Science of the Total Environment 550 (2016) 285–296

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Study of particulate matter from Primary/Secondary Marine Aerosol and anthropogenic sources collected by a self-made passive sampler for the evaluation of the dry deposition impact on built heritage

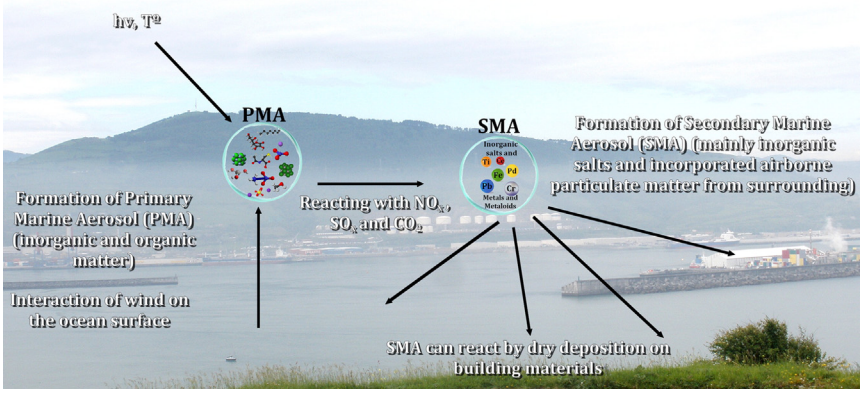
Héctor Morillas [a,*], Maite Maguregui [b], Cristina García-Florentino [a], Iker Marcaida [a], Juan Manuel Madariaga [a]

[a] Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, Basque Country, Spain
[b] Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU, P.O. Box 450, 01080 Vitoria-Gasteiz, Basque Country, Spain

HIGHLIGHTS

- Primary Marine Aerosol was simulated evaporating the seawater in the laboratory.
- Self-made passive sampler was developed to characterize Secondary Marine Aerosol.
- In the Secondary Marine Aerosol, different airborne particles are also suspended.
- Dry deposition is a key factor on the conservation state of cultural heritage.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 October 2015
Received in revised form 26 December 2015
Accepted 13 January 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Dry deposition
Marine aerosol
Raman spectroscopy
SEM-EDS
Sulfate
Nitrate
Chloride

ABSTRACT

Dry deposition is one of the most dangerous processes that can take place in the environment where the compounds that are suspended in the atmosphere can react directly on different surrounding materials, promoting decay processes. Usually this process is related with industrial/urban fog and/or marine aerosol in the coastal areas. Particularly, marine aerosol transports different types of salts which can be deposited on building materials and by dry deposition promotes different decay pathways. A new analytical methodology based on the combined use of Raman Spectroscopy and SEM-EDS (point-by-point and imaging) was applied. For that purpose, firstly evaporated seawater (presence of Primary Marine Aerosol (PMA)) was analyzed. After that, using a self-made passive sampler (SMPS), different suspended particles coming from marine aerosol (transformed particles in the atmosphere (Secondary Marine Aerosol (SMA)) and metallic airborne particulate matter coming from anthropogenic sources, were analyzed. Finally in order to observe if SMA and metallic particles identified in the SMPS can be deposited on a building, sandstone samples from La Galea Fortress (Getxo, north of Spain) located in front of the sea and in the place where the passive sampler was mounted were analyzed.

* Corresponding author. Tel.: +34 946018297.
E-mail address: hector.morillas@ehu.es (H. Morillas).

http://dx.doi.org/10.1016/j.scitotenv.2016.01.080
0048-9697/

1. Introduction

Many of the studies dealing with the characterization of building materials from historical sites close to the sea, conclude that marine aerosol exerts high influence on their conservation state (Stefanis et al., 2009, Urosevic et al., 2010, Torfs and Van Grieken, 1997, Zezza and Macri, 1995, Martinez-Arkarazo et al., 2007, Morillas et al., 2012, Morillas et al., 2013, Morillas et al., 2015a, Morillas et al., 2015b, Morillas et al., 2015c, Morillas et al., 2016). To understand the formation of marine aerosol, the main soluble compounds present in seawater must be known. As many authors point out, the main ions that are present in seawater, from a higher to lower percentage, are chloride (Cl^-), sodium (Na^+) sulfate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), bicarbonate (HCO_3^-), bromide (Br^-), borate ($H_2BO_3^-$) and strontium (Sr^{2+}) (Culkin, 1965, Dyrssen and Sillen, 1967). Marine Aerosol is made out of inorganic salts and organic matter dissolved in water, and comprises primary (PMA) and secondary aerosol (SMA) particles. PMA results mainly from the interaction of wind over the oceans' surface. The generation of whitecaps and the resulting jet drops via bubble-bursting of the whitecap generated, gives as a result the formation of sea-spray particles ranging from the submicrometer scale, up to a few micrometers. SMA production involves the growth of formed particles; this process can follow two different ways: (i) after the formation of stable clusters from 0.5–1 nm, by nucleation, condensation processes lead to larger size particles, and (ii) via heterogeneous oxidation reactions in aqueous phase of dissolved gases in the existing aerosol particles (O'Dowd et al., 1998; O'Dowd and Hoffmann, 2005; O′Dowd and de Leeuw, 2007). Apart from dissolved salts, marine aerosol can also transport trace metals and nutrients from oceans to the atmosphere, through wet and dry depositions (Baker et al., 2007).

Considering that most of the suspended particles present in PMA and SMA have sizes below 10 μm, techniques that allow high magnifications are necessary for their characterization. Nanometric scaled structures, as well as aerosol particles are often characterized using transmission electron microscopy (TEM) equipped with a variety of analyzers such as bright field and dark field imaging, selected area electron diffraction (SAED), electron energy loss spectroscopy (EELS) and energy dispersive spectrometry (EDS) (Chen et al., 2006, Pósfai et al., 2004). Apart from these, other techniques are able to detect and quantify the mixed particulate matter from marine aerosol. For example, in order to characterize small clusters present in marine aerosol, a combination of SEM-EDS with TEM-EDS and STXM-NEXAFS can be used (Ault et al., 2013). Besides elemental characterization, molecular characterization using Raman micro-spectroscopy has been reported as a useful tool to determine composition of airborne marine aerosol (Deng et al., 2014). Other authors had reported the use of infrared spectroscopy (FTIR) for the molecular characterization of inorganic and organic compounds in aerosol samples collected using Teflon filters (Coury and Dilner, 2008, Shaka and Saliba, 2004). Organic compounds present in marine aerosol, had been widely determined by GC/MS (Kawamura and Sakaguchi, 1999). A combined use of FTIR and Raman spectroscopy is also a good alternative to perform a complementary molecular characterization (Gaffney et al., 2015).

Nowadays, different sampling methods for collection and analysis of aerosol particles can be found. In general terms, these sampling methods are expensive and require regular maintenance (Wagner and Leith, 2001a). As an example of those kinds of sampling methods, cascade impact can be mentioned. With this kind of sampling methods, airborne particulate matter can be separate according to their size (e.g. PM_{10}, $PM_{2.5}$). In this case, a pump must be used to impulse the air to the sampler. The first "low cost" aerosol sampler was described in 2001 (Wagner and Leith, 2001b, Wagner and Leith, 2001c). It was small, lightweight, cheap, easy to operate and also very efficient. After the sampling (from hours to months), the sampler was covered and brought to the lab.

According to the inorganic compounds in the suspended marine aerosol particles, the deposition of solid NaCl, KCl, SiO_2, Fe_2O_3, Na_2SO_4, K_2SO_4, $CaCO_3$, and $CaSO_4$ is widely known. The most abundant particle that can be found are carbonaceous and $(NH_4)_2SO_4/NH_4HSO_4$-containing particles, followed by minerals (e.g., aluminosilicate, SiO_2, $CaCO_3$), sea salt (NaCl etc.), K-rich particles (e.g., K_2SO_4 and KCl), Fe-rich particles, flying ash and transition or heavy-metal-containing (e.g., $ZnSO_4$, $ZnCl_2$, $PbSO_4$) particles (Geng et al., 2010). Apart from them, nitrates such as $Mg(NO_3)_2$, KNO_3, $NaNO_3$ can be also present (Ro et al., 2001). Among the other compounds above mentioned, marine aerosol also carries a high load of sulfates mainly in form of magnesium sulfate or magnesium mixed sulfates (Maskey et al., 2011, Zhao et al., 2006).

The effect that marine aerosol exerts on the environment is high. Thus, buildings that are close or immersed on coastal areas, will suffer the effects of marine aerosol in the form of dry deposition. These dry marine aerosol depositions promote different decaying processes on the building materials (Stefanis et al., 2009, Urosevic et al., 2010, Zezza and Macri, 1995). For example, the inorganic salts mentioned above can migrate to the inside of building materials through their pores promoting new salts formations or crystallizations (sub-efflorescences) within the porous matrix with its consequently material degradation (Zhao and Gao, 2008, Abdalmogith et al., 2006).

In this work, a self-made passive sampler (SMPS) was developed for direct airborne particulate trapping coming from a marine and a direct urban-industrial environment. The trapped particles were then characterized using SEM-EDS and Raman micro-spectroscopy. Along with that, inorganic salts formed from the direct evaporation of sea water were also characterized in order to determine what is the composition of PMA particles, which of them could lead to the formation of SMA particles, that are going to be the trapped in the SMPS. Finally, a correlation between the composition of the trapped particles and those deposited on the surface of the sandstone from La Galea Fortress (Getxo, Basque Country, north of Spain), located in front of the sea will be establish, in order to evaluate the negative consequences that this kind of depositions can cause on the conservation state of building materials such as sandstone.

2. Experimental section

2.1. Samplings

To determine the composition of the salts present in seawater, a sample from the Abra Bay (Getxo, north of Spain) was collected. This seawater (1 ml) was evaporated over an aluminum pin stub covered by a carbon conductive tape in open air conditions (22 °C). The SMPS developed consisted on several aluminum stubs as described above, on the bottom of a 10 cm polystyrene cylinder that allows us to collect airborne particulate matter from the other end (see Fig. 1A). The SMPS was fixed during two months (12th March 2015 to 12th May 2015) to the South-southeast side (just in an open window for protect it of the rainfalls) of La Galea Fortress' tower in Getxo (north of Spain) using silicone adhesive (see Fig. 1B and C). Thanks to the SMPS design, a previous pretreatment of the conductive tape is not required. Moreover the main advantages of the SMPS are the low cost to built it, the low size and finally is easy to operate. In this way, after the sampling the aluminum stubs are saved in a little crystal box and brought to the lab. Thanks to the data collected in an atmospheric station that takes place just to 200 m from our sampling point (http://www.ingurumena.ejgv.euskadi.eus/r493614/es/aa17aCalidadAireWar/datohistorico?locale=es), the averages of different meteorological parameters during the two months were the following: the average of wind velocity was 1.53 m/s and the average of wind direction was 173.5°. The atmospheric pressure was 1013.1 mBar, the relative humidity (RH %) was 74.5% and the average temperature, 13.85 °C.