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Black soiling of an architectural limestone during two-year term exposure to urban air in the city of Granada (S Spain)

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ABSTRACT

A two-year term aging test was carried out on a building limestone under different urban conditions in the city of Granada (Southern Spain) to assess its Cultural Heritage sustainability. For this purpose stone tablets were placed vertically at four sites with contrasting local pollution micro-environments and exposure conditions (rain-sheltered and unsheltered). The back (rain-sheltered) and the front (rain-unsheltered) faces of the stone tablets were studied for each site. The soiling process (surface blackening) was monitored through lightness (ΔL^*) and chroma changes (ΔC^*). Additionally atmospheric particles deposited on the stone surfaces and on PM10 filters during the exposure time were studied through a multianalytical approach including scanning electron microscopy (SEM-EDX), transmission electron microscopy (TEM) and micro-Raman spectroscopy. The identified atmospheric particles (responsible for stone soiling) were mainly soot and soil dust particles; also fly ash and aged salt particles were found. The soiling process was related to surface texture, exposure conditions and proximity to dense traffic streets. On the front faces of all stones, black soiling and surface roughness promoted by differential erosion between micritic and sparitic calcite were noticed. Moreover, it was found that surface roughness enhanced a feedback process that triggers further black soiling. The calculated effective area coverage (EAC) by light absorbing dust ranged from 10.2 to 20.4%, exceeding by far the established value of 2% EAC (limit perceptible to the human eye). Soiling coefficients (SC) were estimated based on square-root and bounded exponential fittings. Estimated black carbon (BC) concentration resulted in relatively similar SC for all studied sites and thus predicts the soiling process better than using particulate matter (PM10) concentration.

1. Introduction

Stone decay in polluted urban atmosphere is an outstanding problem with paramount cultural and economic consequences that have attracted the attention of extensive research during decades (see Doehne and Price, 2010 for a comprehensive review). In fact, the effect of air pollution on stone decay is still a major problem even though acidic pollutant levels have considerably decreased since the early 1990s (Doehne and Price, 2010). The danger to Cultural Heritage from air pollution comes from several main sources such as increasing corrosion induced by gases from the atmosphere (Charola and Ware, 2002; Cardell-Fernández et al., 2002; Sabbioni, 2003), soiling of light-colored stone surfaces due to black particles, i.e. black soiling (e.g. Grossi et al., 2003; Hamilton and Crabbe, 2009), and crystallization of soluble and insoluble salts inside the porous network that eventually leads to stone disaggregation and surface recession (Scherer, 1999; Doehne, 2002 and references therein). Moreover, surface recession can be also enhanced by the occurrence of sulfates and nitrates as a consequence of the rain effect (Sabbioni and Zappia, 1992; Bonazza et al., 2009; Siegesmund and Snetlage, 2011). The development of black crusts is a well-known process associated with surface deposition of complex mixtures of atmospheric particles and gases derived from the combustion of fossil fuels together with varieties of environmental dust, salts including marine aerosols, and microbial fauna (Watt et al., 2009 and references therein). The blackness of these gypsum crust layers is commonly explained by absorption of carbonaceous particles such as soot (e.g. Sabbioni and Zappia, 1992). Additionally, it has been argued that carbon soot and metal-rich particles (e.g. V, Fe, Ni, Cu, Mn and Cr-rich particles derived from anthropogenic sources) catalyze the oxidation of SO_2 (Camuffo et al., 1984; Rodríguez-Navarro and Sebastián-Pardo, 1996; Maravelaki-Kalaitzaki and Biscontin, 1999; Böke et al., 1999, 2002; Maravelaki-Kalaitzaki, 2005), although the additional catalytic effect of bacteria is not discarded. Further assessment of the link between anthropogenic activities and black soiling has been provided by quantitative data of organic and elemental carbon (OC and EC) in damage layers on historic buildings worldwide (Sabbioni and Zappia, 1992; Sabbioni et al., 2003; Bonazza et al., 2005, 2007; Ghedini et al., 2006).

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One approach followed to address the above issues combines detailed observations of already weathered construction materials from polluted cities with *ad hoc* experiments under controlled laboratory conditions (e.g. Rodríguez-Navarro and Sebastián, 1996; Simão et al., 2006). Experimental data are later extrapolated to 'real' urban conditions. The diversity of tested stone materials under different environmental conditions has provided considerable understanding of their main weathering mechanisms. However to ensure measurable results in relatively short times, these experiments are usually conducted under extreme environmental conditions which are usually far from those prevailing in urban conditions. Therefore a direct extrapolation to natural conditions is not straightforward and leads to several uncertainties in the estimation of decay rates, which are an important issue in the sustainability of Cultural Heritage. Furthermore many factors both intrinsic (stone-related properties) and extrinsic (environmental-related variables such as exposure and micro climatic conditions, pollution, etc.) are still challenging to be reproduced experimentally.

For these reasons, an important amount of research has been focused on field tests in order to address long-term sustainability of architectural materials (e.g. Delalieux et al., 2002; Viles et al., 2002; Sabbioni, 2003; Viles and Gorbushina, 2003; Grossi et al., 2003, 2007). Pioneering long-term field aging tests designed to study the soiling effect of atmospheric aerosols on building stones were conducted by Beloin and Haynie (1975) using changes in reflectance to asses the stone weathering process. Similar studies were carried out by Creighton et al. (1990), Hamilton and Mansfield (1992) and Pio et al. (1998), which discussed several fitting equations of experimental data relating decreased reflectance to exposure time. Further systematic research has been carried out to develop robust fitting parameters of larger dataset with the aim to improve dose–response functions (Brimblecombe and Grossi, 2004; Kucera, 2005) which are appropriate for long-term predictions of soiling. Although to be essential to design conservation policies of vulnerable Cultural Heritage legacy (Grossi and Brimblecombe, 2004; Brimblecombe and Grossi, 2004, 2005, 2007, 2009), these kinds of studies are still limited to few places around Europe (Grossi and Brimblecombe, 2007).

This study is aimed to investigate the black soiling of a carbonate stone (i.e. a porous limestone used to replace similar historic carbonate stones in monuments in Andalusia, South Spain) under Granada urban conditions during a two-year term exposure test (period of 2008 and 2009). The city of Granada is considered a relatively non-polluted city in terms of NO_x, CO, SO_2 and O_3 (average values are below the EU normative) but significantly exceeds the EU normative limit values for particulate matter concentration (PM10) even if the effect of frequent mineral dust-rich Saharian intrusion is discounted (Lyamani and Bravo Aranda, 2009, 2010; Kontozova-Deutsch et al., 2011). Therefore most of the architectural heritage of Granada, built with carbonate stones, is rather prone to weathering and darkening under its urban conditions. Assessment of soiling was qualitatively and quantitatively estimated by chromatic changes at the porous limestone surfaces through spectrophotometric measurements. Additionally, atmospheric particles deposited on the stone surfaces and filters were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and micro-Raman spectroscopy (MR). Based on observed lightness changes (ΔL^*) the effective area covered by dark particles (EAC) was estimated. Moreover, soiling coefficients were determined by assuming several empirical models.

2. Materials and methods

2.1. Materials

A porous limestone (carbonate stone) from the *Escúzar* quarry situated ~20 km to the SW of the city of Granada, Southern Spain (Urosevic et al., 2011) was selected for this study. The main constituents (>80–90 vol.%) of this limestone are fossil fragments (allochemical component). Fragments of bioclasts include molluscs, echinoderms, briozoan, red algae and foraminifera. The allochemical grain size ranges from 1 mm to 4 mm (Urosevic et al., 2011) thus the geological term biogenic calcirudite is preferred in most of the cases. Following Folk's scheme *Escúzar* limestone is classified as 'sparry biogenic calcarenite/calcirudite' or simply 'biosparite/biorudite' (Folk, 1981). This stone is texturally very heterogeneous, highly porous (29.30 ± 7.6% on average) and scarcely cemented (sparry and micritic calcitic cement). These features, together with the high calcite proportion in its matrix, make this stone very prone to weathering under polluted environments by dissolution processes induced by acid rain and gypsum crust formation. Moreover the lower grain size of the micritic calcite in the matrix and therefore its high specific surface area enhances calcite dissolution in the matrix compared the less reactive sparitic domains. This process commonly leads to desegregation and differential surface erosion, typical of bioclastic limestones (such as the *Escúzar* porous limestone).

This porous limestone is commonly used in modern architecture in Andalusia as well as in monuments replacing the historic *La Escribana* bioclastic calcarenite widely used in ancient buildings of the city of Granada such as the Cathedral, the Charles V Palace and the San Jerónimo Monastery (Rodríguez-Navarro, 1994; Rodríguez-Navarro and Sebastián, 1996; Cardell, 1998; Cardell et al., 2008; Rodríguez-Navarro et al., 2008).

2.2. Environment and sample location

Granada is a non-industrialized, medium-sized city in Southern Spain with a population of around 300,000 (double for the entire urban area). It is about 50 km from the Mediterranean Sea and around 200 km from the African continent. Granada is located in an intraorogenic basin surrounded by mountains with the highest elevations (up to 3500 m) located to the southeast. Due to its topography in combination with the prevailing low wind speeds, heavy traffic and intensive construction works (e.g. Metropolitan works during the test period of 2008 and 2009), pollutants and soot particles often accumulate in the air of Granada. Indeed, around 9% of black carbon (soot) was detected in particles in the city center by Kontozova-Deutsch et al. (2011). Granada has a near-continental climate with cool winters, hot summers, and high diurnal temperature variability. Most rainfall occurs during winter and spring seasons, leading to re-suspension of dust particles predominantly in the dry seasons. The average annual precipitation in the area during the test was $427\ L\ m^{-2}$. When the wind direction is southerly (S and SW are the prevailing wind directions) marine particles can be expected. Additionally meteorological conditions prevailing in spring and summer favors the arrival of Saharan and Sahel air masses. During autumn and winter the number of Saharan dust episodes is reduced while Atlantic and continental air masses are dominant (Lyamani et al., 2004, 2008, 2010). Regarding atmospheric pollutants, the European legal limits for SO_2, CO, and NO_2 emissions were not surpassed during the test in clear contrast to the O_3, PM10 (particulate matter with an aerodynamic size ca. 10 µm) and soot particles emissions, particularly the latter two (Lyamani and Bravo Aranda, 2009, 2010).

For the two-year exposure test, porous limestone tablets of $10 \times 10 \times 2$ cm (cut from the same limestone slab) were placed vertically at four different sites in the city of Granada (see Fig. 1 for sample location and Table 1 for details). The selected site locations ensure a representative spectrum of microclimatic conditions and thus stone weathering environments ranging from very high (site 4), to high (site 1) and to low polluted areas (sites 2 and 3), as inferred from proximity to heavy traffic streets and data monitored through several stations placed in the city (Fig. 1). Outdoor- and indoor-looking stone faces (here named 'front face' and 'back face' respectively) were distinguished for each site. Comparatively the back faces were more sheltered from rain-wash and sunlight than the front faces. In this work the term "black soiling" always refers to blackening of stones