondary heterogeneous reactions could, with some time delay, cause changes to the deposit. One should also be aware that the deposited liquid layer of PM represents a medium, where different types of reactions can elicit a change in the chemical composition of the deposit, affecting the color of the deposit, and eventually influencing the soiling. Anaf (2014) gives a straightforward example of this process, where soiling and atmospheric damage are overlapping. He demonstrated that bigger particles, even temporarily deposited on the surface, can adhere more strongly to the surface. The PM rich in calcium under the influence of water can cause the redeposition of calcium in the form of microcrystalline calcite, which cements the particles to the substrate surface. Anaf (2014) concluded that for this process, the RH and the liquid water content (LWC) play a crucial role. In fact, he set up a relationship between the hygroscopicity of the particles and their cementation process; this process could represent an important overlap between soiling and atmospheric damage.

In support of this, Brimblecombe et al. (2009) investigated the cementation ability of coarse PM on textile. They recognized that such PM becomes attached to the surface at high RH due to microcrystalline calcite cement formation. It was further shown that similar process can happen on any material (Anaf 2014). Initially, deposited coarse mode PM is, in general, easily removed from the surface; however, it has been shown that after a certain time, such PM is firmly bound to the surface. This behavior is again attributed to the formation of microcrystalline calcite, which cements the particles to the surface of cultural heritage material. Calcite may leach from the deposited PM or migrate from the substrate (if it is a material rich in $CaCO_3$). Dew and RH are the most critical factor for this process. Once formed, such a patterned cemented layer may act as a new (passive) surface for PM deposition in the same way as the gypsum-rich crust. Palomino et al. (2008) investigated the effect of kaolinite-clay and $CaCO_3$ on the cementation process of various particles. They postulated that the behavior of mineral mixtures can be significantly different form the behavior of individual components due to differences between the mechanical and chemical properties of individual minerals and their resultant effects on interparticle interactions. They further concluded that the presence of carbonate controls the pH of mixtures and that the particle aggregation takes place due to electrostatic interaction between the positively charged calcium carbonate and the negatively charged kaolinite particles at carbonate-controlled pH conditions. This process should be more thoroughly investigated and connected to the atmospheric damage and soiling in upcoming research.

Similar processes are also established for iron oxide, silicon dioxide, and clay minerals, which can be found in atmospheric particles (especially during dust events). Borggaard (1983) showed that iron oxide may have a role in the aggregation process of different soils by dissolution and recrystallization of iron. The authors also speculated that iron-organic complexes can contribute to the cementation process.

Another idea, where atmospheric damage and soling might overlap can be found in the review article by Price and Doehne (2011). Water-soluble $(NH_4)_2(SO_4)$ and NH_4NO_3 particles, deposited onto the surface, can dissolve and migrate into the substrate, supposing that the re-migration of such hydrated salts to the surface (stone material) is faster than the drying rate. In that case, the crystals deposit on the top of the external surface and form visible efflorescence, which does not damage the stone mechanically; deposited crystals containing different inclusion can cause soiling or act as an additional surface for PM collection. Moreover, Roth and Anaya (1980) showed that small water-soluble particles such as halides (NaCl or KCl) can be dissolved by condense moisture at high RH or by dew exposure at the surface and subsequently recrystallize into larger individual particles. Again, the so-formed particles or layer act as an alternative surface for PM deposition.

Matteini and Moles (1986) and Matteini et al. (1994) identified different salts of oxalic acid on outdoor monuments. They first thought that these salts were directly deposited from the atmosphere and that the yellow-ochre patina acted as a protective layer. Fassina et al. (1996) and Rampazzi (2019) found a correlation between oxalic acid in black crust and calcium oxalate patina. Cariati et al. (2000) showed with laboratory experiments that the oxalate salts are most probably formed on the surface after oxalic acid has been deposited. Siegesmund and Snethlage (2011) postulated that calcium oxalate found on limestone could result from biogenic oxalic acid production. Vendrell Saz et al. (1996) reported that the oxalate film found on different monuments in Spain had a common biological origin. They found that the oxalate film on different monuments had the same color and probably originated from fungi and bacteria pigmentation. The films also showed the same mineralogical features and chemical composition, with a stratigraphy resembling the stromatolitic structure layers of biological origin. Moreover, they found calcium phosphate inside of the oxalate films, which were infiltrated by microflora and were independently formed from the stone surface. Hence, the oxalate film may originate from metabolism by products and organic matter on the substrate, which is derived from the atmosphere. The twofold origin of the oxalate film was confirmed by Martin-Gil et al. (1999). However, argumentation against the atmospheric origin of oxalate films can be found (Benzzi et al. 2008). The main argument is the low concentration of oxalate. The authors believed that the oxalic acid of atmospheric origin would not be sufficient to form extensive films. Watchman (1991) related the oxalate patina formation with the dissolution reaction of oxalic acid (biological or atmospheric origin) and calcareous stone. The formed oxalate is even less soluble than the parent mineral calcite, such that the crust is also formed on the exposed surface. Del Monte et al. (1987) found on marble and limestone monuments in Italy two main oxalate crystal types whewellite ($CaC_2•H_2O$) and weddellite ($CaC_2•2H_2O$). It was also documented that the calcium oxalate patina could be covered with PM. Even if calcium oxalate is naturally white in color, the formed oxalate patina film on limestones and marble may vary from ochre to black and may be shiny or opaque. The color of the formed oxalate is probably due to the presence of iron-based silicate compounds possibly originating from the airborne PM emended in the formed film (De Buergo and González 2003; Matteini and Moles 1986). Although in the literature clues can be found that PM can be responsible for oxalate salt patina formation and that the formed oxalate patina can act as a passive collector of PM, this process has never been put in the perspective of combined effect of soiling and atmospheric damage.

To better understand the influence of air pollution, especially the influence of PM on cultural heritage material deterioration, it is of utmost importance to include such intuition in future research of soiling and atmospheric damage. Based on today's knowledge of atmospheric PM, many similar processes that fall in the category of overlapping soiling and atmospheric damage can be anticipated. Particular attention should be given to the OC, as it is the dominant carbonaceous fraction of atmospheric PM, not only because of its physical properties (e.g., light absorption) but also due to its chemical properties and the ability to react with the surrounding atmosphere and the substrate to form new compounds, which can act as soling or atmospheric damage agents.

Summary of the main gaps in current knowledge and future directions of research

Atmospheric damage and soiling are recognized as two pivotal forms of deterioration of cultural heritage material caused by air pollution. Acidifying pollutants and hygroscopic carbonaceous particles are considered the major actors of these processes.

Atmospheric damage

The role of air pollution in atmospheric damage, where mostly gaseous pollutants are involved, is well established and recognized through different international programs and projects (ICP-Material, MICA, ISOCORRAG, Multi-Assess, and Cult-Strat). As the pollution situation changed during the past decades, new strategies to quantify the air pollution effect have emerged. Therefore, in the *Multi-Assess* project, the multi-pollution situation was considered. It was demonstrated that after the decreased level of SO_2, HNO_3 also presents a significant threat to the cultural heritage in terms of atmospheric damage. HNO_3 affects the corrosion of all metals by acting as an acidifying agent. In the case of stone material, HNO_3 can be very harmful, particularly for the calcareous stone, where soluble nitrate salts are formed and washed away from the surface. Although HNO_3 has probably taken over the main role in the atmospheric damage, no commercial instruments exist today to monitor it. Therefore, there is an urgent need to develop novel, sensitive, portable, and robust detection systems for HNO_3 (for all phases), which will provide accurate and real-time data.

The importance of PM in atmospheric damage was recognized for the first time in the frame of *Multi-Assess* project. However, the influence of PM on atmospheric damage was considered only for three materials, i.e., carbon steel, cast bronze, and limestone. In future investigations, more attention should be paid to the PM and its composition. The atmospheric damage effect of PM is rather complicated; its variable composition affects the atmospheric damage by providing aggressive substances that accelerate the atmospheric damage process. In general, PM causes corrosion of metals since they are hygroscopic and contain corrosive substances at ambient relative humidity. More attention should also be given to the organic part of PM, particularly to the organic acids that can have an important (direct) role in metal corrosion However, other organics present in the atmospheric PM should not be neglected. Even if other organics do not affect the corrosion directly, adsorbed at the metal surface, they can affect the ability to wet the surface. Consequently, the thickness and continuity of moisture film are undoubtedly significant parameters. To better understand and mitigate the effect of organics in the atmospheric damage processes, more experimental, theoretical chemistry, and corrosion modeling studies are required in the forthcoming era.

Soiling

Soiling is a kind of material deterioration defined as a visual effect that results from the darkening of exposed surfaces following the deposition and accumulation of atmospheric PM. Even if it was recognized a long time ago, its definition and knowledge have not changed much for several decades. In the past, it was thought that BC is the main soiling agent and that the change of the reflectance can affectively measure the soiling.

In general, soiling is managed by two different processes: (i) transport of PM to the surface and (ii) interaction of PM with the surface. Because the interaction is almost immediate, the transport step is the rate-limiting step and defines the overall soiling rate. Following this, models describing the rate of soiling were derived. Only two models for soiling based on different physical principles exist. It is important to consider that a model can be useful in terms of policy only if it is based on physical principle rather than being solely statistical. It is worth mentioning that also empirical models exist for soiling prediction. However, due to the shortcoming associated with the condition at which these models are derived, they can be used only under limited circumstances.

Fred H. Haynie and Roel W. Lanting are two pioneering researchers in the field of soiling of cultural heritage material. They postulated the only existing theory of soiling independently, whereby each author used a different physical principle for its derivation. Haynie believed that different size fractions of PM have different deposition velocities and therefore have different influences on the soiling. At the same time, Lanting presumed that only BC is responsible for soiling. The developed theoretical models can be used to reliably predict the soling rate under different conditions (sheltered and unsheltered). Though the theoretical models are the artificial oversimplification of real processes, in the future, they need to be supplemented in accordance with new knowledge about specific processes. This is especially important in the case of the pollution situation change in the atmosphere and emergence of new soiling agents, which need to be included in the models, making them more reliable in prediction.

Using models developed by Haynie and Lanting, later, the DRFs for soiling of different materials were developed. The knowledge about DRF is vital to connect the effective environmental monitoring with the condition of cultural heritage objects. As DRFs represent the response of material as a function of exposure (air pollution and environmental factors), it is crucial that in the future, the exposure is well grounded and defined within theoretical models which will include all possible species and condition influencing the response.

In the future investigations of soiling, few things should be definitely considered. Both, Haynie and Lanting started with the assumption that soiling can be measured by the change in reflectance, which depends on the amount of BC and particle size. However, at that time, under the term reflectance, only the lightness was considered and measured, which was fair enough for the pollution where BC dominated. With the change of pollution situation, the lightness measurement does not represent the degree of soiling correctly, and in the future, a need for a new methodology for soiling quantification will occur. Although the OC represents the major fraction of non-carbonate carbon of the *black crust*, most papers report only the lightens measurement to indicate soiling, which is only partially correct. However, a certain fraction of OC (known as brown carbon, BrC) can also absorb light in the near UV and visible range, and thus affects the color of the deposit. According to the change of the pollution situation, where OC dominates over BC, the overall color change would represent a better approach to characterize the soiling process. It is already recognized that the color of buildings becomes more yellow-brownish rather than black. Hence, in the future soiling studies, the overall color change through the *CIE lab* system should be analyzed and reported.

The chemical characterization of the soiled layer would also improve the understanding of soiling processes and help to redefine soiling itself. It should be kept in mind that almost 70% of BrC compounds are water-soluble. Therefore, if such compounds are deposited on different surfaces, rain can dissolve and redistribute them, causing an even stronger soiling effect.

Overlaps between soiling and atmospheric damage

In numerous studies, soiling and atmospheric damage are treated separately, even if these two phenomena can act together. The best example, where soiling and atmospheric damage act together is *black crust* formation. Besides, some ideas of what might happen when air pollutants interact with the surface of cultural heritage material can be found in the literature. For example, the PM deposit cementation by calcium ions can form a new surface at which PM causes further soiling. Another example is the recrystallization of water-soluble salts, which also form a new surface for PM deposition. It has been also recognized that at the surface of stone materials (particularly $CaCO_3$ rich stones), different calcium organic salts can be formed. Notwithstanding, no systematic studies exist on the synergy between soiling and atmospheric damage caused by atmospheric PM.

Therefore, in the forthcoming investigations on the impact of air pollution on cultural heritage material, the overlaps between soling and atmospheric damage should be considered.

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