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Dry deposition effect of marine aerosol to the building stone of the medieval city of Rhodes, Greece

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ABSTRACT

Continuous exposure to marine aerosol of the historic buildings of the medieval city of Rhodes (Greece) has produced severe weathering of the building stone (biocalcarenite). The aim of the research was to investigate the effect of marine aerosol dry deposition on the architectural surfaces. Particles were collected in a cascade impactor, on stone samples collected at the buildings and on fresh quarry samples exposed at the monitoring positions. Meteorological conditions were constantly monitored in situ. Collected samples were analysed by SEM/EDX and chemical techniques to acquire information on their morphology and chemical composition. According to their morphology and composition, collected particles were classified into four major groups. Deposited and suspended particles were compared to determine their possible sources. The production of marine aerosol is favoured when north, high-speed winds prevail. Sea-salt is deposited having different morphologies. The zone mostly influenced by the deposition of sea-salt lies within 100 m from the northern fortification wall of the city. Stone mass loss was determined for different monitoring positions and was found to be proportional to sea-salt concentrations. Relative humidity fluctuations permit NaCl deliquescence/crystallisation cycles. Macroscopic examination of the buildings confirmed that the positions with the highest chloride concentrations present severe damage.

1. Introduction

The research has been undertaken at the medieval city of the island of Rhodes in Greece, which is located at the south-eastern part of the Aegean Sea. In 1988, the medieval city of Rhodes was characterised by UNESCO as a World Heritage City due to its wealth of architectural heritage [1]. All the buildings of the medieval city are constructed of the local stone, a porous material susceptible to the action of soluble salts. Although Rhodes stone has been historically and commercially known as sandstone, it is in fact a bioclastic limestone. The exposure to marine aerosol has produced significant weathering of the building stone. The aim of this work is to investigate marine aerosol dry deposition on the monuments of Rhodes in order to evaluate the impact of the atmospheric environment to the exposed building stone. The way to achieve this is by associating suspended particles to their source, meteorological conditions to the aerosol species produced, deposited particles to suspended ones and deposited sea-salt to stone mass loss.

These associations were achieved by developing a methodology, which was based on measurements conducted in the field. By applying the presented methodology, the meteorological conditions favouring marine aerosol production and deposition in the area were studied, the deposited sea-salt was quantified, and marine aerosol deposition was correlated to stone weathering. In the adopted approach, the description of soluble salt decay mechanism and aerosol deposition [2–17], as well as the study of the types and forms of the decay of building materials caused by soluble salts [17–23] were incorporated. In addition, an attempt was made to study the long-term effect of marine aerosol deposition on buildings dated to the 14th century. Through this holistic approach, the production of marine aerosol, its transformation to a weathering factor, its action and effect on Rhodes stone are interrelated, associating the historic building to its surrounding environment.

2. Experimental

2.1. Methodology

The medieval city of Rhodes is built at the northern part of the island and its coast lies to the north and east. To the west and south, the modern city expands. A green zone of 150 m in width, created by parks, separates the modern city from the medieval, leaving the latter exposed to all directions. Local stone was

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extensively used in medieval times as the main building material. Typically, Rhodes stone has a high open porosity (10–40%), with a pore distribution discriminating above 10 μm, low tensile strength (0.5–0.9 MPa) and high values of water absorption coefficient (0.23–$2.14\,kg\,m^{-2}\,s^{-0.5}$) [24,25]. The rock fabric affects the petrophysical properties of porous stones which in turn control the behaviour of the material during weathering processes [26,27]. Petrographic observations were carried out to find out the possible occurrence of clay minerals in the stone matrix, as the presence of clay minerals in the cementing material of sedimentary stones, have been reported to act synergistically with salt weathering [28,29].

In order to study the phenomena that control sea-salt aerosol deposition and to correlate them with building stone weathering, a monitoring network was set up around the medieval city of Rhodes (Fig. 1). The monitoring period was 1 year, from October 2004 to September 2005, in order to acquire seasonal data. During this period, environmental conditions were monitored, airborne particles were collected, freshly quarried stone samples were positioned on the fortifications of the city and historic stone samples were obtained from the architectural surfaces in order to study the deposited particulate matter. This network provided all the necessary data to describe the production and deposition of marine aerosol on the building stones. The following methodology was carried out in order to study the atmosphere and the phenomena that promote the production and deposition of airborne particles.

Six monitoring positions were selected on the fortifications of the city according to their distance from the sea and their orientation (Fig. 1). Monitoring "Position 1" was a medieval tower at the northern walls of the city. It is the highest point of the fortifications and open to every direction. In order to confirm the atmospheric origin of the particles deposited on stone surfaces and to study their chemical composition and morphology, aerosol sampling was carried out at "Position 1". Sampling was carried out when there was no precipitation, in order to acquire results exclusively on the dry deposition of marine aerosol [30]. Suspended particles were collected by a 10-stage cascade impactor (MOUDI Model 110 by MSP Corporation) with nominal cut-points 18 (inlet), 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10 and 0.056 μm at a flow rate of $30\,l\,min^{-1}$. At each stage collected particles were deposited uniformly over the entire impaction plate, which was rotated automatically relatively 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 °C for 90 min [31]. Twelve sampling events spread over the monitoring period were conducted at "Position 1". The duration of each sampling event was 12 h in order to minimise the risk of large alteration of the meteorological conditions. One hundred and thirty-two impaction substrates corresponding to 11 different particulate size fractions of the 12 sampling events were collected for the particular period.

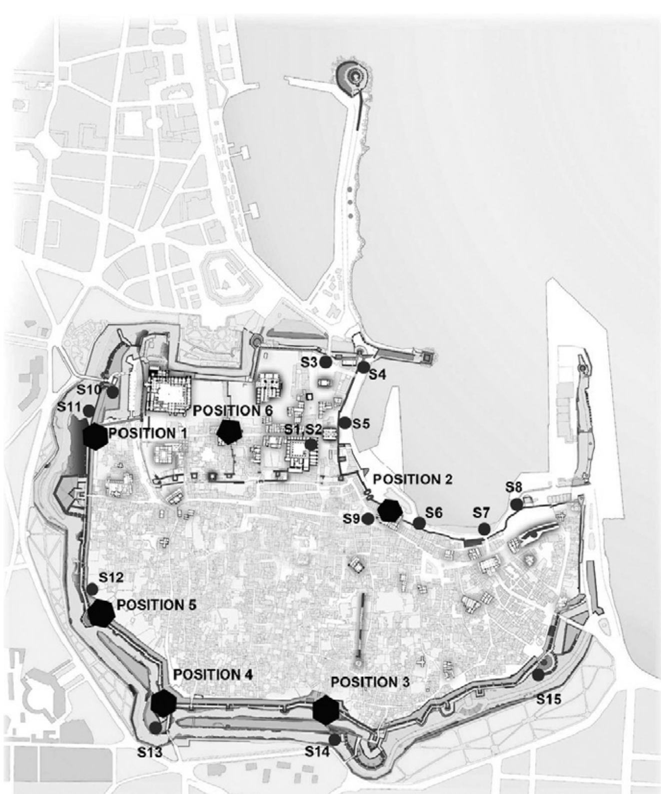

Fig. 1. The monitoring network which was set up at the medieval city of Rhodes (map provided by the Archaeological Service of Rhodes).

In order to study the influence of meteorological conditions on the production and deposition of marine aerosol, wind direction, wind speed, ambient temperature and relative humidity were monitored in situ. It was essential to obtain information on these parameters at the monitoring site and not from the nearest meteorological station, which is located at the airport, about 20 km from the city, due to the fact that microclimatic conditions can be different within this range of distance. Wind direction and wind speed monitoring was conducted by the use of an anemometer (by Thies Clima and Wittich & Visser Prf) which was placed at "Position 6" located at the highest point of the city, at the roof of the Spanish quarters (Fig. 1). This position was only used to collect anemometric data. The data logger of the anemometer (Stylitis 41 by Symetron) collected data on wind speed and wind direction on a 24-h basis. Data were then processed by "Wind Rose" software, which was developed by the Greek Centre for Renewable Energy Sources. Temperature and relative humidity were monitored by means of Gemini Tiny Tag data loggers, which were placed at Positions 1 and 2 (Fig. 1). The reading logging interval was 1 h. Acquired data were processed using Gemini Tiny Tag software.

In order to examine the morphology and chemical composition of the deposited particles, 15 freshly quarried stone samples with dimensions $5\,cm \times 5\,cm \times 1\,cm$ were prepared. Fresh samples were washed with deionised water and then placed vertically and sheltered from rainfall at iron racks at Positions 1–5 on the fortifications around the medieval city (Fig. 1). A similar approach was applied to the study of the airborne particulate matter in the Cathedral of Burgos in Spain, which was adopted and proved efficient in Rhodes as well [32]. The stone used to produce fresh samples was carefully selected from the historic quarry in order to use material having the same physicochemical and mechanical characteristics as the one used for building purposes in medieval times. The characteristics of the monitoring positions are presented in Table 1.

The distance of the positions from the sea, ranged from 20 to 650 m and the iron racks orientation followed those of the buildings that were attached upon. Fresh samples were placed in position contemporaneously with the initiation of aerosol sampling, in order to correlate the results acquired from studying suspended and deposited particles. Fresh samples were collected after being exposed for 3, 6 and 12 months during the monitoring period, in order to study the particle deposition rate.

To investigate the cumulative effect of sea-salt deposition on stone surfaces, 16 historic stone samples were obtained from the