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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.

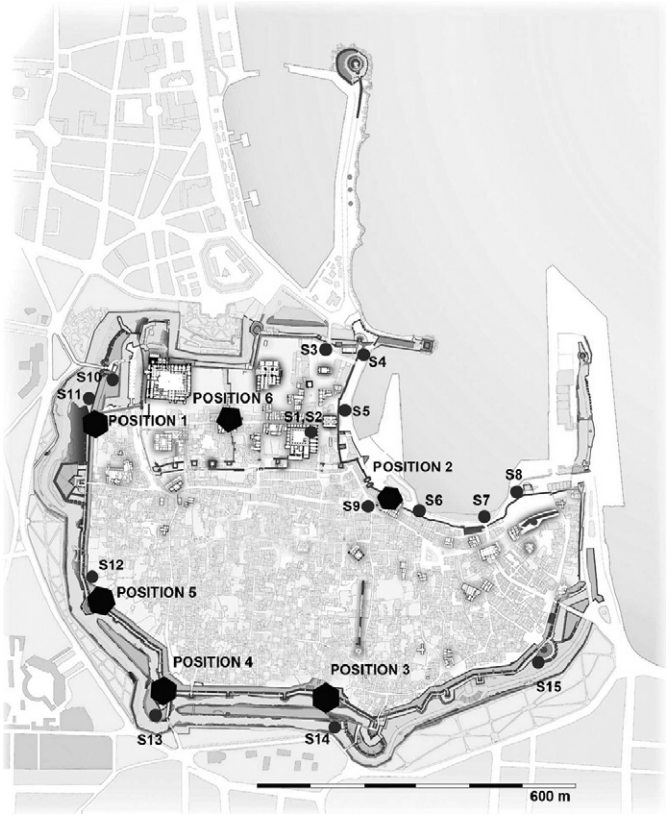

Fig. 1. The monitoring network which was set up at the medieval city of Rhodes (map provided by the Archaeological Service of Rhodes).

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 × 5 cm × 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

medieval buildings and recent restorations around and inside the city fortifications. It must be noted that historic samples were deliberately obtained from the highest parts of the constructions, having a height of at least 10 m, in order to exclusively study the deposition of particles transferred through the atmosphere. Sampling positions are indicated in Fig. 1 by the letter "S" and their characteristics are presented in Table 2. Historic samples were acquired from the surface of buildings dated from the 14th century to restorations of the 20th century in order to compare the concentration of sea salt between stones of different age. The orientation of the walls and their age were important in order to correlate them with marine aerosol deposition. Furthermore, historic samples S6, S11, S12, S13 and S14 were deliberately obtained at the monitoring positions where fresh samples had been placed, in order to compare the results from the deposited particles analysis (Fig. 1).

2.2. Sample analysis techniques

Petrographic examination of Rhodes stone was performed at samples obtained from the buildings. Thin sections were prepared and examined under a Leica DM-LP petrographic microscope. Images were captured by a Color View IIIu digital camera and were processed by analySIS-getIT software.

All the impactor substrates used to collect suspended particles, fresh stone samples and historic stone samples were studied by means of scanning electron microscopy coupled with an energy dispersive X-ray analyser (SEM/EDX). The instrument used was a JEOL JSM-5310 with an OXFORD-LINK Pentafet 6587 EDX unit which was operated under the following conditions: accelerating voltage 20 kV, probe current 6×10^{-10} A, detector distance 50 mm, working distance 20 mm, accumulation time 30–100 s, dead time 10–25%. Samples were observed at different magnifications in order to obtain results on their morphology and physical state. EDX analysis was then applied at each sample, in order to study their chemical composition. Furthermore, X-ray mappings were acquired in order to support the elemental analysis results. Mineralogical characterisation of the collected particles was based on the EDX semi-quantitative analysis since X-ray diffraction could not be performed due to the small quantity of the samples.

SEM photomicrographs and X-ray elemental mappings of the particles collected by the cascade impactor were processed by "Image-Pro Discovery" software developed by Media Cybernetics Inc, which was used to process the information of the photomicrographs, facilitating the study of the physical characteristics of the samples. "Image-Pro Discovery" is an image-processing package that detects, counts, measures and analyses features of a digital image, such as an SEM photomicrograph of collected particles. It is widely used for the morphological analysis of particles and pore sizes of rocks and minerals. During the application of SEM analysis, all the photomicrographs were obtained aiming at their processing in order to discriminate individual particles deposited on the collection substrate.

In order to determine the accumulation of sea-salt on fresh and historic samples, chloride concentrations were measured by potentiometric titration of aqueous extracts from the stone samples with silver nitrate solution ($AgNO_3$) [33]. The technique has been extensively used in the determination of ionic species in archaeological and building materials giving credible results [34,35]. Potentiometric titration was carried out by using a silver ion-selective electrode and a mercury/mercury sulphate reference electrode (Thermo-Russel) connected to a pH/voltmeter (Orion) [36]. Calibration was performed by titrating a potassium chloride (KCl) solution of known concentrations (2.16 and 0.216 g l^{-1}). The ionic strength adjustment buffer that was used both in calibration and in measurements was a 5 M solution of sodium nitrate ($NaNO_3$). pH was buffered using a solution of sodium hydroxide (NaOH). The determination of the concentration of chlorides in the samples was performed as follows: 10 g from the surface of each fresh sample (~1 cm in depth) were obtained and crushed into a fine powder. The powder was left in 100 ml of deionised water for 24 h. The solutions were then filtered and 10 ml of each extract was potentiometrically titrated with a silver nitrate solution of known concentration, 0.1 or 0.01 N, depending on the estimated concentration of chlorides in the extract. The concentration of chlorides was initially estimated in mg l^{-1} using Cl^- concentration strips by Merck.

Table 1
Characteristics of the main monitoring positions

Position	Building	Orientation (°)	Distance from the sea (m)
1	Cannon Gate Tower	N 350	500
2	Marine Gate	NE 25	20
3	St John's Gate	S 190	440
4	Tower of the Virgin	NE 65	570
5	Spanish Tower	W 260	650

Table 2
Characteristics of the historic stone sampling positions

Sample	Building	Construction date	Orientation (°)	Distance from the sea (m)
S1	Knights' Hospital	1440–1489	E 90	65
S2	Knights' Hospital	1440–1489	E 90	65
S3[a]	Freedom Gate	1932–1936	NE 30	70
S4	Arsenal Gate	1461–1467	W 280	15
S5	Maritime Walls	1360	E 90	15
S6	Maritime Walls	1360	NE 45	10
S7[a]	Maritime Walls	1985–2000	NE 45	10
S8[a]	Maritime Walls	1985–2000	NW 310	10
S9	Castellania	1507	W 265	75
S10	D' Amboise Gate	1500–1525	W 280	490
S11	Cannon Gate Tower	1500–1550	W 285	520
S12	Medieval moat	1500–1550	W 280	610
S13	Tower of the Virgin	1500–1550	S 165	640
S14	St John's Gate	1500–1550	SE 210	510
S14a[a]	St John's Gate	1985–2000	SE 210	510
S15	Carreto Tower	1513–1521	S 175	150

[a] Samples obtained from restored parts of the buildings.

3. Results and discussion

3.1. Petrographic examination of the building material

Rhodes stone is a bioclastic porous (10–40%) limestone formed, almost exclusively, by detrital bioclasts (biocalcarenite). It presents scarce micritic to sparitic cement, which coats partially the bioclasts leaving large (100 μm) pores (Fig. 2). The occurrence of clay minerals or other related impurities in the matrix is negligible. This excludes the possible synergistic action of other damage mechanisms related to clay minerals, which are linked to wetting and drying stress generation and damage [28,29,37].

3.2. Meteorological conditions

Meteorological conditions were monitored throughout the whole experimental period, in order to correlate them with the marine aerosol production and deposition. The conditions at the time of aerosol sampling events are presented in Table 3.

3.3. Aerosol sampling

Suspended particulate matter sampling was performed by using the cascade impactor. Particles collected at the cascade impactor substrates during the aerosol sampling events have been categorised according to their morphology and chemical composition into four major groups.

- *Marine particles*: Pure marine salts or salt mixtures were identified as particles of marine origin. EDX analysis showed that the dominant elements of these particles were either chlorine or sulphur. Halite (NaCl) crystals of a well-formed cubic shape, ranging in dimensions from 1 to 15 μm, were observed under the SEM, and represent chlorine particles. These particles were found either isolated or in most cases in clusters, crystallised after the evaporation of a seawater droplet onto the collection substrate (Fig. 3). In many cases, halite particles were associated with Mg, Al, Si, S, K, Ca and Fe producing homogenous particles of round shape (1–40 μm) as shown in Fig. 4. The main peaks of these coagulated particles at EDX analysis were Na, Cl, Ca, S and Si, and followed by Al, K, Mg, probably indicating a mixture of halite, gypsum ($CaSO_4 \cdot 2H_2O$) and sylvite (KCl) along with alumino-silicates.

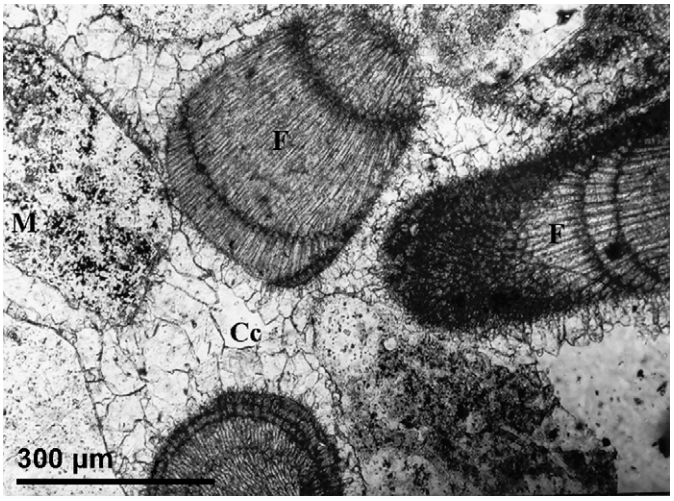

Fig. 2. Thin section photomicrograph of Rhodes stone (crossed polarisers) indicating microfossils (F), mineral grains (M) and the sparitic calcite cementing material (Cc).

Table 3
Meteorological conditions at the time of aerosol sampling events

Sampling event (SE)	Date	T (°C)	RH (%)	WS ($m\,s^{-1}$)	WD (°)
SE01	26 November 2004	7.3	73.1	1.9	NE 40
SE02	4 December 2004	16.2	55.3	9.0	SE 140
SE03	29 January 2005	14.8	93.0	1.8	SE 150
SE04	1 February 2005	9.6	90.9	3.2	NW 315
SE05	12 March 2005	8.4	79.4	2.4	N 20
SE06	5 April 2005	13.7	61.3	2.7	N 10
SE07	26 May 2005	21.7	80.3	1.9	W 260
SE08	3 June 2005	23.4	66.7	4.3	W 270
SE09	9 June 2005	22.9	80.1	5.0	W–NW 290
SE10	2 July 2005	25.7	75.6	2.3	W–SW 225
SE11	3 August 2005	29.6	56.3	8.5	NW 320
SE12	16 August 2005	27.1	89.0	7.0	S 190

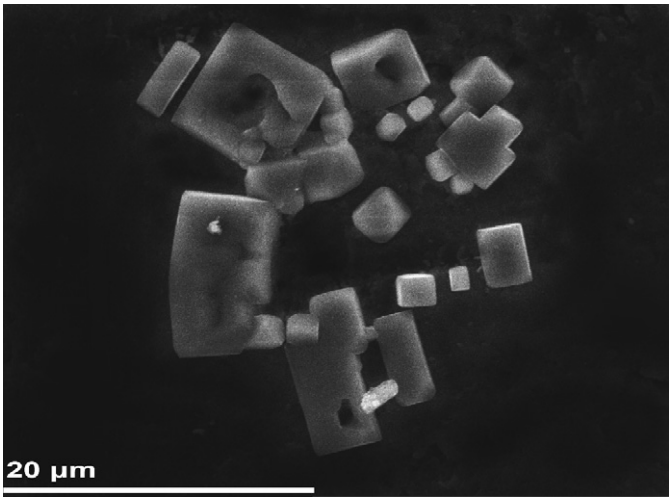

Fig. 3. SEM micrograph of halite cubic crystals in a cluster coming from the evaporation of seawater droplet on the collection substrate of the 10 μm filter of the impactor (January 2005 sample).

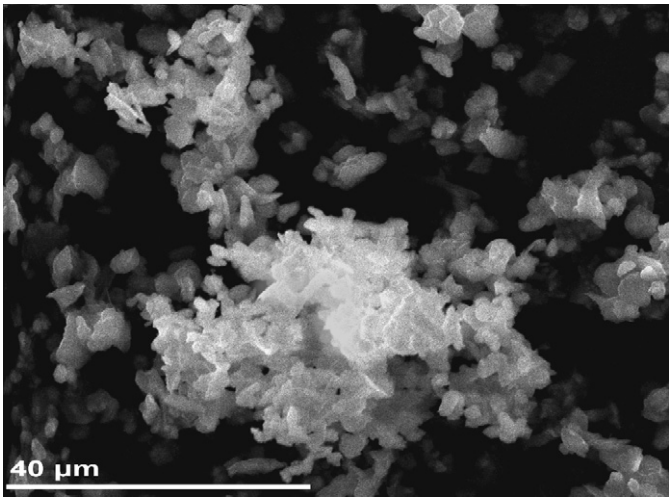

Fig. 4. SEM photomicrograph of coagulated particles of marine origin deposited on the collection substrate of the impactor's inlet (August 2005 sample).

Particles rich in sulphur are represented by thenardite (Na_2SO_4), which was observed either in entangled rods or in isolated rods scattered on the surface of the collection substrates. At all samples the individual rods length varied

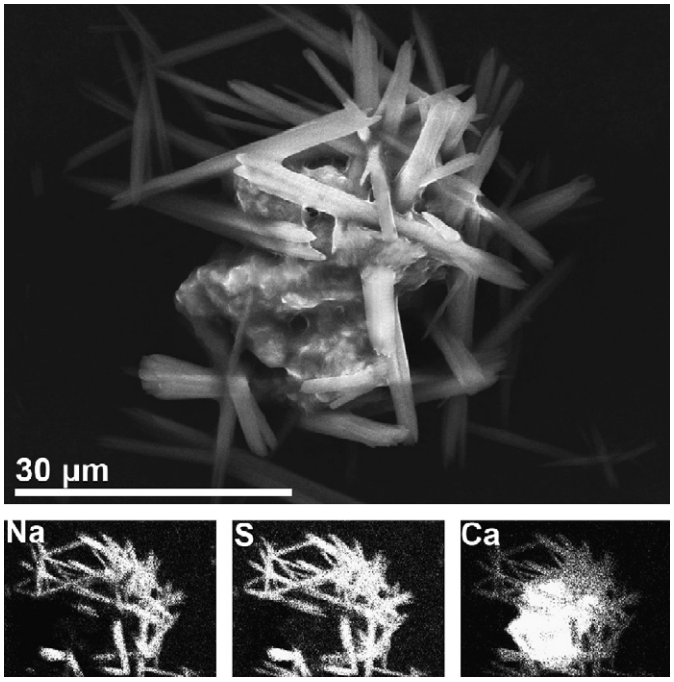

Fig. 5. SEM photomicrograph and X-ray elemental mapping of a particle consisting of a core rich in calcium and of thenardite efflorescence rods on its surface deposited on the collection substrate of the impactor's inlet (June 2005 sample).

from 0.20 to 5 μm. It is possible that halite of marine origin reacts in the atmosphere with sulphuric acid coming from the oxidation of atmospheric sulphur dioxide leading to the production of thenardite, which was found deposited on the collection substrates [38,39].

- *Detrital particles*: Particles of this category had a distinct irregular and angular shape. Their sizes ranged from 0.10 to 100 μm and the dominant elements in their chemical composition were Ca, Al, and Si followed by S, Cl, and Fe. Particles rich in calcium are probably calcite ($CaCO_3$). Traces of Al and Si were also identified in these particles. Alumino-silicates have also been identified.
- *Mixtures of marine and detrital particles*: These particles had sizes ranging from 1 to 50 μm. They consisted of mixtures of halite crystals with detrital material and of thenardite efflorescence rods usually on calcium-rich particles (Fig. 5). The length of thenardite efflorescences was up to 30 μm, which is much larger compared to the length of the individual thenardite rods of pure marine particles. The production of mixtures can be interpreted by the impact of seawater droplet on detrital particles either in the atmosphere before sampling or on the collection substrate after their deposition.
- *Biogenic particles*: EDX analysis of the collected matter has identified the presence of biogenic particles with characteristic elements S, P, Cl, K and sizes ranging from 2 to 20 μm. Anthropogenic particles which are usually represented by fly-ash rich in carbon and sulphur were not identified.

All the particles deposited on the collection substrates of the impactor had sizes ranging from 0.10 to 100 μm. Particles were not identified at the last stage of the impactor.

"Image-Pro Discovery" was applied at the images acquired by X-ray elemental mappings of the particles, in order to calculate the percentage of each group of particles on the collection substrates for each sampling event. All images acquired from the analysis of all collection substrates (132) were processed in order to associate results for the 12 sampling events (Fig. 6).

The most significant percentages of marine particles were collected during sampling events SE01 (25%), SE02 (72%), SE03 (66%), SE11 (47%) and SE12 (67%). These particular sampling events were performed under different meteorological conditions, indicating that marine aerosols are produced under variable wind speed and wind direction conditions, since particles of marine origin were collected at all sampling events. Their production is favoured when winds of high speed prevail within the sector of 190–320° (S–NW). The greatest percentage of detrital particles was collected during SE01 (52%), SE04 (80%), SE05 (77%), SE06 (75%), SE07 (70%), SE08 (65%), SE09 (75%), SE10 (65%) and SE11 (53%). Wind direction during the particular sampling events was within the sector of 40–225° (NE–SW). Such a broad sector, suggests that particles of detrital origin are suspended in the atmosphere under variable conditions but their concentration is increased when inland south winds prevail.

At all sampling events, except SE11, mixtures of marine and detrital particles were present. The highest concentration percentages were identified at SE01 (14%), SE02 (16%), SE03 (12%), SE05 (11%) and SE12 (16%). The percentage of biogenic particles at all sampling events was between 0% and 15%.

For all sampling events, the average percentage for each group of particles was 31.5% for marine particles, 54.4% for detrital particles, 9.8% for mixtures of marine and detrital particles and 4.1% for biogenic particles. Thus, particles having a marine origin constitute about one third of the total suspended particles.

Marine particles were mainly produced during SE02, as opposed to SE04, where their production was minimal. The question lies whether these particles are capable of being transferred at long distances and be deposited on buildings, which are far from the seashore. Since the principal phenomenon controlling sea-salt deposition on building surfaces is inertial impaction, particle size is an important parameter when considering aerosol transportation and deposition. Characteristic SEM photomicrographs of particles collected at the 11 collection substrates of the sampling events SE02 and SE04 were processed by "Image-Pro Discovery", in order to measure and count the collected particles. Acquired data were further processed to yield particle size distributions. During SE02 the collected particles were coarser than those collected during SE04 (Fig. 7). The concentration of particles on the impactor substrates ($N\,mm^{-2}$) during SE02 was higher as opposed to SE04 (Fig. 8).

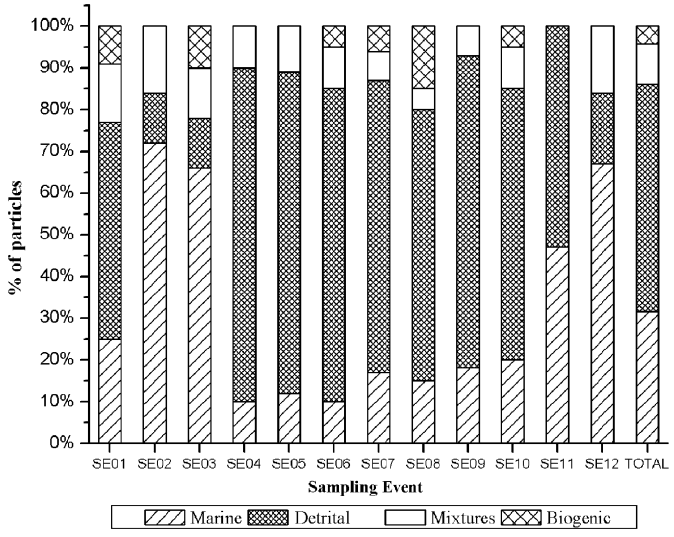

Fig. 6. Percentage (N%) of each group of particles for all aerosol sampling events (SE) performed during the experimental period. The percentage of each particle category found deposited in every collection substrate for each SE, has been added.

Therefore during SE02, particles coarser and higher in number were produced compared to those of SE04. The total collected mass of particles in SE02 is also higher than that of SE04 (Table 4). During SE02 high speed, southeast winds originating the sea were dominant. The winds produced and transferred primarily marine aerosols to the fortifications of the city. The conditions were much different during SE04 where low-speed, northwest winds prevailed. The winds produced mainly fine detrital particles and a small percentage (10%) of coarser marine particles. The results indicate that the area of the medieval city of Rhodes is dominated by the presence of marine aerosols. Their physical characteristics and their concentration in the atmosphere vary according to the prevailing meteorological conditions. The mass of suspended marine particles, when the conditions favour their production and transportation, is large and some times even larger than the mass of other groups of particles. But even when the conditions favour the production of other particles, marine particles and their mixtures still exist in the atmosphere and can potentially be deposited on architectural surfaces.

3.4. Particles deposited on fresh stone samples

Deposited particles on the surface of fresh samples were analysed by means of SEM/EDX. Microscopic observations and EDX microanalysis have identified particles belonging to marine, detrital, mixtures of marine and detrital and biogenic groups. The chemical composition, morphology and size of the deposited particles were identical to the ones collected on the substrates of the impactor. All four groups of airborne particles with their specific physicochemical characteristics, as described, were identified deposited on the stone surfaces. Detrital particles and thenardite crystals were difficult to identify due to the interferences derived from the stone surface characteristics. In three fresh samples (two placed at "Position 4" and one at "Position 5"), in addition to the morphology described for the aerosol sampling, a different morphology of halite crystals was observed. Halite had formed from deposited seawater droplets, which then had crystallised in an anhedral state with rounded external surfaces, covering in each case an area ranging from 0.6 to 1 mm^2 (Fig. 9).

In order to determine the halite content of each of the fresh samples, chloride concentration was determined by applying potentiometric titration. The results for chloride concentration of the fresh samples at each position were plotted as a function of their exposure time and are presented in Fig. 10. The fresh sample with the greatest concentration of chlorides was the one placed at "Position 2". This can be explained both by the proximity to the sea which is only 15 m, and by the northern orientation of the wall that was placed upon which makes it vulnerable to the prevailing winter winds coming from northwest. Furthermore, halite was mainly crystallised in clusters, indicating sea-water droplet deposition. Deposition of sea-salt at this position continues throughout the year.

At "Position 1", the concentration of chlorides was lower but still the second higher compared to all other positions. During

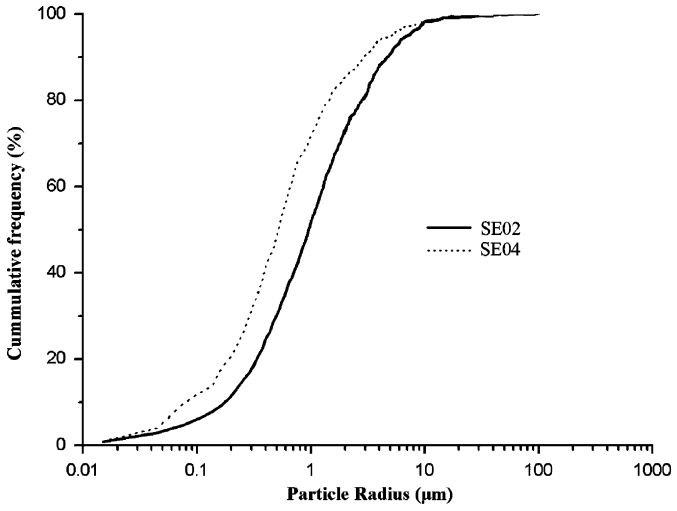

Fig. 7. Cumulative frequency of the particle radius distribution for the sampling events SE02 and SE04.

Table 4
Mass of collected particles during each sampling event at all collection substrates

Sampling event (SE)	*m* (mg)
SE01	6.5
SE02	12.1
SE03	7.3
SE04	2.3
SE05	3.3
SE06	4.8
SE07	9.8
SE08	10.4
SE09	8.6
SE10	4.3
SE11	5.7
SE12	11.9

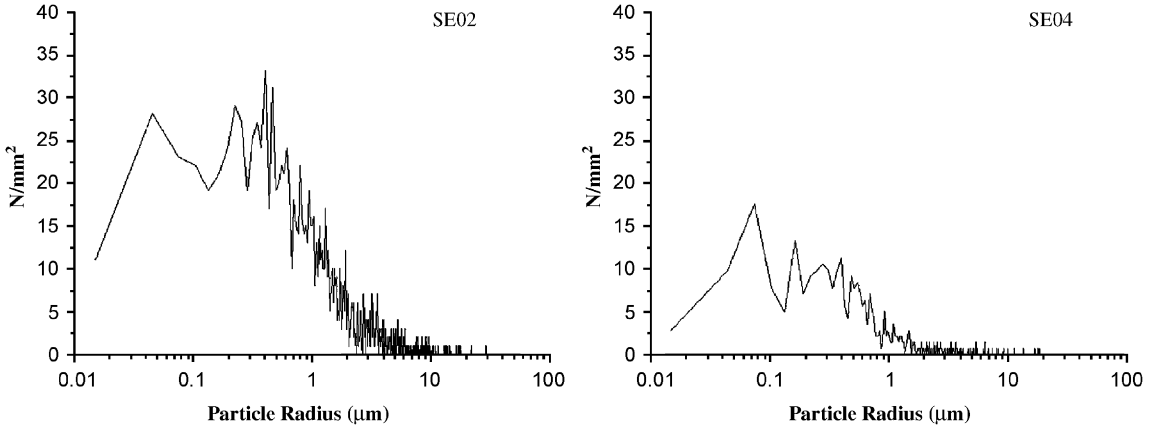

Fig. 8. Concentration of particle sizes on the collection substrates of the sampling events SE02 and SE04.

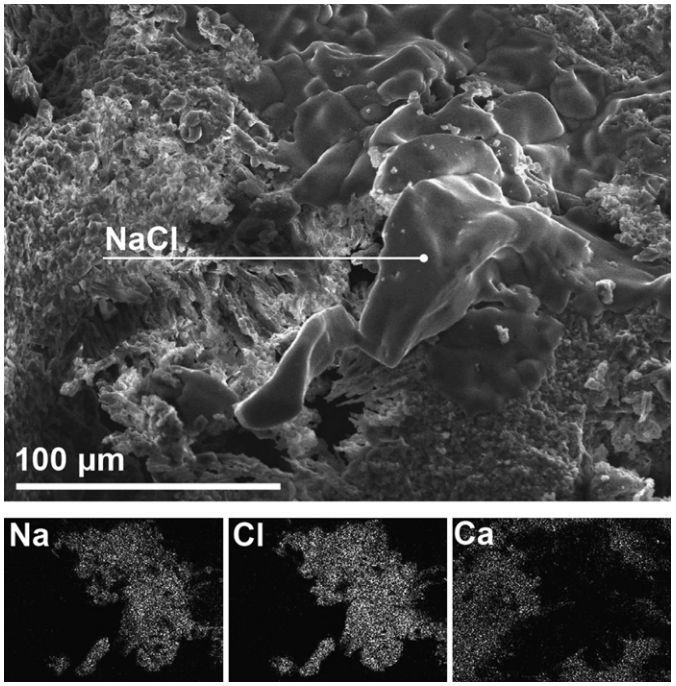

Fig. 9. SEM photomicrograph and X-ray elemental mapping of anhedral halite crystal deposited on the surface of a fresh sample which was placed at "Position 4" for 3 months.

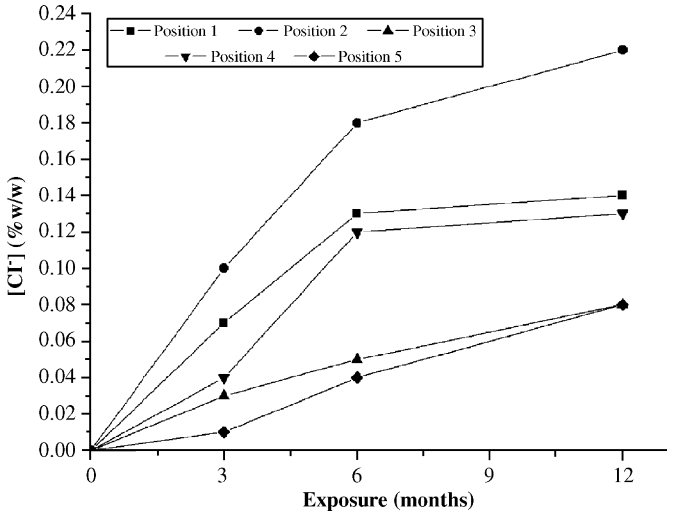

Fig. 10. Chloride concentration of fresh samples at each position versus fresh sample's exposure time.

winter and spring, marine aerosol was deposited at a distance of 500 m. Again, the northern orientation of this position, as well as its topography which, as described before, is the highest point of the medieval city, with no obstacles between the sea and the tower, are considered the main factors to influence the deposition of marine aerosol. During summer and autumn, the deposition of sea-salt is reduced.

Sea-salt was also deposited on the fresh sample placed at "Position 4", having a northeast orientation and distance from the sea 570 m. The characteristics of this position are identical to "Position 1" and, although the concentration of chlorides is lower, the plotted values follow the same pattern.

Finally, at Positions 3 and 5, chloride concentrations are much lower but seem to have a constant rise. The most significant factor influencing the deposition of sea-salt is the orientation of the positions, which is south and west, respectively. Especially for "Position 5", a significant parameter is also the distance from the sea, which is the greatest of all positions.

3.5. Particles deposited on historic stone samples

All the historic samples collected from buildings were analysed by means of SEM/EDX. The characteristics of the deposited particles, such as chemical composition, physical state, morphology and size were identical to the ones of the particles collected from the atmosphere and of the particles deposited on fresh samples. Once more, detrital material and fine particle identification was complex due to the surface roughness of the stone. Gypsum was also identified on the surface of the samples, indicating the action of sulphur but it cannot be solely contributed to the deposition of thenardite of marine origin, as anthropogenic sources can be influencing the production of sulphur-rich products. As far as halite deposition is concerned, both cubic crystals and anhedral halite crystals were observed, having the characteristics described for fresh samples. At samples S1, S3, S4, S7, S8, S11 and S13, anhedral halite crystals were identified, but there is no correlation with either the orientation of the buildings or their distance from the sea. Halite crystallisation of this type is not affected by these factors but by the microclimatic conditions prevailing at the position where the seawater droplet is deposited. The fact is that halite which was crystallised after seawater droplet deposition and evaporation, was found on S13, which was obtained within the medieval moat, 640 m inshore.

In order to determine the halite content of each of the historic samples, chloride concentrations were determined by applying potentiometric titrations. The results are presented in Table 5. Chloride concentrations for each historic sample were plotted as a function of distance from the sea and the result is presented in Fig. 11. The results indicate a constant supply with sea-salt of the fortifications and the buildings which are close to the sea. Chloride concentrations drop dramatically 100 m inshore. Of course, the orientation of the walls is a critical factor. As with fresh samples, historic samples having greater chloride concentrations were the ones obtained from buildings with northern exposure. Furthermore, samples collected from building stone used for restoration purposes, such as S7 and S8, have high chloride concentrations and present superficial damage.

Finally, it was observed that the historic samples obtained from buildings at the monitoring positions (S6 at Position 2, S11 at Position 1, S12 at Position 5, S13 at Position 4 and S14 at

Table 5
Chloride concentrations of historic samples obtained from buildings

Sample number	$[Cl^-]$ (%, w/w)
S1	0.26
S2	0.23
S3[a]	1.20
S4	2.92
S5	2.94
S6	3.55
S7[a]	2.88
S8[a]	2.34
S9	0.08
S10	0.14
S11	0.34
S12	0.11
S13	0.14
S14	0.12
S14a[a]	0.06
S15	0.09

[a] Samples obtained from restored parts of the buildings.

Position 3) and the fresh samples placed at the same monitoring positions had proportional chloride concentrations (Table 5 and Fig. 10). This fact indicates that the rate of deposition of sea-salt and especially the quantity of sea-salt deposited is constant for these positions.

3.6. Correlation between marine aerosol deposition and stone weathering

Procedures leading to stone surface weathering include mass loss, colour and texture alterations, and structural failure [40]. The methods used to quantify the decay of stone include gravimetric changes or changes in surface composition as well as macroscopic and microscopic examination [41,42]. In order to examine the effect of marine aerosols on the surface of the building stone, the mass loss of the fresh samples that were exposed for 12 months was determined. It should be noted that fresh samples were placed on iron racks on the surface of the monuments and the only weathering factor affecting the state of the stone was the deposited soluble salts crystallisation cycles. Any other factor, such as salt transportation in aqueous solutions through capillary rise, or alveolar weathering was excluded since fresh samples were sheltered and not directly attached to the walls. Before their placement, fresh samples were immersed in deionised water for 24 h in order to remove any soluble constituents that may have existed from the mother rock. Then they were placed in an oven at 80 °C for 24 h and their initial dry mass (m_i) was weighted. Fresh samples were placed at their positions for 12 months and after their removal, they were placed in an oven at 80 °C for 24 h and their final dry mass (m_f) was weighted. The difference in mass (Δm) was calculated and the results are presented in Table 6. The fresh sample that was placed in "Position 2" is the one with the greatest mass loss. This is interpreted by the fact that "Position 2" is constantly supplied with marine aerosol throughout the year and the fresh sample placed there had the greatest percentage of chlorides. The correlation of total fresh stone mass loss at each position (Table 6) to the concentration of chlorides found at the fresh samples placed at the same positions (Fig. 10) indicates that stone mass loss is proportional to the quantity of chlorides determined, for all positions. At periods where the deposition of marine aerosol is decreased, further stone mass loss could possibly result in the reduction of the sea-salt content of the stone. On the other hand, results obtained from the correlation of chloride concentration of fresh and historic samples, showed that

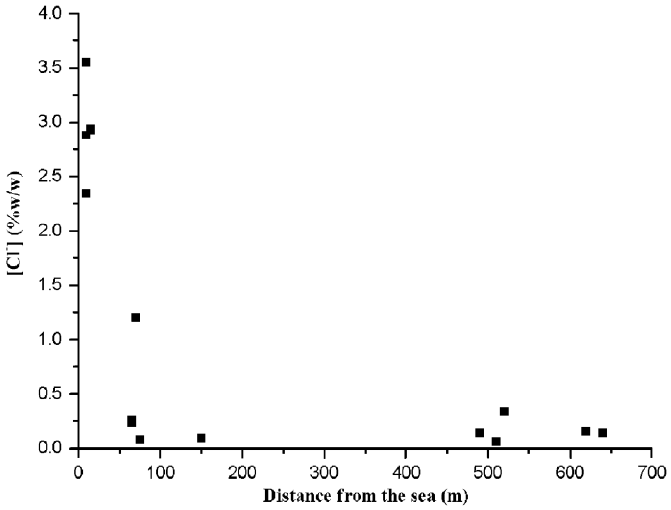

Fig. 11. Chloride concentration of historic samples versus their distance from the sea.

Table 6
Dry mass of fresh samples before and after the 12-month exposure

Position	Sample number	m_i (g)	m_f (g)	Δm (g)	Δm (%)
1	1B9S	64.98	62.84	2.14	3.3
2	2B9S	61.69	58.46	3.23	5.2
3	3B9S	63.71	61.99	1.72	2.6
4	4B9S	60.85	58.86	1.99	3.2
5	5B9S	59.97	58.86	1.11	1.8

Fig. 12. Building stone preservation state at "Position 2". Severe weathering followed by granular disintegration and material loss is presented.

sea-salt is deposited throughout the year at all monitoring positions. Thus, it is the long-term effect of marine aerosol deposition that constitutes stone mass loss proportional to the concentration of sea-salt. In order to confirm this conclusion, in situ macroscopic investigation of the building walls was performed.

At "Position 2", where the highest chloride concentration was measured both in fresh and historic samples, 90% of the building stones present mass loss to a great extent. The decay is so severe at this position, that the structural integrity of the wall is endangered (Fig. 12). The cumulative effect of the weathering factor at this position is unambiguous, since it has been acting for more than six centuries. At "Position 1", in which the second highest concentration of chlorides was measured, stone is highly decayed presenting material loss. More than 65% of the stones used in the building have lost their cohesion. Building stones at "Position 4" are better preserved and 20% of them present material loss. Sea-salt concentration of the historic sample obtained from this position, was lower than that measured for Positions 1 and 2. Finally, at "Position 3" and "Position 5", which present the lowest concentrations of chlorides, building stones are only superficially decayed (Fig. 13).

Macroscopic investigation confirms that sea-salts deposited through the atmospheric pathway significantly affect the preservation state of Rhodes stone. The environment of Rhodes plays a key role in the weathering process since the medieval city is dominated by a variety of microclimatic conditions affecting stone decay mechanisms. Relative humidity fluctuates around the annual average value of 74.8%, permitting NaCl crystallisation occurring below 75%, which is the equilibrium relative humidity of this salt. Forty-five percent of the relative humidity values obtained during the monitoring period, corresponding to 167 days, were between 26.4% (the minimum value measured) and

75% (Fig. 14). As expected, these values were mainly recorded during summer and autumn. Halite precipitation on and beneath the stone's surface depends on the solution supply and evaporation rate, which are controlled by the prevailing microclimatic conditions. As long as the rate of transport of fresh salt solution to the surface equals the rate of evaporation, the deposition of the salt occurs on the surface of the stone. This phenomenon is usually observed during spring and autumn. During the summer, when relative humidity decreases even more and intense drying of the walls is achieved, more water evaporates from the masonry. The transport of solution to the exposed surface becomes too slow and does not compensate for the escape of water at the surface, resulting to salt crystallisation beneath the surface.

The above-mentioned macroscopic investigation is consistent with the initiation of the deterioration of the Rhodes stone with the detachment of the grain aggregates and it proceeds to selective pitting resulting to the formation of deep interconnected cavities (Fig. 15). The stone appears to have suffered an irregular loss of material, which follows the alveolar weathering pattern (Fig. 12). It has been documented that the crystallisation pressure exerted by NaCl against the pore walls of Rhodes stone overcomes the tensile strength of the stone, leading to its disruption [11].

Fig. 13. The preservation state of the building stone at "Position 5" is adequate. Decay can be detected on the external surface of the stone.

4. Conclusion

At the medieval city of Rhodes, local stone is the dominant building material which due to its physico-mechanical properties is susceptible to the action of soluble salts. The purpose of this work was to evaluate the atmospheric contribution and to study the phenomena that promote sea-salt deposition leading to the weathering of the stone used as the building material for the monuments. For this reason, an aerosol production and deposition-monitoring network was set up on the fortifications of the city. This network consisted of airborne particles sampling, collection of meteorological data, exposure of fresh quarry stone samples and collection of historic stone samples. The application of instrumental and chemical analytical techniques supported the aim of identifying aerosol dry deposition.

The properties of the cementing material of Rhodes stone do not justify synergistic action of damage. Deposition of marine aerosol was investigated as the predominant weathering factor. Collected particles were classified into marine, detrital, mixtures

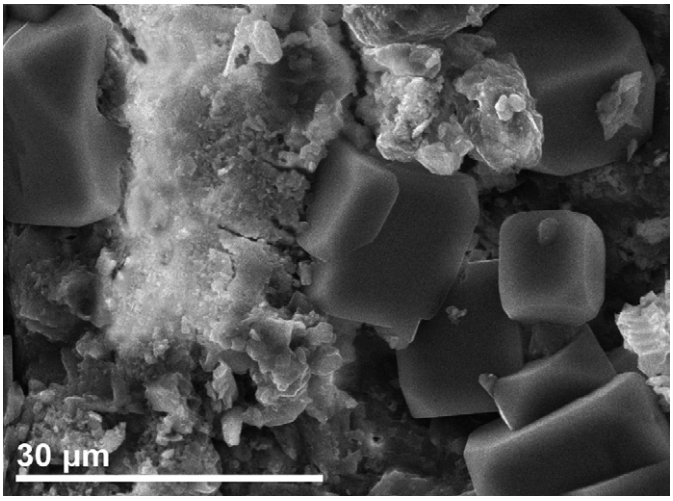

Fig. 15. SEM photomicrograph of halite crystals developed by the deposition of marine aerosol on the surface of a fresh sample, which was placed at "Position 1" for 12 months. The cohesion between the stone's grain aggregates is lost due to the pressure exerted by the confined halite crystals.

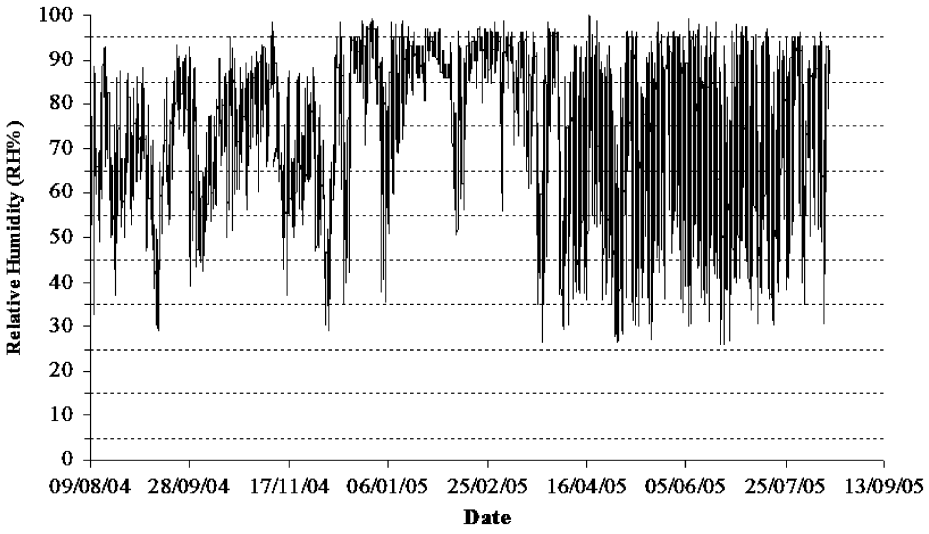

Fig. 14. Relative humidity variations recorded in situ during the monitoring period.

of marine and detrital, and biogenic according to their chemical composition and morphology. Marine particles, with dominant elements Cl and S, have sizes ranging from 0.20 to 40 μm and are produced throughout the year. They constitute about one third of all suspended particles. Their morphology and size depend on the prevailing meteorological conditions. Halite of marine origin is produced and transferred on the buildings surface under variable meteorological conditions. Its concentration in the atmosphere is increased when strong north winds prevail, deriving directly from the sea. Fine thenardite crystals were collected at the presence of west winds. Their production is probably attributed to the presence of sulphates in sea water and to anthropogenic sources since the commercial centre of the modern city of Rhodes lies to the west side of the medieval city. Mixtures of marine and detrital particles have sizes ranging from 1 to 50 μm.

Deposited particles on fresh samples are characterised by the same chemical composition, morphology and size as the particles directly collected from the atmosphere. Sea-salt is transferred and more easily deposited at high wind speeds on surfaces having a northern orientation. The distance from the sea affects the deposition rate but as far as there are no obstacles between the sea and the surface, sea-salt can be deposited even at remote buildings in the form of seawater droplets. The phenomenon takes place throughout the year but it is more intense during winter and spring. South oriented surfaces are less susceptible to the deposition of sea-salt.

The examination of historic samples collected from buildings having different orientation and age showed that deposited particles have the same physicochemical characteristics and sizes as the particles collected from the atmosphere and the particles deposited on fresh samples. Marine aerosol is directly deposited onto the buildings having a northern orientation and a small distance from the sea. Furthermore, stone used for restoration purposes during the last 20 years is already affected by the deposition of sea-salt. The zone influenced by the deposition of sea-salt lies within 100 m from the northern fortification wall of the city. The supply of the building stone with sea-salt is constant. Except the deposition of sea-salt, sulphur-rich particles are also deposited onto the stones leading to the production of gypsum but their source was not identified.

In general, sea-salt is produced and deposited having different morphologies, such as in a cluster of well-formed halite crystals, in coagulated particles, in a mixture of particles of detrital and marine origin and in anhedral halite crystals.

Marine aerosol deposition affects the preservation state of the stone. Once marine aerosol has been deposited on the stone surface, and according to the microclimatic conditions, soluble salt dissolution and precipitation cycles take place, leading to the pore fracture and stone decay. Macroscopic investigations of the original architectural surfaces were correlated with the experimental results to demonstrate that the degree of weathering of the building stone is proportional to the sea-salt content. This is of great significance since no other results are available on the rates of damage to medieval building materials in Rhodes due to marine aerosol.

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