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EFFECTS OF DIFFERENT SOURCES OF AIR POLLUTION ON THE CARBONATE STONE SURFACE OF RELEVANT EUROPEAN MONUMENTS

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This contribution focuses on spectrometric analyses carried out on black crust samples, collected from buildings and churches belonging to the European built Heritage, i.e., the Corner Palace in Venice (Italy), the Cathedral of St. Rombouts in Mechelen (Belgium), the Church of St. Eustache in Paris (France) and the Tower of London (United Kingdom). Such monuments, all built in carbonate stones, were selected for their historic and artistic relevance, as well as for their location in different urban contexts (exposed to intense vehicular traffic or pedestrian areas)[1].

For a complete characterization of the black crusts, an approach integrating complementary techniques was used, including optical (OM) and scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS), Fourier transform infrared spectroscopy (FT-IR) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The complete characterization of the damage layers provided information on their chemical composition, the state of conservation of the underlying substrates and the interactions between crusts and stones. In particular, the geochemical study in terms of trace elements revealed that all crusts are enriched in heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, Ti, V, and Zn) compared to substrates. The different concentrations of such elements in all analyzed crust samples can be ascribed to several factors, such as: height of sampling, morphology of the sampled surfaces (vertical or horizontal), exposure to atmospheric agents, exposure to direct (road or boat traffic) or indirect (industries) sources of pollution, accumulation time of pollutants on the surfaces, wash out and particulate air pollution[2-3]. Specifically, the crusts collected at lower heights (some samples of the Corner Palace, Cathedral of St. Rombouts and Tower of London) resulted to be mainly influenced by mobile sources of pollution (vehicular or boat traffic), while samples taken at higher heights (Church of St. Eustache and some samples of the Corner Palace) are generally mostly affected by stationary combustion sources [4-6]. In some cases, the detailed analysis of multilayered crusts (Palazzo Corner) contributed to recognize the variation of combustion sources responsible for the deterioration of surfaces over time. In addition, the possibility of analyzing altered portions of the substrate (Tower of London) permitted to observe that some elements (Zn, Cu and Ni) show concentrations similar and, sometimes, higher than the overlying crusts. This result can be explained by the geochemical mobility [7-9] of such elements (at specific environmental conditions), which accelerate the process of sulfating, rapidly creating new layers of crust.

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In conclusion, the study of black crusts and altered substrates in terms of trace elements may provide information useful to understand the influence of the pollutants in the genesis of such degradation forms.

References

- [1] Bonazza A., Sabbioni C., Ghedini N., 2005. Quantitative data on carbon fractions in interpretation of black crusts and soiling on European built heritage. Atmos. Environ., 39: 2607-2618.
- [2] Belfiore C.M., Barca D., Bonazza A., Comite V., La Russa M.F., Pezzino A., Ruffolo S.A., Sabbioni C., 2013. Application of spectrometric analysis to the identification of pollution sources causing the cultural heritage damage. Environ. Sci. Pollut. R., 20: 8848–8859.
- [3] La Russa M.F., Belfiore C.M., Comite V., Barca D., Bonazza A., Ruffolo S.A., Crisci G.M., Pezzino A., 2013. Geochemical study of black crusts as a diagnostic tool in cultural heritage. Appl. Phys. A., 113: 1151–1162.
- [4]Rodriguez-Navarro C. and Sebastian E.,1996. Role of particulate matter from vehicle exhaust on porous building stone (limestone) sulfation. Sci. Total Environ., 187:79-91.
- [5]Harmens H., Norris D.A., Koerber G.R., Buse A., Steinnes E., Rühling A., 2007. Temporal trends in the concentration of arsenic, chromium, copper, iron, nickel, vanadium and zinc in mosses across Europe between 1990 and 2000. Atmos. Environ., Issue 31, 4: 6673-6687.
- [6] Winther M. and Slentø E., 2010. Heavy Metal Emissions for Danish Road Transport. In: *National Environmental Research Institute* ed. Neri Technical Report, Aarhus University, no. 780.
- [7]McAlister J.J., Smith B.J., Neto J.B., Simpson J.K., 2005. Geochemical distribution and bioavailability of heavy metals and oxalate in street sediments from Rio de Janeiro, Brazil: a preliminary investigation. Environ. Geochem. Hlth, 27: 429–441.
- [8]McAlister J.J., Smitha B.J., Tőrők A., 2006. Element partitioning and potential mobility within surface dusts on buildings in a polluted urban environment, Budapest. Atmos. Environ.,40: 6780–6790.
- [9]McAlister J.J., Smitha B.J., Tőrők A., 2008. Transition metals and water-soluble ions in deposits on a building and their potential catalysis of stone decay, Atmos. Environ.,42: 7657–7668.