THE DECAY EFFECTS OF SEA-SALT AEROSOL ON THE SURFACE OF HISTORIC BUILDINGS

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EXTENDED ABSTRACT

The deposition of airborne particulate matter on the surface of historic buildings causes a number of physicochemical decay processes, leading to the deterioration of the building materials. Particularly in coastal areas, marine aerosol intensifies the process of weathering through the deposition of sea-salt particles, which is controlled by various environmental parameters. A study is being carried out at the medieval city of Rhodes, where most of the buildings are constructed of local sandstone, focusing on the revelation of the building material's decay mechanism due to sea-salt aerosol. A specific interest is directed on the environmental factors that affect the deposition rate of sea-salt particles and enhance the weathering procedures. In order to address the environmental effect on historic buildings, meteorological data was collected and combined with the results obtained by monitoring the aerosols and the total deposition. Aerosols were collected using a 10-stage impactor and dry deposition was monitored on stone specimens. Stone samples, taken from dated positions, were examined in order to assess the deterioration degree and to study the total deposition rate. The components of the collected particulate matter were analysed by means of SEM-EDX in order to study their composition and physicochemical characteristics. The synergistic effect of sea-salt aerosol and anthropogenic airborne particulate matter is discussed through the results of the analyses. A correlation between the collected data and the environmental parameters that control marine aerosol production, its physicochemical transformation in the atmosphere and its deposition, is performed in order to explain the weathering phenomena that cause characteristic decay patterns due to soluble salt crystallisation. In the present paper the methodology used to monitor the environmental parameters and the production of aerosols is presented, the initial outcomes of the research are analysed and the targets set for its completion are presented.

Key words: marine aerosol, deposition, building materials, sandstone weathering phenomena, environmental parameters, particle analysis

1. INTRODUCTION

Rhodes is located at the southeastern part of the Aegean Sea. The medieval city begun to modulate at the end of the 7th century AD, on the remains of a brilliant Hellenistic settlement. In 1988 the medieval city of Rhodes was characterised by UNESCO as a World Heritage City [1].

All the buildings of the medieval city are constructed of local sandstone, a material susceptible to the action of soluble salts crystallisation cycles [2]. In Rhodes there is a constant infusion of the building materials with soluble salts, through the course of production, transportation and deposition of sea-salt aerosols on architectural surfaces. Rhodes sandstone is fossiliferrous biocalcareous porous of low strength. Different qualities of the same stone, with different behavior in weathering process have been used. Nevertheless, deterioration appears as an irregular loss of material, following an alveolar weathering pattern. NaCl crystallisation causes granular disintegration of the stone [3].

The aim of the project is to establish a correlation between the environmental factors, marine aerosol properties and building materials weathering. The environmental phenomena that determine the deposition of sea-salt aerosols and stone decay mechanisms are associated in order to investigate the action of soluble salts originating from marine aerosols.

2. ENVIRONMENTAL SETTING

The area of the Eastern Mediterranean is affected by three main aerosol sources: the sea, the Sahara desert and industrialized areas of N-NE Europe [4]. The environment of the medieval city of Rhodes is marine and urban, with varying microclimatic conditions. The climate of Rhodes is characterised by mild temperature, high relative humidity and high sun exposure (over 200 d yr^{-1}). Temperature is ranging, in average, between 8 and 28.7 ^{o}C, whilst the mean annual temperature is 19 ^{o}C. Relative humidity (RH%) varies in the range of 45.5 to 86.4%. Rainfall (728.70 mm yr^{-1}) is more abundant in the winter (December, 164 mm; January, 158 mm) with a minimum in the summer (July, August 0.2 mm). The number of dry days is between 125 and 150 with the driest period between April and September. The wind direction during the winter is 2-5 BF South, Southeast with a great percentile of stillness, whilst during the summer is 3-6 BF West, Northwest with a small percentile if stillness [5]. The medieval city of Rhodes creates an interesting combination and a variety of microclimatic conditions controlling the crucial mechanisms, which lead to distinct decay patterns of the building materials [3].

2. EXPERIMENTAL

A monitoring mechanism has been set up around the medieval city, to study the phenomena that control sea-salt aerosol deposition and to correlate them with the stone weathering mechanisms caused by soluble salts. Environmental conditions are monitored, airborne and deposited particles are collected in order to create a database that will be used in describing the phenomena causing building materials to decay. The project involves the study of the environment and the atmosphere around the monument so as to reveal the phenomena taking place on its surface. The following methodology is carried out in order to study the atmosphere and the phenomena that promote the formation and deposition of particles.

Wind direction and wind speed monitoring is conducted by the use of an anemometer which is placed at the north part of the city. The data logger of the anemometer collects data on wind speed and wind direction on a 24h basis. Data is processed by Wind Rose software. Temperature and relative humidity are monitored by means of Gemini Tiny Tag data loggers.

Sampling of particles is carried out at a small tower at the fortifications of the city facing the sea and the ring road within the sector 270^{o}-90^{o}. Suspended particles with aerodynamic equivalent diameters (Dp) ranging from 18μm to 0,056μm were collected by a ten-stage cascade impactor (MOUDI Model 110, MSP Corporation) at a flow rate of 30

L/min. At each stage the collected particles are deposited uniformly over the entire impaction plate by rotating the impaction plate relative to the nozzles. The impaction substrate used was aluminium foil in order to achieve a stable tare weight. The substrates were coated with No 11025 silicon spray (Cling-Surface Co., Inc., Angola, NY) in order to reduce particle bounce. After the oil application the substrates were placed in an oven at 65 ^{o}C for 90 min [6]. An SEM stub was attached onto to impaction substrate that facilitates the observation and analysis of the samples by SEM-EDX.

Eight sampling runs over a period of one year (autumn 2004 – autumn 2005) have been designed for the same sampling location. The scope is to study the environmental effect on the formation and transportation of sea-salt aerosol particles. Sampling is carried out when N-NW and S-SW wind is prevailing respectively, at each season. The duration of the sampling exercise is 24h in order to minimise the risk of any conditions' change. The collected particle mass is enough to conduct all the necessary analyses. Four, longer sampling runs, of about 200h spread over a period of ten days at each season have also been designed and conducted in order to acquire a better understanding of the phenomena when the environmental conditions change.

Sandstone and marble specimens (5cm x 5cm x1cm) were placed vertically and sheltered from rainfall in iron racks at five positions on the fortifications around the medieval city. The distance from the sea ranges from 30 to 520 m and their orientation follows the exposure of the buildings that have been placed upon. Specimens are collected after an exposure period of three, six and twelve months. On these specimens deposited particles are studied and any surface change, as well as any deposition rate will be analysed.

Glass collectors have been placed at the monitoring positions. Particles deposited on glass collectors are supposed to be the same as those deposited on stone specimens but with no interferences derived from the stone's surface characteristics.

Sandstone samples were collected from buildings dated from the 14th to the 20th century around and inside the city fortifications. The orientation of the walls and their age are important in order to study the deposition rate, the decay extend and morphology.

4. RESULTS

A compartmentation of the detected elements in the cascade impactor occurred in all of the sampling exercises. Collected particles were characterised by means of SEM-EDX [7]. The scanning electron microscope used was a JEOL 6100 with a microanalysis unit LINK eXL 100. At the first three stages (18-5.6μm) the detected elements were mainly calcium, silicon, aluminium, potassium, iron and magnesium indicating eroded material particles. At the next four stages (3.2-0.56μm) sodium and chorine were detected along with the above-mentioned elements, whereas at the last four stages (0.32-0.056μm) sulphur was combined with other elements depending on the environmental conditions. Sodium chloride crystals were observed on stone specimens exposed for three months as well as deposited particles derived from soil and sandstone erosion (calcite and Al-silicates). As mentioned above, aerosol sampling was performed when the environmental conditions were steady in order to correlate sea-salt aerosol production and deposition with the environmental factors. 'Sampling I' was performed at high relative humidities and temperatures caused by S-SE winds, whereas 'Sampling II' was performed at low relative humidities and temperatures caused by N-NW winds. The wind direction for the whole sampling period was S-SE, N-NW and NE.

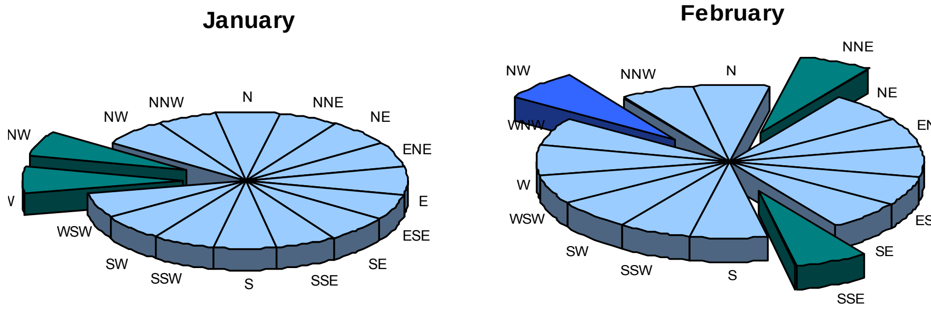


Figure 1: Wind direction frequency during sampling period

The mean ambient temperature during ‘Sampling I’ was 15 ^{o}C and the mean RH 80%, whilst during ‘Sampling II’ the values were 10 ^{o}C and 35% respectively. Conditions variation occurred within 48h, influencing the physical state of airborne and deposited particles.

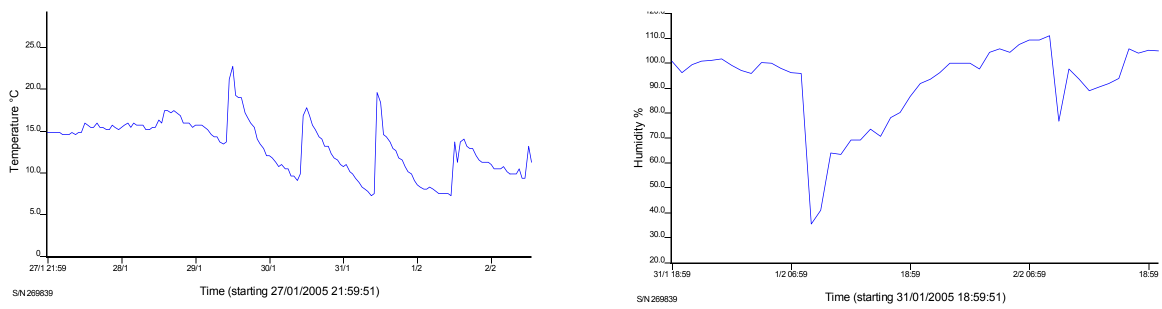
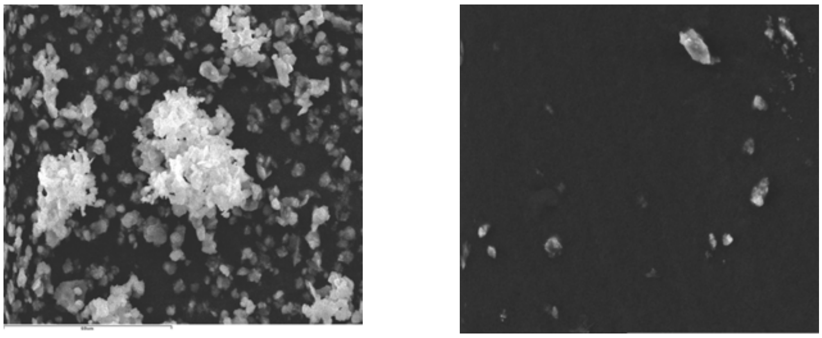


Figure 2: Temperature and relative humidity variations at the time of aerosol sampling

4. DISCUSSION

South winds produce and carry coagulated particles composed of eroded material and sea-salt. High RH promotes the phenomenon of condensation, especially on the surface of hygroscopic soil particles carried by the south winds to Rhodes [8]. SEM observations and EDX microanalysis have identified particles composed mainly of Ca, Si, Mg, Fe, Al Na, and Cl of this form, that deposit directly on architectural surfaces. Particle sizes range from 10 to 60μm. North winds on the other hand, carry fine particles (~0.1μm) composed of Ca, Si, Mg, Fe, Al, Na and S. Low relative humidity does not promote condensation thus water molecules do not interfere with the transformation of aerosol particles. Crystals of sodium sulphate were identified at the lower stages of the impactor. The formation of Na_2SO_4 under the particular environmental conditions is to be investigated since it depends on the interaction between sea-salt aerosols and anthropogenic emissions. NaCl is only capable of crystallisation damage, while Na_2SO_4 can cause both crystallisation and hydration damage [9]. The decahydrate mirabilite ($Na_2SO_4 \cdot 10H_2O$) occupies 314% higher volume than the anhydrous form thenardite (Na_2SO_4) [10]. The ring road is north of the sampling position and it seems that sulphur produced of exhaust emissions is carried along with sea-salt producing Na_2SO_4. Because of the fine size of the particles, they can be deposited directly within the pores of the stone as opposed to NaCl crystals that were observed on the surface of the stone specimens. There is of course, a quantitative relation over NaCl, which although it forms coarser particles, especially when combined with eroded material, its total deposited mass is higher than that of Na_2SO_4. Equilibrium RH has to be considered as well, since the RH_{eq} for Na_2SO_4 is 95% and for NaCl is 75% [11] indicating that in dry conditions both salts are deposited in their crystalline form, whereas NaCl in humid conditions is transferred in a solution with a great potential of penetrating the stone matrix.



a b

Figure 3: SEM micrographs of (a) coagulated particles, (b) fine calcite and quartz particles

Specific environmental conditions cause the formation and deposition of particles with properties that correspond to the factors influencing their production [12] [13]. When the conditions were not stable a clear separation of eroded material and sea-salt particles occurred. A sampling exercise of 180h with the wind direction alternating between NW and SE followed by a change in temperature and relative humidity, showed that NaCl had formed separate crystals. It can be assumed that the same phenomenon occurred on the surface of the stone specimens, since they are exposed to alternating environmental conditions.

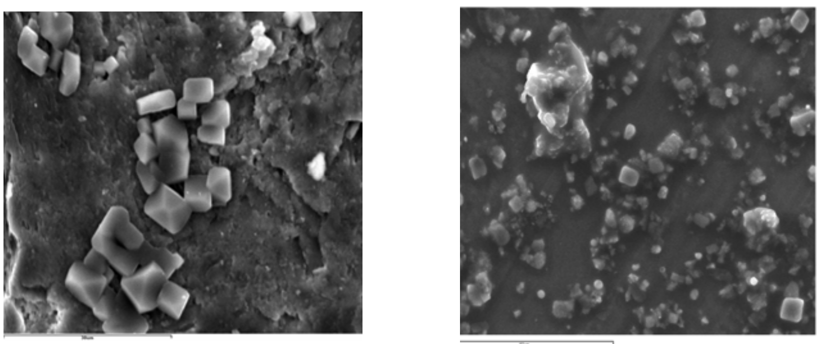


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Figure 4: SEM micrographs of (a) NaCl crystals on stone specimen, (b) NaCl crystals and dust particles

Research is continuing with the study of stone samples collected from original architectural surfaces. Different decay morphology should be expected between samples taken from walls facing north and those facing south. Finest particles are usually the most damaging ones. Their high specific area and chemical composition enhances their action as they can retain the humidity of the stone and facilitate the deposition of other particles.

Environmental monitoring and aerosol sampling will continue in order to investigate the influence of seasons on the deposition of sea-salt aerosols and the crystallisation cycles of soluble salts.

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