Characterization of pollutant deposits: possible relationships between areas of origin and degradation of marble monuments.

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The formation of pollutant deposits on artistic and architectural materials may derive from particulate matter present in urban and industrial smog. In our case, in the city of Genoa, also to be considered is the deposition of salts transported by marine aerosol to coastal areas – hence, adding to deposit formation. In this analytical approach it is proposed that a portable X-ray spectrophotometer be employed so as to carry out screening investigations on deposits of pollutants and black crusts. Thus, a sampling procedure will be formulated, aimed at completing subsequent in-depth analyses and at implementing, in so far as is possible, a conservative method. In particular, marble used in the installation of window sills and terraces in two historic sites of the University of Genoa and marble used for statue construction and similar in the Monumental Cemetery of Staglieno are taken into consideration. The analyses, completed directly *in situ*, focus on samples drawn from black dust and crusts, avoiding any subsequent analytical response of the substrates which could alter the results on the actual compositions of the sampled matrices.

Introduction

Before approaching the analytical phase, it is appropriate to be familiar with the main components of marine aerosol and atmospheric pollutants. As many authors point out (Morillas et al., 2016), seawater contains ionic species such as chlorides (Cl^-), sodium (Na^+), sulphates ($SO4^{2-}$), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), bicarbonate (HCO_3^-), bromine (Br^-), borates ($H_2BO_3^-$) and strontium (Sr^{2+}). The effects exerted by marine aerosol on the environment are considerable *re* buildings just by the sea or not so far from the sea. Such buildings are affected by aerosol contribution, especially in the form of a dry deposit, which causes various processes of decomposition in the materials. For example, this can occur as a result of the migration of inorganic salts which can form from the ionic species mentioned. Once absorbed through the porosities present in a given material, there ensues an increase in the rate of degradation (Zhao et al., 2008; Stefanis et al., 2009).

In the past, attention was mainly focused on the contribution of sulphur dioxide (SO_2); recent emissions of this compound have, however, been significantly reduced.

In our age, the contribution of vehicular traffic has significantly increased; hence, we strive as much as possible to monitor the level of ozone, nitrogen oxides and suspended particulate matter produced by combustion processes and industrial production (Valotto et al., 2018).

The geographical diversity that characterizes the city of Genoa makes it possible to study different micro-climates in city areas located at distances of up to a few kilometres from each other. On the one hand, the city overlooks the Gulf of the Ligurian Sea and, on the other, rises into the mountains of the Ligurian Apennines behind. This entails dramatic temperature changes between the coastal area and the inner city - some areas much windier than others and a constant relative humidity during the year, this latter being more substantial in the spring and summer seasons.

This pilot study focuses on finding a preliminary analysis approach for various components of these degradation factors in historical and artistic monuments. Resulting preliminary data will guarantee the formulation of initial hypotheses apt to "guide" subsequent sampling and in-depth analytical phases - endeavouring appropriately to maintain the integrity of any work in question by way of a conservative procedure. The preliminary analyses are carried out with the aid of an FP-EDXRF (Field Portable Energy Dispersive X-ray Fluorescence), which yields compositional data *in situ* with reasonably rapid times.

Sampling

For this pilot study, two areas in the city were identified – both famed all over the world for their historical and artistic importance. The historic centre, the largest in Europe, and the Monumental Cemetery of Staglieno. These two areas were chosen for their contrasting exposure to all the main climatic factors (wind, rain, humidity) and possible causes of deterioration (marine aerosol, proximity to factories, proximity to particularly busy roads, proximity to the sea port etc.).

In the historic centre, the study focused on the marble applied for windowsill covering in two offices of the University of Genoa: The Bishop's Palace within the Department of Architecture and Design (DAD - site 2 Fig. 3) and Via Balbi, 2, hosting The Department of Italian Studies, Roman Studies, Ancient History and Arts and Entertainment (DIRAAS - site 1 Fig. 3). The choice of these two sites was determined by the fact that the first one (DAD) directly overlooks the sea and, more specifically, looks directly onto the Genoese port and shipyards; the second (DIRAAS) is located in the historic Via Balbi, now closed to private traffic, but once subject to the passage of city traffic directed to the west of the city.

The second site identified for study consisted in the walkways in the Monumental Cemetery of Staglieno (site 3 - Fig. 3). The choice of this site was decided upon because Staglieno Cemetery boasts a most valuable collection of sculptural art and it constitutes the best example for the study of marble sculpture degradation throughout time – be the works restored and not.

The inspections carried out established the type of matrix to be sampled and subsequent chemical analyses. As regards the DAD, the atmospheric deposit present in abundance on a marble terrace with archivolts on the sea side of the Department (via di Santa Croce) was tested. It was possible to obtain a homogeneous dusty matrix composed only of atmospheric dust, presumably due to the deposit of marine aerosol and to the particles deriving from the work in the shipyards. Furthermore, the dust in question is also characterized by the presence of particulates deriving from the discharges of public and private means of transport in two large city arteries: Corso Quadrio and Strada Aldo Moro. In addition, the contribution made by the naval traffic of the port of Genoa should not be underestimated.

At the site in Via Balbi 2, however, the black crusts deposited and stratified over the decades on the windowsills of the building and in particular on the presumed nineteenth-century marble columns were sampled. In this case, the contribution of marine aerosol and naval traffic is less, since the road is sheltered from the wind coming from the sea. On the other hand, a more or less substantial contribution resulting from city traffic is plausible, the dust of which could stagnate in the area, due to the limited width of the street.

The sampling area of the Monumental Cemetery of Staglieno turned out to be the most extensive; first of all, attempts were made to take samples along the entire perimeter of the area of interest and in areas with different exposure (Fig.2). The walkways complex, rectangular in shape, lies open to all the cardinal points, each of which has a different exposure to inclement weather, city traffic, vehicular traffic which flows on the A12 motorway (European Road E80) in the immediate vicinity and there are also the mountains which rise on the fringe of the cemetery. For this reason, some samples were collected along the walkways and some outside – the purpose being to evaluate any possible variation. In this specific case sampling was carried out on both the dust, deposited on various monuments over the years, and the black crusts which have formed and caused high degradation - as can be witnessed from many works inside the complex.

For sampling, classic restorer tools were used: brushes, scalpels and spatulas; the dust and crusts were then inserted into sterile plastic sample-containers, so as to prevent polluting elements (such as the aluminium of the metal films that are often used to collect samples) from interfering.

Each sampling area was documented through photographs and marked on the city and cemetery maps.

Instrumental characteristics and analysis procedure

To carry out the chemical analyses in this pilot study, portable X-ray spectrophotometer (FP-EDXRF - Field Portable Energy Dispersive X-ray Fluorescence; XMET7500 - Oxford Instruments) from University of Genoa spin-off GeoSpectra srl was employed. The detection limits and the instrumental characteristics are shown in Tab.1.
To carry out the chemical analyzes in this pilot study, an X-ray portable spectrophotometer was used (FP-EDXRF - Field Portable Energy Dispersive X-ray Fluorescence; XMET7500 - Oxford Instruments) of the spin-off of the University of Genoa GeoSpectra srl. The instrumental characteristics and the detection limits are shown in Tab.1.
The chemical analyses were carried out by placing the sampled matrices inside specific specimen containers for XRF analysis (XRF Sample Cup - Chemplex CAT.NO:1430), sealed with a film suitable for analysis and not interacting with the beam (Poly -MHP - High Performance XRF Sample Film, Oxford Instruments, Part No. L77). This procedure, which can be carried out *in situ*, is employed due to the necessity to effect analytical screenings on samples which are as homogeneous as possible. In addition, the analysis thus performed is designed to prevent interference from the elements constituting the material from which the black crusts and dust were drawn.
Three analyses of 120s duration were carried out for each sample, sufficient to determine the relevant concentrations.
The determination of the chemical components in the samples was carried out with instrument internal methods defined as Mining_LE_FP (Mining_Light Elements_Foundamental Parameters) and Soil_FP (Soil_Foundamental_Parameters). Both methods are essential because, through the application of different energies (13 kV and 45 kV) to the matrices, they guarantee that preliminary data covering the detection limits will be obtained, as shown in Tab 1.

X-ray tube	45 kV, Rh target
Detector	NEW large area silicon drift (SDD)
Primary beam filters	5 position filter charger
Element range	Mg-U
Battery life	10-12 hours
Computer	Integrated
Weight	< 1.8 kg

Tab. 1 - Detection limits (LOD) for the analysed elements (expressed in ppm - mg / kg).

Results

The results obtained are reported in Tab. 2; the averages of the results obtained on the three repeats carried out on the samples considered most representative (11 in total) are reported. Concentrations are reported in ppm (mg / kg).

	Staglieno (Area 3)								DIRAAS (Area 1)		DAD (Area 2)
Name	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Major Elements (wt%)											
SiO_2	**19,27**	**10,63**	**7,40**	**9,87**	**2,18**	**2,46**	**7,43**	**6,12**	**30,91**	**6,51**	**34,29**
TiO_2	**0,88**	**0,41**	**0,28**	**0,36**	**0,01**	**0,04**	**0,33**	**0,29**	**1,39**	**0,37**	**2,62**
Al_2O_3	**3,75**	**2,38**	**2,06**	**2,04**	**2,17**	**2,57**	**1,99**	**1,84**	**5,58**	**1,61**	**6,33**
MgO	*B.D.L*	*B.D.L*	*B.D.L*	*B.D.L*	**7,86**	**7,65**	*B.D.L*	*B.D.L*	*B.D.L*	*B.D.L*	*B.D.L*
Fe_2O_3t	**9,68**	**5,05**	**3,14**	**4,40**	**0,22**	**0,42**	**4,67**	**4,08**	**14,06**	**3,54**	**20,82**
MnOt	**0,11**	*B.D.L*	*B.D.L*	*B.D.L*	*B.D.L*	*B.D.L*	*B.D.L*	*B.D.L*	**0,20**	**0,01**	**0,24**
CaO	**34,82**	**42,17**	**45,00**	**43,23**	**79,98**	**76,81**	**44,65**	**48,60**	**28,38**	**52,64**	**20,46**
K_2O	**1,97**	**0,94**	**0,76**	**0,81**	*B.D.L*	*B.D.L*	**0,68**	**0,76**	**2,72**	**0,71**	**2,66**
P_2O_5	**0,83**	**0,40**	**0,54**	**0,41**	**0,30**	**0,29**	**0,33**	**0,38**	**1,20**	**0,42**	**0,84**
Secondary and Trace Elements (mg/kg)											
S	**244359**	**333642**	**361528**	**342285**	**24375**	**49238**	**353171**	**333088**	**112457**	**289771**	**70556**
Cu	**456**	**281**	**96**	**159**	*B.D.L.*	*B.D.L.*	**72**	**175**	**1931**	**1177**	**9468**
Zn	**1635**	**430**	**113**	**112**	**13**	**13**	**171**	**269**	**5348**	**1047**	**7124**
Sn	*B.D.L.*	**83**	**98**	**88**	*B.D.L.*	*B.D.L.*	*B.D.L.*	*B.D.L.*	**271**	*B.D.L.*	**285**
Pb	**1710**	**845**	**506**	**464**	*B.D.L.*	*B.D.L.*	**1071**	**818**	**1717**	**3319**	**565**

Tab. 2 - Results of chemical analyses carried out by FP-EDXRF (B.D.L. - Below Detection Limits).

Discussion of the results

In atmospheric deposits and black crusts there is a great variety of chemical elements; their concentration varies according to the origin of the particles and their nature. The possible sources of each element are shown below (Tomasi et al.; Heintzenberg et al; Biancotto et al.):
- magnesium (Mg) derives from fly ash produced by combustion processes;
- aluminium (Al) derives from soils and rocks, but is also present in marine aerosol and in the iron and steel processes;
- silicon (Si) derives from soils and rocks, but in the form of oxide it can also be found among the main components of fly ash, due to combustion processes;
- phosphorus (P) is part of the fly ash deriving from the combustion processes;
- sulphur (S) is contained in the marine aerosol, but is also released into the air by various industrial activities and emitted by diesel engines;
- potassium (K) derives from soils and rocks, but is also found in fly ash deriving from combustion processes;
- calcium (Ca) derives from soils and rocks, but in the form of oxide it is one of the main components of fly ash due to combustion processes;
- titanium (Ti) could derive to a small extent from soils and rocks, but its higher concentration is due to its presence in marine aerosol and in fly ash from combustion processes;
- manganese (Mn) is a derivative of iron and steel smelting processes;
- iron (Fe) derives from soils and rocks and it is one of the main components of fly ash deriving from combustion processes;
- copper (Cu) is one of the elements introduced by various industrial activities, such as the steel smelting processes;
- zinc (Zn) is released from various industrial activities and from the combustion of wood;
- lead (Pb) was previously present in fuels, even if today its presence is mainly due to the combustion of lead-containing waste.

The data obtained show that the further the distance from the coastal area, the seaport and the intense traffic of the two arteries present (C.so Quadrio and Strada Aldo Moro), then the more the decrease in the concentrations of the elements due to combustion and industrial processes. A significant example is given by iron: sample 11 (DAD) has the highest concentration, presumably due to the immediate vicinity of the shipyards, the port and very busy roads. The concentration of this element slightly decreases in sample 9 (DIRAAS): Via Balbi is now closed to private traffic, even if it is still open to public transport. Furthermore, despite being in the immediate vicinity of the port, it is sheltered by the surrounding urbanization. In Staglieno Cemetery, iron concentrations decrease even further; they are, nonetheless, higher in the samples taken in the monuments most exposed to climatic factors in general and to the winds which transport soil rich in iron, a characteristic of the soils and rocks of the surrounding mountains.

Another interesting fact is constituted by sulphur concentrations; these are high in almost all the samples tested. The data revealed *re* Staglieno Cemetery are, it is presumed, due to the conservative state of the works under study; in fact, some works present a heavy state of degradation, where the calcium carbonate ($CaCO_3$) constituting the marble undergoes sulphatization reactions, turning into gypsum ($CaSO_4$). Results presumably due to an anthropogenic contribution are revealed in the two sites of the University of Genoa which show concentrations of sulphur (DIRAAS - samples 9 and 10) and iron (DAD - sample 11) above the limit. These elements are attributable to the smog deriving from diesel engines of public transport, most abundant at DIRAAS. In addition, the accumulation of this element in this area could, in part, also derive from the contribution of the factories sited in the port, from naval traffic and, to a lesser extent, from the sulphate content in marine aerosol.

In assessing the presence of various elements found either in abundance or as traces, the numerous factors to be considered include: morphology of the sampled surface (vertical or horizontal), exposure to atmospheric agents, direct or indirect exposure to sources of pollution, such as the aforementioned vehicular and naval traffic, and the presence of factories. The precise time of pollutant accumulation should also be considered; thus, a seasonal and annual monitoring of the sites considered might be necessary (Comite et al., 2014). In Staglieno Cemetery there was also a lower concentration in elements such as copper and zinc, both coming from the emissions of industrial activities, present near the DIRAAS and the DAD, but absent near the cemetery

The lack of chlorine in the results obtained is to be further researched, in the light of the immediate proximity to the sea of areas 1 and 2 (DIRAAS and DAD) and the prospects of chlorine detection within the scope of the two analytical methods used.

Conclusions

The analyses carried out in this pilot study highlight the correlation between the geographic and urban characteristics of the city of Genoa and the type of deposit of pollutants which could lead to varying degrees of serious damage to historical and cultural artefacts. It can be seen that the distance from the sea (about 3 km) and from major traffic arteries leads to a sharp contrast in some element impact in the case of Staglieno Cemetery. Elements such as copper and zinc with their geochemical mobility (in certain environmental conditions) could speed up the degradation process, accelerating the sulphatization processes and creating new layers of crust more quickly (Comite et al., 2014).

The results obtained through this analytical technique cannot be employed to define the origin of the elements constituting the sampled matrices, but to define the state of conservation of the works, define which samples should be subjected to further investigation with more specific instruments so as to start the best cleaning, conservation or restoration treatment. The samples to be subjected to in-depth investigations can be significantly reduced in number through screening analyses - a factor that should not be underestimated in the various fields of application of this technique, not less so in the field of cultural heritage.

From the results found *in situ*, now conscious of which elements characterize the deposits of dust and black crusts, interested researchers might endeavour to formulate hypotheses for the protection of the works and infrastructures – aiming, therefore, to avoid future contamination as much as possible andthe recurrence of the same related problems.

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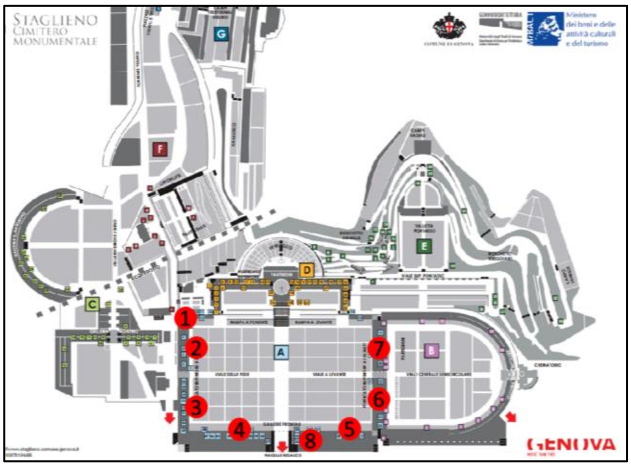
Appendix.

Fig. 1 - Some sampled sites in the Monumental Cemetery of Staglieno and at the DIRAAS (bottom right)



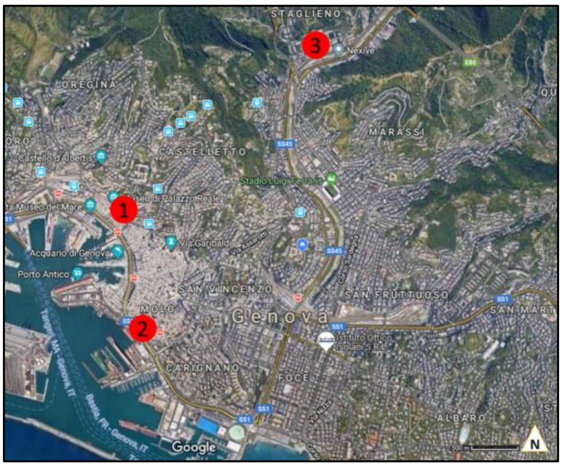


Fig. 2 – sampling points in the Monumental Cemetery of Staglieno. In red.
Fig. 3 – sampling points in the city of Genoa. In red.