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Assessment of the effects of air pollution on european monuments through a geochemical characterization of black crusts

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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 environments.
For an exhaustive account of the sampled black crusts, an approach integrating complementary techniques was used, including OM, SEM-EDS, FT-IR and 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 as well as to direct (road or boat traffic) or indirect (industries) sources of pollution, accumulation time of pollutants on the surface, wash out and particulate air pollution. Specifically, the crusts collected at lower heights (Corner Palace, Cathedral of St. Rombouts, 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 Corner Palace) are generally mostly affected by stationary combustion sources. 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 of such elements (at specific environmental conditions), which accelerate the process of sulfating, rapidly promoting the formation of new layers of crust.
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.