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Trentepohlia algae biofilms as bioindicator of atmospheric metal pollution

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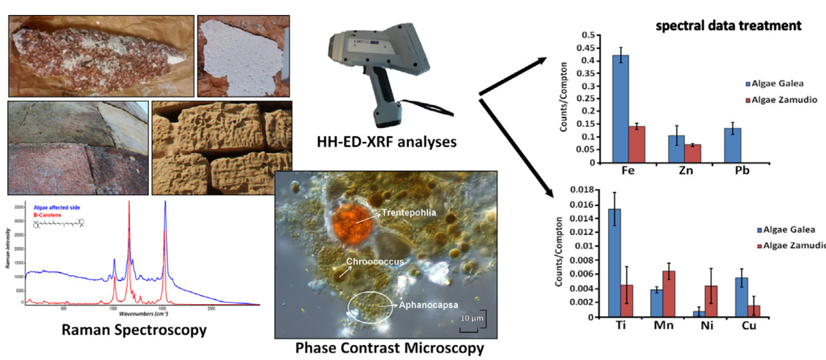
HIGHLIGHTS

- *Trentepohlia* algae biofilms as bioindicator of atmospheric metal pollution
- *Trentepohlia* algae biofilms over buildings as bioacumulators of metals
- A fast in situ X-ray fluorescence methodology for characterizing atmospheric metal pollution
- Principal Component Analysis as a fast X-ray fluorescence spectral data treatment
- Differentiation between possible metals inside the structure and particles deposition over the algae by means of SEM-EDS

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a reddish biocolonization composed mainly by *Trentepohlia* algae affecting a synthetic building material from a modern building from the 90s located in the Bizkaia Science and Technology Park (Zamudio, North of Spain) was characterized and its ability to accumulate metals coming from the surrounding atmosphere was evaluated. To asses if these biofilms can act as bioindicators of the surrounding metal pollution, a fast non-invasive in situ methodology based on the use of hand-held energy dispersive X-ray fluorescence (HH-ED-XRF) was used. In order to corroborate the in situ obtained conclusions, some fragments from the affected material were taken to analyze the metal distribution by means of micro-energy dispersive X-ray fluorescence spectroscopy (μ-ED-XRF) and to confirm the presence of metal particles deposited on it using Scanning Electron Microscopy coupled to an Energy Dispersive Spectrometer (SEM-EDS). In order to confirm if *Trentepohlia* algae biofilms growing on the surface of building materials could be a fast way to in situ provide information about the surrounding metal pollution, a second *Trentepohlia* algae biofilm growing on a different kind of material (sandstone) was analyzed from an older historical building, La Galea Fortress (Getxo, North of Spain).

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1. Introduction

The biodeterioration of the construction materials is referred to the destruction process of material due to living organisms or to products of their metabolism (Sand, 1997). Sometimes, biodeterioration has been considered the following process after chemical deterioration. These chemical processes, such as SO_x attacks, were considered to be responsible of structural changes and to contribute to the enrichment of inorganic and organic nutrients in the materials that boost the growth of microorganisms in building materials (Warscheid and Braams, 2000) even though they can also occur synergistically. Recent investigations, especially those regarding the surface-covering biofilms formed by microorganisms to protect themselves against harmful environmental factors, have found that biofilms can also be detected in well-preserved materials or just in their early stages of their environmental exposure (Warscheid and Braams, 2000).

Algae, cyanobacteria, heterotrophic bacteria and fungi are the most usually found microorganisms in the superficial biofilms in calcareous materials; protozoa are also frequently present. The phototrophs (algae and cyanobacteria) have been considered to be the primary colonizers, conditioning the material for the growth of the heterotrophic organisms such as fungi (Crispim et al., 2003). Normally, in the biodeterioration processes many groups of microorganisms co-exist at the same time in the same material, as a result of complex microbial interactions (Crispim et al., 2003).

The bioreceptivity of a material depends on the chemical composition, physical structure and geological origin. The intensity of the biodeterioration processes is strongly influenced by water availability. This water availability is determined by both, material-specific parameters, such as porosity and permeability, as well as environmental conditions and the exposure to them (Warscheid and Braams, 2000). High porosity values allow deep penetration of moisture into the material promoting the microbial colonization. The size of the pores also affects to the kind of colonization. Large-pore sandstones, promote temporally colonizations due to their short water retention ability, while small-pore stones, with longer water retention time, offer a better environment for the growth of long-lasting microorganisms. The pH of the material and the nutrients sources related to the chemical composition of the material are also important parameters to take into account (Warscheid and Braams, 2000). The presence of significant amounts of carbonate compounds (e.g. >3% w/v $CaCO_3$) in the stone, as in the case of the calcareous stones, lime mortars and concretes, results in the buffering of biogenic metabolic products producing a constant suitable pH for biological growth (Warscheid and Braams, 2000).

The biofilms can also be defined as a consortium of microorganisms encased in a complex 3D gelatinous matrix of extracellular material secreted by the inhabiting organisms. These biofilms are responsible of the aesthetically unaccepted coloured patinas appearance due to the excretion of organic pigments (e.g. chlorophylls, carotenoids and melanins) as an adaptation to increase the resistance against environmental stress. In addition, the presence of extracellular polymeric substances can cause stress to the mineral structure due to shrinking and swelling cycles of the colloidal biogenic slimes inside the pore systems. This can alter the pore size distribution in the material resulting in changes of moisture circulation patterns and temperature response (Warscheid and Braams, 2000). It has also been demonstrated that the early presence of biofilms on exposed stone surfaces accelerates the accumulation of atmospheric pollutants (Thiel et al., 1993). These polymeric substances that can cause the damage of the material are also responsible of the metal biosorptive properties of some bacteria, fungi and algae (Gadd, 2000). The biosorption is the process by which metals are sorbed and/or complexed to either living or dead biomass (Lovley and Coates, 1997). For example, it has been demonstrated in in vitro experiments, the Zn biosorption to *Rhizopus Arrhizus* fungi predominantly to its wall chitin and chitosan in solution (Gadd, 2000; Lovley and Coates, 1997; Zhou, 1999). This ability of the microbes is being studied in order to use it as bioremediation in the field of metal contamination especially in removing metals from contaminated water or waste streams, sequestering metals in soils and sediments or solubilizing metals to aid in their extraction (Lovley and Coates, 1997). Anyway, there has been little investigation into the use of microorganisms for the remediation of metal contamination because until recently, the studies on the use of microorganisms for environmental restoration have been focused on microbial degradation of organic contaminants by oxidizing them into carbon dioxide (Lovley and Coates, 1997). It is well referenced that mosses and lichens can act as bioindicators of air pollutants. Concretely, different works asses the usefulness of these organisms to monitor the atmospheric metal pollution by collecting and exposing them to the environment of the city in bags (Adamo et al., 2003; Harmens et al., 2008). In other cases the presence of some microorganisms in stones or other building materials can also act as a bioprotective barrier (Ariño et al., 1995; Liu et al., 2012; Morillas et al., 2015) instead of being a degradation factor. However, the in situ ability of some biofilms over building materials as bioindicators of the metal pollution of the surrounding environment of the construction has not been studied yet.

In this work, a reddish biocolonization affecting a synthetic building material from a modern building from the 90s located in the Bizkaia Science and Technology Park (Zamudio, North of Spain) was characterized in order to know the nature of the main colonizers present in the biofilm. Apart from that, the influence of its presence in the conservation state of the building material and its ability to accumulate metals coming from the surrounding atmosphere were also studied. To asses if this biofilm can act as bioindicator of the surrounding metal pollution, a fast non-invasive in situ methodology based on the use of hand-held energy dispersive X-ray fluorescence (HH-ED-XRF) was used. In order to corroborate the in situ obtained conclusions, some fragments from the affected material were taken to analyze the metal distribution by means of micro energy dispersive X-ray fluorescence spectroscopy (μ-ED-XRF) and to confirm the presence of metal particles deposited on it using Scanning Electron Microscopy coupled to an Energy Dispersive X-ray fluorescence Spectrometer (SEM-EDS). In order to confirm the ability of these biofilms as a fast source of information about the environmental pollution, the same kind of biocolonization previously characterized by Morillas et al. (2015) was also studied. In this second case, the biofilm was affecting the sandstone used in the historical construction of La Galea Fortress (Getxo, North of Spain), a building from the 18th century diffusely influenced by marine traffic due to the presence of Bilbao harbour close to this construction and also influenced by different industries in a diffuse way.

2. Experimental procedure

2.1. Description of the constructions and the surrounding environment

A red biofilm was present in the North oriented façade of a building from the Bizkaia Science and Technology Park in Zamudio (North of Spain). This town is located at 17 km inwards from Getxo coast and at 2 km from the airport of Bilbao. Thus, the building is under the influence of airplanes and road traffic. The conservation state of the building material is good, except for the aesthetic change promoted by the reddish biofilm. The building material employed was a kind of calcareous artificial material with thermal insulating properties. This special characteristic of the material can promote a temperature increase of the external surface of the façade that is ideal for the growth of microorganisms. The measurements in this building were mostly performed in situ, but some fragments affected and non-affected by the biofilm were also collected in order to characterize the main colonizers of the biofilm and also to confirm the obtained in situ results.

The same red biofilm present in La Galea Fortress and previously characterized by Morillas et al. (2015) was also studied with the aim to corroborate the same tendency of metal accumulation. La Galea