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Micro-Raman and SEM-EDS analyses to evaluate the nature of salt clusters present in secondary marine aerosol

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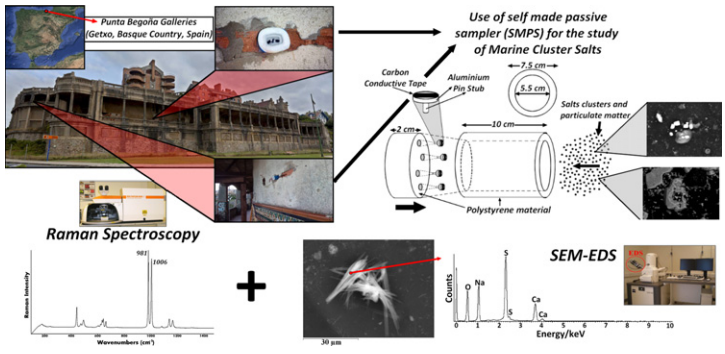
HIGHLIGHTS

- Secondary Marine Aerosol carries high amount of salt clusters.
- Self-made passive sampler was developed to characterize salt clusters.
- Analytical methodology based on SEM-EDS and Raman spectroscopy has been used.
- The conservation state of the buildings close to the sea is influenced by salt clusters.

GRAPHICAL ABSTRACT



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ABSTRACT

Marine aerosol is a complex inorganic and organic chemistry system which contains several salts, mainly forming different type of salt clusters. Different meteorological parameters have a key role in the formation of these aggregates. The relative humidity (%RH), temperature, CO, SO_2 and NO_x levels and even the O_3 levels can promote different chemical reactions giving rise to salt clusters with different morphology and sizes. Sulfates, nitrates and chlorides and even mixed chlorosulfates or nitrosulfates are the final compounds which can be found in environments with a direct influence of marine aerosol. In order to collect and analyze these types of compounds, the use of adequate samplers is crucial. In this work, salt clusters were collected thanks to the use of a self-made passive sampler (SMPS) installed in a 20th century historic building (Punta Begoña Galleries, Getxo, Basque Country, Spain) which is surrounded by a beach and a sportive port. These salt clusters were finally analyzed directly by micro-Raman spectroscopy and Scanning Electron microscopy coupled to Energy Dispersive X-ray spectrometry (SEM-EDS).

1. Introduction

One of the most important natural aerosols from the Earth is the marine aerosol, which is one of the responsible and it contributes significantly to the Earth's radioactive budget, biogeochemical cycling and even to air quality (O'Dowd and de Leeuw, 2007). Marine aerosol is a mixture that comprises different primary and secondary aerosol components (Rinaldi et al., 2010). The Primary Marine Aerosol (PMA) is formed due to the interaction of wind with the ocean surface (O'Dowd and de Leeuw, 2007). The result of this interaction is the mechanical production of sea spray (inorganic sea salts and organic

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matter). Sea spray is produced when the bubbles from the generated whitecap burst (O'Dowd and de Leeuw, 2007). This process originates a jet of saline drops commonly known as Sea Spray Aerosol (SSA) (De Leeuw et al., 2011). This aerosol carries particles of submicrometre size up to a few micrometres (Rodriguez-Navarro et al., 1999). It is estimated that whitecap formation occurs when the wind reaches the speed of 4 $m \cdot s^{-1}$ (O'Dowd and de Leeuw, 2007). One of the physical characteristics of the sea aerosol is the size of its suspended particles (>1 μm), which depends on the wind speed, sea-air water transfer, etc. (O'Dowd and de Leeuw, 2007). The global annual mass emission of Primary Marine Particles (PMP), or sea aerosol, is estimated to range from $2 \cdot 10^{12}$ to $1 \cdot 10^{14}$ Kg $year^{-1}$, which is comparable to that of dust aerosol (Textor et al., 2006). Apart from this, the SSA has a key role in chemical reactions such as the coupled cycles of sulfate-sea salt (O'Dowd et al., 1999a, 2000) and nitric acid-sea salt (Sørensen et al., 2005). Apart from that, other authors focused their attention on the study of SSA role in the climate change (Intergovernmental Panel on Climate Change (IPCC), 2001). SSA has also been linked to the Marine Boundary Layer (MBL) cycle through the activation of halogens, leading to ozone depletion (O'Dowd et al., 1999b; Vogt et al., 1996; McFiggens et al., 2000).

The Secondary Marine Aerosol (SMA) production consists on cluster particle formation resulting from gas to solid particle conversion (O'Dowd and de Leeuw, 2007). The sulfur species present in the atmosphere (e.g. SO_x) and coming from the anthropogenic emissions are closely related with the SMA formation. The SMA formation occurs in two steps. In the first one, the new particle formation via the nucleation of 0.5–1 nm stable clusters takes place. Once these clusters are formed, they can grow to larger sizes via condensation. During the second step, the clusters growing via different heterogeneous reactions and aqueous phase oxidation of dissolved gases in existing aerosol particles happens. In terms of the sulfur cycle, dimethylsulphide (DMS), a waste produced by phytoplankton, is released from the ocean into the atmosphere where it undergoes oxidation by the OH radical to form SO_2, which is further oxidized to H_2SO_4 (Charlson et al., 1987). H_2SO_4 is thought to participate in binary homogeneous nucleation with H_2O, and in ternary nucleation with H_2O and NH_3. Apart from this, in coastal zones where regular and significant particle nucleation takes place, iodine oxides have a key role in clusters nucleations and growth (O'Dowd et al., 2002).

According to the different sizes that aerosol particles can raise, marine aerosol clusters can have 1000–10,000 nm volume diameter size (Heintzenberg et al., 2003).

Although the main mass fraction of marine aerosol is inorganic sea salts, organic matter is also present and can contribute to the overall mass (Claeys et al., 2010). Usually, marine aerosol carries organic residues from the decomposition of algae, plankton and salts. The most abundant salt carried on marine aerosol is sodium chloride, but other types of chemical compounds like sulfates and nitrates can be also present (Zhao and Gao, 2008; Abdalmogith et al., 2006).

Apart from chlorides, sulfates and nitrates, other ions are also present in a suspended way such as Ca^{2+}, K^+, Mg^{2+}, Fe^{3+}, Al^{3+}, Sr^{2+}, NH_4^+, HCO_3^- and Br^-. Usually, organic matter has also high importance because it represents around the 10% of marine aerosol (Chameides and Stelson, 1992; Tervahattu et al., 2005). Additionally, $P.M._{2.5}$ and $P.M._{10}$ airborne particulate matter can be transported by the marine aerosol including metals such as Pb, Cd, Cr, Mn, Cu, Mo, Rh, Ni, As, Ti, V and Hg (Calparsoro et al., 2017; Arruti et al., 2011; Morillas et al., 2016a, 2016b). The source of these heavy metals can reside in the influence of maritime traffic, port activities and also industry or even road traffic (Gómez et al., 2005).

Taking into account the high amount of salt clusters present in marine aerosol, it is clear that this environmental factor has influence on the surrounding landscape. One of this is the surrounding built heritage. In this sense, there are many chemical reactions involved in the interaction between marine aerosol and building materials (García-Florentino et al., 2016; Morillas et al., 2012, 2013, 2015a, 2016c, 2016d) and besides of marine aerosol it can be extended in general to salt crystallization into building materials in particular to those belonging cultural heritage (Gómez-Laserna et al., 2015; Godts et al., 2017; Benavente et al., 2015; Maguregui et al., 2008).

In this work, a self-made passive sampler (SMPS) was tested as a tool to collect salt clusters coming from Secondary Marine Aerosol (SMA). The SMPS was installed in a 20th century historic building (Punta Begoña Galleries, Getxo, Basque Country, Spain), which is surrounded by a beach and a sportive port. This building shows a wide variety of pathologies (salts crystallizations, black crust formation, etc.) which some of them would be originated by the impact of acid gases and airborne particulate matter. In order to determine the nature of the salt cluster particles and to analyze them without any sample treatment, non-invasive techniques such as Scanning Electron Microscope coupled to Energy Dispersive X-ray Spectrometry (SEM-EDS) and micro Raman spectroscopy were selected.

2. Materials and methods

2.1. Installation of the self-made passive sampler (SMPS) in Punta Begoña Galleries

The passive sampler design used and successfully tested in the Punta Begoña Galleries has been previously described elsewhere (Morillas et al., 2016a). This passive sampler basically consists in a polystyrene cylinder where several pins stubs covered with carbon tapes are inserted inside. Thanks to the natural wind and the nature of the tapes, many different types of suspended particles can be deposited (see Fig. 1). Indeed, the SMPS was installed in the favorable direction of the winds to the façade. In this self-made device, the particulate matter is spontaneously trapped, without artificially pumping the air, in a carbon tape fixed on the surface of a typical SEM pin stub used to fix samples during SEM-EDS measurements (see Fig. 1). Concretely, in the installed passive sampler three pin stubs with the carbon tape were inserted (see Fig. 1). The content of the "pin stubs", mainly particulate material adhered to it, can be characterized directly without any

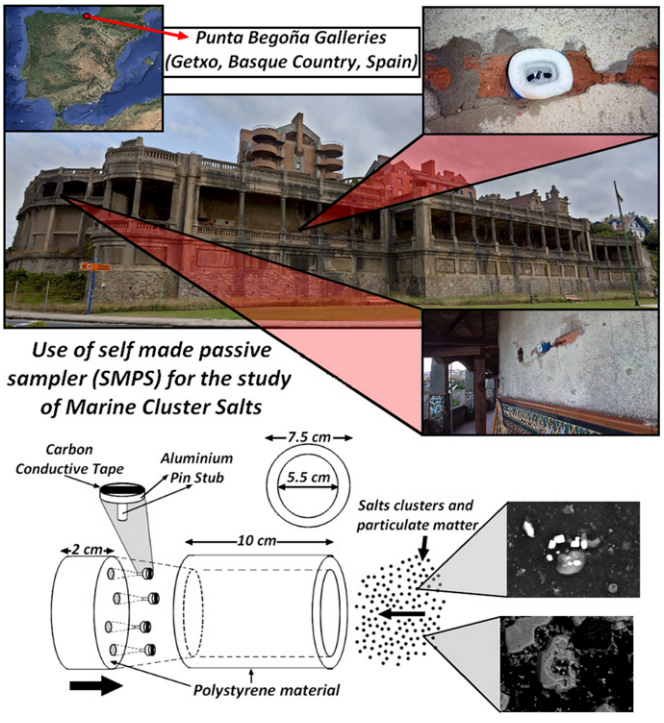

Fig. 1. a) Scheme of the Punta Begoña Galleries sampling and b) self-made passive sampler (SMPS) scheme.