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In situ long-term monitoring of recolonization by fungi and lichens after innovative and traditional conservative treatments of archaeological stones in Fiesole (Italy)

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ABSTRACT

The research complements a study (Pinna et al., 2012) carried out to evaluate the effectiveness of mixtures of consolidants and water-repellent products (tetraethylorthosilicate, methylethoxy polysiloxane, Paraloid B72), with biocides (tributyltin oxide, dibutyltin dilaurate, copper nanoparticles) applied in situ to prevent biological growth on stones. The mixtures were tested over time on trial areas of three substrates - marble, sandstone, and plaster – in the archaeological site of Fiesole (Firenze, Italy). The 8-year-long study showed that the recolonization of the three substrates after the conservation treatment related mainly to their bioreceptivity and to the climatic conditions. Although the mixtures of water repellents and consolidants with biocides and copper nanoparticles were effective in reducing the recolonization, they did not play a crucial role in preventing biofilms and lichens growth. This study demonstrated that it was not possible to draw common conclusions regarding the products' performance on the examined stones. Copper nanoparticles proved to be a suitable alternative to traditional biocides because they did not alter stones colour and contributed to the prevention of recolonization. The study provided information on the succession of fungi and lichens on untreated and treated stones, as well as on the variations of water repellency of treated stones.

1. Introduction

A growing number of studies has considered the recolonization after treatment as one of the most challenging aspects nowadays in conservation of cultural heritage objects. Particularly demanding are the following issues: the recolonization of bare surfaces after the removal of biofilms and lichens, and the recolonization of surfaces treated with consolidants and/or water repellents that can be useful in preventing biofouling (see review in Pinna, 2017). These substances can inhibit microbial growth by reducing the degree of saturation of the stone and limiting the amount of water available to organisms. As consolidants and water-repellents are currently applied in the final steps of restoration/conservation processes, the development of microorganisms on treated surfaces is worthy of investigation. Two water-repellents, the products Rhodorsil H224 and Protectosil SC Concentrate, efficiently prevented the biological colonization for 2 years on limestone samples located outdoors in a park in Belgium, while tetraethoxysilane (TEOS, a consolidant) mixed with the antimicrobial agent Chitosan was not effective (Eyssautier-Chuine et al., 2014). A 160-day-long laboratory test evaluated the ability of water-repellents (silane and fluorinated compounds) to prevent colonization of the alga *Graesiella emersonii* on mortar samples (Martinez et al., 2014). The treatment notably reduced the progression of colonization compared with that obtained with the control specimens.

Drawbacks can occur after the application of these products, however. A study observed that the hydrophobicity provided by water-repellents on marble statues inhibited the spreading of raindrops over the surfaces (Charola et al., 2007) and created preferential water paths that favoured the accumulation of biomass and eventually the development of localized biofilms. The formation of these preferential water routes depended strongly on the structural characteristics of the stone surfaces. In fact, autoclaved aerated concrete samples treated with alkylalkoxy silane showed streaking patterns of colonization when tested with an accelerated fouling experiment, while white concrete specimens treated with the same water-repellent did not show any streaking (De Muynck et al., 2009). According to these authors, the low

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roughness of the latter substrate allowed an even distribution of products impeding the formation of preferential water flow paths.

Statues housed in parks of Venetian villas (Italy) and of the National Palace of Queluz (Portugal) were treated with consolidants and/or water-repellents after the removal of lichens and biofilms with biocides (Nascimbene and Salvadori, 2008; Nascimbene et al., 2009; Delgado Rodrigues et al., 2011). These studies showed that, besides the usual factors favouring biological colonization, the type of products and the method of application affected the recolonization rate (Salvadori and Charola, 2011). The regrowth started after a few weeks on statues treated with a fluorinated polymer, whereas it took several years to occur on those treated with silane and/or polysiloxane.

Some studies suggested that the application of mixtures of hydrophobic compounds and biocides was an effective brake on the microbial recolonization of stones (Malagodi et al., 2000; Ariño et al., 2002; Nugari and Salvadori, 2003; Urzì and De Leo, 2007). Urzì and De Leo (2007) showed that water-repellent plus biocide combination had a protective effect, especially against algae and bacteria, when used on mortar samples exposed to outdoor environments.

Other studies (Ditaranto et al. 2011, 2015; Zhang et al., 2013; Bellissima et al., 2014) experimented with nanoparticles mixed with water-repellents and consolidants to inhibit microbial growth. Although primarily addressed to buildings, they reported that the polymers mixed with nanoparticles can also be useful for the preservation of historic monuments. Although the results on application of nanoparticles mixed with water-repellents and consolidants for preventing biological growth on stones are promising, and the topic is very important having strong connections with maintenance and minimum intervention strategies, it is not possible to draw general conclusions because most research was performed under laboratory conditions. Therefore, controlled in situ trials of the potential for biodeterioration of these new coatings are a good subject for future applied research.

The research described herein complements a study that started in late 2008 and was aimed at evaluating the effectiveness of mixtures of (i) consolidants and water-repellent products with (ii) biocides applied to prevent biological growth on stone heritage objects. Besides traditional chemicals, copper nanoparticles were experimented. Copper is known to be one of the most effective biocides and Cu compounds have been tested previously, but not in the forms used in this study. Henriques et al. (2007) tested mortar samples containing 0.35% by weight of copper powder. The samples, located outdoors in a place prone to biocolonization, did not show any biological growth for over nine years.

This study was conducted in the archaeological area of Fiesole (Firenze, Italy), chosen for the widespread lichen colonization. A previous article assessed the bioreceptivity of untreated and treated sandstone, marble, and plaster over a period of almost three years (Pinna et al., 2012). Growth of fungi was identified by that study as the main cause of darkening of marble surfaces.

The present article describes and discusses the results of the monitoring of the surface treatments in the period succeeding the original study (2012–2016). Biological growth - fungal and lichen colonization – was investigated by microscopy and cultivation methods. The study also analyses the results of the whole period (2008–2016), providing relevant information on stones recolonization after a conservation treatment by examining the bioreceptivity of untreated and treated stones.

2. Materials and methods

2.1. Description of the site

The archaeological site is located in Fiesole (Italy), a village on a hill not far from Firenze. The area features dried and sunny summers: the average relative humidity (RH) is around 66% and the average temperature of July (the hottest month) is 24 °C. Winters are cold and wet, with average RH of about 75% and average temperature of 7 °C in January (the coldest month). In winter, however, occasionally sunny and windy days with RH around 55% occur. In June and July, high temperatures up to 35 °C with low RH (about 30%) can occur quite often during the day. According to the bioclimatic classification proposed by Pesaresi et al. (2014), the area is classified temperate with bioclimate type Oceanic and variant sub-Mediterranean.

The archaeological site includes three monumental structures: the Etruscan temple (III century B.C.), the Roman theatre and the Roman baths (I century B.C.). The natural and artificial stones of the site are marble, sandstone and plaster covering bricks. The Roman theatre and the Etruscan temple are mostly made of a local sandstone, *pietra serena*, a feldspathic greywacke with a clay matrix and little carbonate cementing material (about 7%). There are some original slabs of white, homogeneous, fine-grained marble cladding on two sandstone bases in the Etruscan temple area. The original plaster of the Roman baths used to line and waterproof one of the two swimming pools was made with a homogeneous mixture of a fine local sand charged with finely ground cocciopesto. The binder was obtained by firing local marly limestone (Fratini, 2005).

The tests were carried out on surfaces of different orientation - marble and sandstone ones are horizontal, while the plaster ones are vertical and adjacent to the ground. Sandstone and marble are close to each other and do not have any shelter effect as they are completely exposed. As for plaster, being placed at the bottom of a poll, it is shaded during parts of the day.

2.2. Application of mixtures of biocides with water-repellents and consolidants

The mixtures were applied in situ on marble, sandstone and plaster after cleaning them to completely remove the crustose and foliose lichens (Figs. 1–3). Product compositions are listed in Table 1. The product Bioestel by CTS (Altavilla Vicentina, Italy), which consists of a tetraethylorthosilicate (TEOS)-based consolidant mixed with two biocides - tributyltin oxide (TBTO) and dibutyltin dilaurate - was applied on all the lithotypes. Recently organotin compounds, including TBTO, have been withdrawn from use as surface biocides in Europe. TBTO was a very efficient component of antifouling coatings that prevented the growth of marine organisms on the hulls of ships. Laboratory tests showed that concentrations as low as 20 ng/l could damage nontarget aquatic organisms, particularly molluscs, negatively affecting important biological processes such as larval development or reproduction. Organotins use in plastics, silicone and foams results in their occurrence almost everywhere, e.g., clothes, toys, wallpaper, food containers, household piping and medical devices (Sousa et al., 2014). Toxicity data reveal that organotins are endocrine disruptors, immunotoxicants, and carcinogens. Tributyltin is extremely toxic toward a wide range of organisms, from bacteria to mammals, including humans. The European Union moved to the adoption of Directive 2002/62/EC and Regulation 782/2003 for the total interdiction of organotins antifouling paints application on European Union ships after July 1, 2003, and the prohibition of organotins antifouling paints on ships' hulls from January 1, 2008. From this date onward, the prohibition was extended to all ships entering European Union ports. The use of organotin compounds was further regulated in the European Union by the EC Regulation 1907/2006 on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). Organotin compounds are included in Annex XVII of this regulation that restricts the manufacture, placing on the market and use of certain dangerous substances, preparations and articles. According to this directive organotin compounds shall not be placed on the market for use as substances and constituents of preparations when acting as biocides in free association paint. European Commission Decision 2009/425/EC and Regulation No 276/2010 have officially banned specific organotin compounds (including TBTO) in consumer products. Thus, organic–tin or –mercury and other heavy

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