Società Chimica Italiana
Divisione di Chimica
Ambiente e Beni Culturali

"La tutela dell'Ambiente e dei Beni Culturali in un Mondo che cambia"

XVII CONGRESSO NAZIONALE DI CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI

Genova, 24-27 giugno 2018

CONTRIBUTI SCIENTIFICI

SCADENZA 30 APRILE 2016

Il contributo, presentato in lingua inglese, dovrà essere al massimo di 2 pagine, figure e bibliografia comprese, formattato secondo il facsimile riportato nella pagina successiva.

Selezionare la SESSIONE di interesse (una per ogni contributo presentato):

Valutazione di fenomeni di contaminazione ambientale. Monitoraggio e bonifica di siti contaminati	☐
Economia circolare: gestione, valorizzazione dei rifiuti e riduzione dell'impatto ambientale	☐
Inquinamento odorigeno outdoor e da nuove fonti indoor	☐
Inquinanti emergenti nelle acque: antibiotici, PFOAS, micro e nanoplastiche	☐
Inquinamento delle acque industriali e minerarie	☐
Analisi, valutazione e gestione del rischio chimico	☐
Sviluppo e valutazione di materiali avanzati per un packaging sostenibile	☐
Strumenti e indicatori di sostenibilità ambientale	☐
Monitoraggio ambientale e conservazione del patrimonio culturale	☑
Sviluppo di materiali e metodi per la conservazione e restauro dei beni culturali	☐
Metodologie analitiche innovative per la diagnostica applicata ai beni culturali	☐

Tipologia di intervento richiesto: orale ☐ poster☑

N.B. Il comitato si riserva di variare la preferenza espressa dagli autori, in considerazione di valutazioni scientifiche ed organizzative.

Title - Times New Roman, 12

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1. Introduction

The issue of environment protection, including the conservation of the monumental heritage worldwide is related to atmospheric pollution. Anthropogenic multi-pollutants are the main factors responsible for the accelerating damage observed on cultural artifacts exposed to the atmosphere over recent decades [1]. Air pollution is one of the most important causes of surface decay in the urban environment. Currently, emissions from mobile combustion sources are the main agents responsible for pollution, although a significant decrease is expected in Europe within the next decade. Damage to stone surfaces is generated by the combined action of environmental and anthropogenic factors. Many studies in the past have assessed the erosion phenomena of stone surfaces by precipitation using both mechanical and chemical mechanisms and also the phenomena of blackening and sulfation due to the deposition of atmospheric particulate on the stone substrates [2-6]. Therefore, the issue of conservation of the monumental heritage worldwide is mainly related to atmospheric pollution that causes the degradation of stone surfaces. The deposition of particles on the surfaces of works of art of historic and artistic interest is not a simple phenomenon of adsorption to the surface since the powder is often cemented into a physicochemical process that includes the deposition of a thin layer of water, and chemical reactions between the material and the corrosive acids present in this solution can occur [5]. The powder deposits present on the stone monuments reflect the composition of the aerosol particulate matter (PM) to which the surfaces are exposed, so it's the chemical characterization is necessary in order to adopt mitigation measurements which of conservative intervention and maintenance strategies, as well as for the development of emission reduction policies on a larger scale. In the present study Candoglia marble specimens and quartz fiber filters have been exposed at the façade of Milano Cathedral (Duomo di Milano). The field exposure activity started in 2012, few years after the completion of the restoration work of the façade. The objective was to characterize the soiling rate and composition during the very early stages of deposition on reference substrates exposed to the same condition of the actual stone of the façade. . In order to fully characterize those samples, a multi-analytical approach was used. Data acquired on samples have been compared with those collected by the regional environmental protection agency (ARPA Lombardia).

2. Results and Discussion

Candoglia marble specimens and quartz fiber filters (gravitational deposition sampling) have been exposed on the façade of Milano Cathedral. at the exposure sites where placed at different heights and the monitoring time covered the period 2014-2016. Moreover, samples of deposits from real architectural surfaces have also been sampled (6-year accumulation period from the last conservative intervention, between 2008 and 2017). All specimens were exposed in sheltered condition to promote deposit accumulation, samples of real deposits were collected from sheltered areas of the façade as well.. The samples have been analyzed by multi-analytical approach including ion chromatography (IC) for analysis of the anions, Thermal Optical Transmittance (TOT) for the analysis of organic carbon (OC) and elemental carbon (EC) on quartz fiber filters and Thermal Gravimetric Analyses coupled to Differential scanning calorimetry (TGA/DSG) for the quantification of OC and EC on powders samples from real surfaces. The anion average concentrations (reported as %) are shown in table 1. Comparing the two quartz filters series it can be observed that the concentrations of the single species are quite constant overtime. Powders samples from real surfaces show a significantly higher SO_4^{2-} concentration which can indicate that a sulfation process is occurring. Furthermore, taking into account the

accumulation period, it can be observed that the sulfation process does not follow a linear trend. On the contrary nitrate concentrations seem quite constant, the differences depending from the substrate.

Table 1 – Anion averages of the samples expressed in concentration%.

Sample	Exposure time	Concentration Averages %				
		Cl^- %	NO_2^-%	Br^-%	NO_3^-%	SO_4^{--}%
Quartz fiber filters set I	July 2014 - February 2015	1,12±0.08	n.a	n.a	1,98±0.39	3,24±0.67
Quartz fiber filters set II	July 2016 -march 2017	2,89±0.17	0,11±0.06	0,18±0.12	2,63±0.53	3,68±0.74
Powders marble samples A	July 2014 - February 2015	0,23±0.02	n.a	n.a	0,62±0.25	4.00±0.26
Powders real architectural surfaces PO	2009 - June 2017	0,69±0.14	0,02±0.004	n.a	1,11±0.16	10,75±1.45

Comparing the results obtained on quartz filters for OC and EC in the two exposure sites (Central balcony and South pillar) at different heights (19.40 and 9.40 m) it can be observed that both of them are present in a slightly higher concentration at the higher level and this is due to the fact that these species are present in the finer PM fraction that is more easily re-suspended. On the contrary, there are not significant differences in OC and EC concentrations overtime in accordance with what already observed for the main anions. In order to interpret the results obtained, environmental data as regards the main atmospheric pollutants (both particles and gases such as NOx and SO_2) have been collected from ARPA monitoring stations, placed in Milan city center, over the period 2000-2017. The acquired information will allow to elaborate damage functions and the values predicted by the models will be fitted with the experimental results observed for the real surfaces.

3. Conclusions

In this contribution, we discuss the results of a field exposure performed on the Milan Cathedral façade after the last restoration. The analysis carried out on the powders have shown that on the stone surfaces sulfation processes have occurred. A constant chemical composition of the powder collected on the exposed quartz fiber filters has been observed within the two monitoring periods. This information could be useful to evaluate the deposition rate on the actual surfaces of the façade thus allowing to define sustainable strategies for preventive conservation.

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