State-of-th e Art in the Research of Environmental and Operational Influences on Degradation Cultural Heritage in Greece

C.Varotsos, and K.Theodorakopoulou

University of Athens, Dept. of Applied Physics

1. Introduction

1.1 Physical and Human Context

Greece forms the southernmost extension of the Balkan peninsula, in south-eastern Europe. The land territory of Greece totals 130.800 km^2. The mainland accounts for 80% of the land area, with the remaining 20% divided among nearly 3000 islands

Greece has a Mediterranean climate, with mild, wet winters and hot, dry summers. The Hellenides Mountains, extending from north to south, divide the country into a maritime western part and a continental eastern part.

Greek natural resources include modest supplies of bauxite, magnesite and petroleum, and plentiful deposits of lignite.

Greece has a population of 10.6 million. The population density averages 80 inhabitants per square kilometre, but varies greatly across the country, reaching a maximum in Athens of 6700 inhabitants per square kilometre. The Greek population is concentrated on the coastlines, 33% of the people live within two kilometres of the coast, and 86% live in prefectures bordering the coast. In some tourist areas, the population density increases several-fold during the summer. Greece is relatively urbanised, with 60% of the population (6.3 million people) living in settlements with more than 10000 inhabitants. Nearly 30% of the national population lives in Athens, and 10% in Thessaloniki. After exploding in the 1970s, the rate of urban growth has slowed significantly in recent years.

1.2 Air Pollution Situation and Trends

1.2.1 Emissions of atmospheric pollutants

SO_x emissions in Greece totalled 507 kt in 1997, up 0.4% from 1990. About 70% of SO_x emissions in Greece are from power plants, 17% from industry and 9% from transport. In 1996, large combustion plants emitted 360 kt of SO_x.

NO_x emissions amounted to 369 kt in 1997, an increase of 8% from the 1990 level. Transport was the largest contributor (48%), followed by industry (15%) and power generation (20%). NO_x emissions from large combustion sources totalled 60 kt in 1996.

Emissions of non-methane volatile organic compounds (NMVOCs) totalled 442 kt in 1997, 18% higher than in 1990. Transport was the largest contributor (59%), while solvent use accounted for 13%, agriculture 11% and other sources, including waste, 10%.

Carbon monoxide (CO) emissions amounted to 1375 kt in 1997, a 3% increase from 1990. Transport was the greatest contributor (71%), followed by the residential and commercial sector (17%).

Carbon dioxide (CO_2) emissions totalled 95500 kt in 1997, a 12% increase over 1990. The majority of CO_2 emissions come from energy use (92%), and the remainder mostly from industrial processes. Emissions from energy use are attributable to power generation (55%), transport (21%), industry (12%) and other stationary sources (12%).

Consumption of CFCs has significantly decreased, going from 14043 tonnes in 1986 to 1450 tonnes in 1996. In 1997, consumption of HCFCs totalled 300 tonnes.

1.2.2 Ambient air quality

Annual average ambient concentrations of SO_2 in major cities (e.g. Athens and Thessaloniki) have declined by about 23% since 1990. In Athens, the annual median concentration of SO_2 in 1997 was 21 $\mu g/m^3$, well below ambient limit values. In Thessaloniki, hourly average SO_2 concentrations were about half of allowable values in 1997.

Ambient median concentrations of NO_2 in Athens have stabilised in recent years near the ambient air quality limits. In Thessaloniki, NO_2 concentrations are well below limit values.

Ambient concentrations of smoke in Athens at the most of the monitoring urban sites are well within the norms. Concentrations (24-hour averages) of total suspended particulates (TSP), measured at Athens's two stations, have exceeded the World Health Organisation (WHO) guideline value (120 $\mu g/m^3$) since 1993, but the magnitude of exceedance declined to 8-10% over the limit value in 1997.

In Athens, eight-hour average ambient CO concentrations show a decreasing trend, and exceedances of the WHO recommended value are becoming rarer (about 1% of the time). CO concentrations in Thessaloniki also show a decreasing trend, and average concentrations are lower than in Athens.

Ambient concentrations of ground-level ozone (O_3) often exceed the EU limit values between noon and 8 p.m., particularly at monitoring stations on the periphery of Athens. Population warning levels are rarely exceeded, however.

Ambient levels of lead measured in Athens and Thessaloniki have continuously decreased over the last decade as use of unleaded gasoline in motor vehicles has expanded. Lead concentrations are now well below the WHO limit of 0.5 $\mu g/m^3$.

Because of the alkaline nature of its soils, Greece does not face large-scale acidification problems relating to transboundary air pollution or domestic air pollution. The prevailing north winds make Greece a net importer of SO_x. Heavy metal deposition (chrome, lead, nickel, copper and manganese) from lignite-fired power plants is being studied.

1.2.3 Measures to prevent and control air pollution (Regulatory measures)

EU directives form the basis for air management regulation. Numerous decisions by the Council of Ministers have established ambient air quality standards in Greece. Ambient standards for SO_2, NO_2, O_3, suspended particulates and lead have been transposed into Greek law from EU directives, while for CO the WHO recommended guideline is applied. An environmental licensing system for industry has been developed, and legislation has been passed establishing limits for SO_2, NO_x and particulate emissions from large combustion plants, in accord with the relevant EU directives. Emission standards applied to new road vehicles are equivalent to EU standards.

Fuel standards in Greece are approaching EU norms. Leaded fuel is being phased out, and special restrictions have been set regarding the content of aromatic compounds in gasoline. In 1998, unleaded gasoline had an estimated 46% market share. Though sulphur concentration in diesel fuel was recently decreased from 0.3 to 0.2% by weight, this does not yet satisfy the 0.05% limit for 1996, set by EU Directive 93/12/EEC. Heavy fuel oil used in Greece has a sulphur content of 3.2% by weight, except in metropolitan Athens, where it is limited to 0.7%.

Since the mid-1980s, an alternate licence plate system in Athens has restricted use of passenger cars in the central city between 7a.m. and 7p.m: cars with odd-numbered plates may be used only on odd-numbered days, cars with even-numbered plates only on even-numbered days.

In the early 1990s, the government introduced a vehicle scrapping programme to reduce the number of old vehicles in the fleet. Owners of old-technology cars could turn them in and get a significant discount on the purchase of a vehicle with a catalytic converter. Some

350000 cars were turned in at scrapyards before a Ministry of Finance study found that about one-third of these cars were being resold by the scrapyards, and the programme was discontinued.

The Ministry of Transport and YPEHODE (Ministry of Environment, Physical Planning and Public Works) have jointly implemented an exhaust gas emission inspection programme for in-use road vehicles. Passenger cars are tested once a year, and taxis and buses twice a year. Vehicles complying with the emission regulations in force receive exhaust gas control cards. First introduced in Athens in 1995, such programmes now exist in 30 prefectures.

1.2.4 Air quality management and transport

The major modes of passenger transport in Greece are road (64%) and air (19%). Public transport accounts for 13% of passenger-kilometres travelled. The use of private cars for passenger transport has tripled since the early 1990s

The road vehicle fleet consists of some 3.5 million vehicles with four or more wheels, and 550000 motorcycles (over 50cc). Passenger cars (including taxis), which have an average age of 11 years, make up 74% of the four-wheel vehicle fleet. Light commercial vehicles account for 20% of the fleet, and have an average age of 14 years. Heavy commercial vehicles and buses make up the remainder of the fleet, and both have average ages over 17 years. In 1997, road transport was estimated to contribute 19% of total CO_2 emissions from fuel combustion in Greece.

Road congestion in urban areas has been addressed by a range of policy measures, but remains a concern. In Athens, infrastructure improvements aiming to alleviate congestion include expansion of the urban ring road, construction of a number of flyovers, improvement of the traffic light system and creation of restricted access areas in the city centre. In Thessaloniki, a new coastal road diverts transit traffic from the centre. In Piraeus, computerised systems facilitate management of road traffic generated by seaport activities. Other cities have built ring roads to alleviate central congestion. Traffic management planning has been carried out in certain areas, especially those near major tourist attractions.

Public transport in Athens consists of buses and a subway system (metro). Some 1600 diesel buses serve about 420 million passengers per year. An additional 400 electric trolley-buses serve about 62 million passengers per year. In both Athens and Thessaloniki major subway system expansion is under way, with the help of EU funds. In Athens, new subway lines are under construction; the expanded system of three lines will total 44 kilometres. The expansion project is being co-ordinated with the bus and trolley-bus systems and with car parking areas.

1.3 Environmental Performance

1.3.1 Air management

In Athens, ambient air quality has improved remarkably since the mid-1980s as a result of determined and numerous regulatory measures. Fuel quality improvements for industry and households, as well as restrictions on industrial activity and road traffic in the metropolitan area, have been effective. Large reductions have been achieved in ambient air concentrations of SO_2, smoke, CO and lead. Ambient concentrations of NO_2 have stabilised near ambient limits, and exceedances are rare. Overall, despite some remaining concerns with measurement of TSP and O_3, air quality management in Athens has been effective. Preparations for the 2004 Olympic Games should provide additional momentum for air quality improvements.

1.3.2 Air emissions

Given the performance in Athens, it is all the more remarkable that the intensity of air pollutant emissions (kg/unit Gross Domestic Product GDP) of the Greek economy is relatively high overall. This fact reflects the massive reliance of the energy supply on lignite and oil. Stationary source of SO_x emissions have steadily grown in recent years, from 342 kt in 1993 to 359 kt in 1996, and no clear decoupling of SO_x emissions from economic growth has yet been achieved. National emissions of NO_x increased by about 15% over 1987-97, preventing Greece from satisfying the Sofia Protocol. NMVOC emissions are growing at a rate twice as fast as economic growth. Growth in emissions is largely attributable to increases in energy use for heating and cooling in the residential/commercial sector, as well as to electricity generation and road transport.

Total CO_2 emissions nearly tripled over 1970-90. Electricity generation is the largest source of CO_2 emissions; its share in total emissions has increased greatly in recent years, from 32% in 1970 to 55% in 1995, paralleling the increased use of lignite for power generation. Since the mid-1990s, the government has launched a major restructuring of the energy sector, including a range of measures aimed at improving the fuel mix for electricity generation (primarily through the use of natural gas) and promoting energy conservation in the transport, industrial and residential/commercial sectors. These measures should lead to significant environmental benefits and should be pursued with determination.

1.3.3 Pollution control measures

Data on Greek air pollutant emissions from stationary and mobile sources are improving, but remain sparse because Greece lacks systems for comprehensive environmental data collection. Air quality monitoring stations exist in urban areas, but are very sparse in the rest of the country.

Both cleaner fuels and end-of pipe control measures have been used to limit air emissions from the industrial and residential/commercial sectors. The use of cleaner fuels in the residential/commercial sector has helped reduce SO_x emissions. Flue gas desulphurisation equipment has recently been installed at two refineries and at one unit of the Megalopolis lignite-fired power plant.

A wide range of measures has been taken to reduce emissions from road vehicles. Since 1990, exhaust emission regulations have, de facto, required new gasoline-fuelled cars to have three-way catalytic converters. Since 1995, exhaust gas emission inspection programmes for in-use vehicles have been instituted in 30 prefectures. Greek motor vehicle fuels generally conform with EU standards. In the early 1990s, reduced consumer taxes and vehicle registration fees were used to encourage replacement of old vehicles with new, cleaner vehicles; some 250000 vehicles were collected and scrapped through the scrapping programme.

2. Cultural heritage and environmental pollution.

2.1 Protection of cultural heritage from air pollution

Many studies have discussed risk analysis for the protection of cultural heritage from industrial pollution, presenting relevant results for the Sanctuary of Demeter in Eleusis. For instance, (*Moropoulou et al. 1999*) have explored the analysis of the risks, which threaten cultural heritage when exposed to industrial atmosphere, as investigation of the origin of weathering crusts on ancient marbles in relation to the triggering environmental factors. It is noted that the first temple was founded in the Late Helladic period, 1500-1425 BC and the present ruins are the rest of the new Telestirion built during Pericles'reign.*(Preka-Alexandri K,1991)*

Crusts and encrustation samples from the monuments surfaces, as well as aerosols and total deposition samples have been investigated by Ion Chromatography (IC), Atomic Absorption/Atomic Emission Spectrometry (AAS/AES) and Energy Dispersive X-Ray Fluorescence (EDXRF).

The estimation of enrichment factors permits the determination of the possible sources of the identified elements as soil, underlying rock, marine spray and anthropogenic activities.(*Torfs &Van Grieken,1997, Schneider,1987*) The study of sulphur isotopes permits the investigation of the sources of sulphur-rich pollutants triggering gypsum formation. (*Moropoulou et al.1998a, Buzek& Sramek,1985*)

Gypsum crusts and dusts on the monuments marbles and crusts on buildings in the city were sampled, and aerosol samples were collected from the emissions of the nearby industries, like cement industry, refinaries, metallurgies etc.(*Christidis,1995)*

The isotopic ratio $^{34}S/^{32}S$, in terms of delta values ($\delta^{34}S$) of the sulphur- rich pollutants from the industry, shows that the main impact of suspended particles to the archaeological site is caused by the industry- cement industry in particular.

2.2 The role of the atmospheric deposition

One of the most important factors for the degradation of the historical monuments, is the atmospheric deposition. For example in a recent study *(Moropoulou et al,1998b)* is examined the composition of the atmosphere around the ancient ruins of the Demeter Sanctuary in Eleusis, through the characterization of the local total deposition and aerosols in combination with observations concerning the stone decay. (*Zezza F,1996)*

The environmental conditions around the monument have been studied extensively by monitoring, during more than one year, the local total deposition and aerosols. Also, systematic mineralogical, petrographical and chemical examination (*Moropoulou A et al,,1995a),* along with classification of the weathering crusts, have been performed. It is noted that Pentelic marble has been used mainly for the Sanctuary, together with some limestone.

Very high amounts of $\mathbf{SO_4^{2-}}$ are observed in the total deposition, stone crusts and aerosols. The origin of SO_4^{2-} is almost purely anthropogenic and not marine spray. The crust formation on the stones is not merely caused by aerosols, but gaseous SO_2 influences this process. The major part of the collected SO_4^{2-} aerosols must be classified as secondary aerosols and not as originating from sea spray.

$\mathbf{Ca^{2+}}$ found in the weathered stone layer, originates from the Pentelic marble, from deposited calcite particles of the ruins and only part from soil dust.(*Rockens E et al,1988*), $\mathbf{Cl^-}$ in the total deposition originates mainly from the sea, while for the aerosols, other sources of Cl are present beside sea spray (combustion of coal). The Cl that is found in the stone layer can be attributed mainly to a marine source. The deposition **of Pb, Zn, Cu** and **Cr** is most distinct on the black-grey crusts, black gypsum formation, surface encrustations and dust deposits. Zn and Pb are highly enriched to soil dust and must be attributed to anthropogenic depositions.(*Chester R et al,1993)* The high concentrations of **Mn, Ni, Ti** and **Fe** in the weathered stones are due partly to the underlying rock and partly to industrial activities of the area. Only a small percentage is due to aerosol deposition.

On the wall facing the sea, a high deposition of $\mathbf{Na^+}$ **,** $\mathbf{Cl^-}$ and $\mathbf{SO_4^{2-}}$ is observed on the disintegrated marble. Na and Cl originate from marine spray, while SO_4^{2-} must be related to action of anthropogenic SO_4^{2-} . The washed-out area presents deposition of $\mathbf{Cl^-}$**,** $\mathbf{K^+}$**, Ca**, and $\mathbf{SO_4^{2-}}$**.** The four other weathered stone types (black-grey crusts, black gypsum formations, surface encrustations and dust deposits) present a high deposition level of **Pb, Zn** and $\mathbf{SO_4^{2-}}$, attributed to the effects of the local industry.

The surface analysis of atmospheric polluted ancient marbles can also be done by the use of FT-IR Spectroscopy (Fourier Transform Infared Spectroscopy). A related study has been done concerning marbles taken from the Acropolis *(Anastassopoulou I, et.al,1997)* .From vibrational spectral analysis the presence of sulfur compounds was clear on the surface of the marbles. By observing the spectra and making a spectral analysis, it is quite evident that in surface of the marbles from Acropolis upon weathering and pollution we find on the surface sulphur bound to form disulfides, or bound to hydrocarbons and esters to form sulfoxides, thiols, amines, silyl derivatives, methyl acetals and other dimenthyl or trimenthyl groups. These groups are connected with the refineries of hydrocarbons or pollutants of combustion engines (cars). The refineries maybe those in Eleusis or Pireus that produced these products upon aging of the marbles of the Acropolis.

Another study concerning sea-salts transportation by aerosols and deposition on stones has been made recently for the case of Delos island inCyclades *(Chabas A et al,1997, 1996)*. In order to determine the chemico-mineralogical composition of particles present in the atmosphere of the archaeological site of Delos, 2 field campaigns have been performed in March and July in 1995.The air was filtered through Nucleopore membranes and the particles analysed by x-ray fluorescence spectrometry and analytical scanning electron microscopy. The analytical results show that the concentrations in Na, Cl, ans S are the most important and higher in July than in March. S 'in excess' constitutes the most important part of total s and it is anthropogenic in origin. The individual analysis of particles allows to classify them in 5 classes : marine, terrigenous, mixture of marine & terrigenous , anthropogenic and biogenic. Some species detected in the air are present on the surface of marbles and granites and their role has to be taken into account when studying the weathering processes of Delos.

2.3 Mechanisms of weathering

Several studies have been made concerning weathering mechanisms and their effects to ancient marbles –monuments.

For instance, *Fassina et al 1996* studied the weathering process of the Sanctuary of Demeter in Eleusis. The main decay phenomena that they are observed are:

a) Granular disintegration and detachment, the most general and important weathering, presented at washed out surface areas, or on surface areas facing the sea,

b) biological attack to the stone,

c) chromatic alteration from the white of the Pentelic marble to the rusty-yellow color at the washed out surfaces,

d) soiling are frequently present at horizontal top sides of numerous building stones relief in form of micro-karst,

e) black-grey crust formations formed on hollows,

f) black crust strongly attached at the surfaces, often present in unwashed areas,

g) loose deposition inside hollow and

h) orange-colored crust very thin and attached to the stone surface.

Samples were taken from different parts of the archaeological site according to the following criteria:

1) the degree of decay through macroscopic observation,
2) the orientation of the individual architectural elements,
3) the exposure to direct rainfall (washed-out areas),
4) the degree of sheltering from rainwater (black areas) and
5) black ampoules in the groundfloor.

To assess the different alteration products the following analytical methods were used : a) cross sectioning to separate the different layers on the surface, b) SEM analysis to provide morphological information on crystals, c)EDS depth profile microanalysis on cross-sections, d) X-ray diffraction, e) Ion chromatography, to evaluate the salts that are present in the crust, f) Chemical analysis (AAS/AES, EDXRF)

For the white marble the influence of the heavily polluted atmosphere in a marine environment is varying, resulting in several weathering patterns, mainly in the form of crusts. Rusty, yellow patinas on washed –out areas, firmly attached black-grey crusts in contact with water and cementitious crusts in hollow characterize the various material-environment interactions taking place.

Dust and deposition analysis give indications for the causes of the various crust formations. Cement industry depositions could be related to the cementitious surface encrustations.

Salt crystals embedded give evidence to the characteristic synergy of air-pollution, suspended particles deposition and marine spray producing damage to the stone surface.

Black crusts formed on the hollow are mainly composed by cementitious particles. This type of decay was not generally found and it was ascribed to the deposition of suspended particles emitted from cement industry neighbourhood the site. The hollow are formed by solution processes resulting from accumulation of rainwater reacting with suspended particles deposited during long period of dry deposition.

In order to assess the susceptibility of building stones to weathering in an intense marine and polluted atmosphere, analysis and classification of lithotypes is taking place by employing mineropetrographic studies, physical, mechanical and microstructural analysis of the porous system of the various lithotypes. For instance, (*Moropoulou et al,1995a)* , have performed this method in the Demeter Sanctuary in Eleusis.

Grey micritic limestone, yellow limestone, grey biomicritic limestone, yellow-brown limestone and yellow-brown fossiliferous dolomite with origin from subpelagitian unit of Eleusis area and *white (Pentelic) and white-grey marble* from the autochthonous Attico-Cycladic crystalline complex have been identified. *(Katsikatsos G et.al,1986)* . The building stones present in general low porosity. The marble group attains the highest apparent density and the lowest water absorption, in comparison with the limestone group. The wave velocity, depending on the homogeneity of the stone mass, appears to be higher for the relevant low porous and fine grained limestone, *(Camuffo D 1993, Moropoulou A & Theoulakis P 1991)* that present no microstructural networks, while the most porous limestone presents lower values. Different physical and mechanical properties measured for the same rock type indicate alteration of the sample due to anisotropy and/or weathering.

Consequently, the pore structure becomes the critical factor to evaluate the physicochemical resistance of the various lithotypes to weathering, since it determines its resistance to the mechanical weathering, either caused directly by condensation or salt decay, or indirectly by the action of pollutants and suspended particles in the microfractures of the surface.

The weathering rate and mechanism of decay of building stone in a natural or polluted environment can be studied on a quantitative basis by analyses of run-off water (rain water that has run over a building wall or over a stone slab that is exposed to ambient atmospheric conditions). Such analyses have been made for the pentelic marble *(Delalieux et al,1997, Cooper P,1986 & Torfs K-Van Grieken,1996)*. Since SO_2 is a major factor in the deterioration of these stones, gypsum is the main weathering product on historical monuments composed of limestone, marble and sand stone, containing calcite. Pentelic marble is a metamorphosed limestone, comprised almost of an interlocking polygonal aggregate of calcite grains. The marble has a moderate grainy structure. Individual calcite grains up to 1mm in diameter, can be seen with the naked eye. The porosity is 0.05% by volume.

Dissolution processes proved to be important. Weathering rates about 10μm/year were obtained from the runoff experiments. Statistical data analysis confirmed that dissolution was the most important factor for washed surfaces.

The soluble salts can also cause the decay of building stones. For instance, *(Theoulakis et al,1988)* have studied the the patterns and causes of decay of the building stone of the Medieval city of Rhodes and the relevant mechanism. The city has been built by the Knights of Saint John (1309-1522).

In order to analyze the samples, there have been followed these methods:

a) Optical microscopy,

b) scanning electron microscope-microanalysis,

c) atomic absorption spectrometric analysis and d) X-ray diffraction analysis.

The building material is a fossiliferous calcareous sandstone-typical biocalcarenite with high porosity and calcitic cementing material. It undergoes the destructive action of weathering, with the appearance of a typical alveolar (honeycomb) disease pattern.*(Skoulikidis Th et al,1986, Rossi-Manaresi R et al,1978)*

The absence of the products of chemical attack, as well as the unaffected texture (porosity) of the weathered stone, suggest that the deterioration process is not due to chemical alteration.*(Rossi-Manaresi R & Chezzo C,1978)* The high level of Cl and SO^{2-}_4 concentration found in the decay products and in the outer surface, give evidence of the migration of salts from the sea salt spray and the ground waters through the stone, thus causing its degradation. In few words, the action of the soluble salts transferred into the stone pores, is the main cause of decay.

The deterioration of a building stone can also be connected with frost action and temperature fluctuations. The Temple of Apollo Epicurius at Bassai in Arcadia has to do with this type of deterioration (*Beloyannis N, et al, 1988a).* The temple of Bassai (which Pausanias attributes to Iktinos, the architect of the Parthenon), stands on Mount Cotilion (SW Peloponnese) at an altitude of 1130m. The building stone is a crypto-to micro- crystalline limestone, quarried from the neighbourhood of the monument. The material (which has no primary interconnected pores) is run through by a relatively dense network of calcitic veins.

The actual general image of deterioration is a result of the combined actions of many factors: Frost action, 'external mechanical strain' (earthquakes, structural problems), human factor, dissolving action of rainwater.

The alteration of the building stone is attributed mainly to frost action due to the wide range of temperature fluctuations, as well as to the discontinuities in the structure of stone itself, which facilitate penetration and transportation of water. The veins which contain phylosilicate and clay materials, play the most important part in the evolution of the frost damage (as has been shown by electron microscopy and microanalysis of naturally alterated samples), since they facilitate water penetration and circulation inside the stone.*(Beloyannis N et al,1988b)* The presence of clays (illite) creates conditions of intense mechanical strain inside the capillaries, due to the absorption of water on the surface of illite crystals.

The potential causing water movement may be attributed to:

a) The disturbance of thermodynamical equilibrium caused by supercooling resulting to migration of unfrozen water towards regions with lower vapour pressure,

b) The disturbance of ionic equilibrium caused by freezing, resulting to migration of water due to osmotic pressures.

2.4 Environmental assessment on ancient monuments

Many studies have been done for the environmental assessment on ancient monuments. For example in a recent study *(Moropoulou et al, 1996)* the case of the Sanctuary of Demeter in Eleusis has been examined in order to investigate the various correlations between the heavy polluted atmosphere and the weathering patterns.

In order to achieve a methodology for an intergrated correlation between environmental conditions and crust types, the results of the Energy Dispersive X-ray Fluorescence, X-ray diffraction and porosity analysis along with characteristic weathering products of the crusts, the orientation of the weathered surfaces and their exposure to the rainfall have been included in the data matrix describing the statistical problem, elaborated by multivariate analysis. *(Moropoulou A & Theodoulakis P1995, Moropoulou A &Bisbikou K,1995)* Statistical analysis and especially multivariate methods are used in order to provide a technique for predicting what type of weathering would be expected according to the environmental conditions in heavy industrial and marine atmosphere.

Airborne particles are discriminated to the accumulated depositions in dusts and moreover the reacted ones in the surface encrustations. Variables like Si, S, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Pb play a significant role in that discrimination. Heavy metals discriminate for the accumulated depositions or neoformations but are not sufficiently to provide sub-classifications of the various crusts.

Gypsum is strongly related to loose depositions. Cl is correlated through weaker. Si, Fe and surface orientation are strongly correlated among them and are related to cementitious crusts. Y, Mn and rain exposure are strongly correlated among them related to black gray crusts. High porosity concentrations of recrystallized calcite, presence of Sr and Ca, are strongly correlated among them and related to washed –out surfaces.

The correlation between stone weathering and environmental factors in marine atmosphere has been studied in a recent article *(Moropoulou et al, 1995b)* and refers to the Medieval city of Rhodes.

It is attempted the establishment of a method for a statistically reliable correlation between the particular parameters which compose the microenvironment and the resulting decay form. The Medieval city of Rhodes, where various characteristic types of weathering can be distinguished in relevance with the particular laws governing the relation between environmental and microclimatic conditions and materials acted as a pilot-case. *(Poziopoulos A, 1992)*

The results of Ion chemical analysis of soluble salts along with sea and sun exposure and air flow, which control transport and evaporation of solutions in the stone, have been included in the data matrix describing the statistical problem. Discriminant analysis is employed using as data vector the above variables and entering as classification factor the variable Dectype.

From the statistical analysis is concluded that: a) Cl^-, SO_4^{2-}, HCO^-_3 and ' Sea Exp' are strongly correlated and very important for the decay processes at sampling locations which macroscopically present an alveolar disease. B) HCO_3 has a less strong correlation with 'Sun Exp' and is a very influencia variable for sampling points which present crust formation. C) 'Air Flow' and 'Sun Exp' have a weak correlation and seem to influence sampling points characterized by a selective alveolation due to air flow peculiarities in areas normally decayed by carbonate crust. *(Quayle N,1992)*

The environmental assessment has also been studied on the porous stone masonries of the Rethymnon Fortress. (*Moropoulou et al, 1995c*)

The fortress of Rethymnon is constructed by a susceptible to salt decay biocalcareous porous stone and suffers mainly from salt crystallization and hard carbonate crust formation.

The research concerns various masonry surfaces, as far as position and exposure orientation to various environmental factors are concerned, mainly regarding humidity sources like groundwater's capillary rise and marine salt spray. Stone samples from various positions along the fortress, underwent mineralogical and microstructural examination.

The main weathering phenomena are: 1) Salt efflorescences due to the capillary rise effect on the masonry and the salt spray. The measurements of the permanent humidity in the walls of the fortress has shown low values. Serious problems were identified in those buildings where recent restoration work has been performed. 2) Hard carbonate crust. On the walls of North or South orientation, due to their low sun exposure and good protection from strong winds, the evaporation phenomenon is quite mild, and thus the formation of carbonate crusts is prefered. 3) Biological weathering. In the same positions with the above orientation, grey crusts attributed to biological weathering from algae and leachens, the growth of which is augmented by the relatively high permanent humidity, have been observed. 4) In those walls where the sun exposure is intense and thus a greater evaporation is present, salt decay problems of different intensity are observed

Digital image processing *(Cundari C 1991, Mamillan M, 1991)* has been performed on characteristic surface images from the fortifications, acquired from photograms and restituted in false colors, in order to assess and evaluate the environmental impact to the masonries according to the physicochemical criteria employed for the weathering classification. (microstructure, texture and composition)

3. References

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