Speciale

CONSERVATION OF CULTURAL HERITAGE

Effects of Air Pollution on Materials, Including Historic and Cultural Heritage Monuments

The Int. Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments (ICP Materials) started in 1985. It was initiated in order to provide a scientific basis for new protocols developed within the Convention on Long-range Transboundary Air Pollution. The main aim is to perform a quantitative evaluation of the effects of multi-pollutants and climate parameters on the atmospheric corrosion of materials, including Cultural Heritage. The primary objective is to evaluate dose/response functions and trend effects and use the results for mapping areas with increased risk of corrosion, and for calculating the costs of damage caused by the deterioration of materials. Here we present the study of two UNESCO CH sites: the Parthenon in Athens (Greece), and the building façades in the city centre of Paris (France)

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Introduction

Air pollutants, together with climatic parameters, are of major importance for the deterioration of many materials used in cultural monuments. They are emitted by industrial activities and by the transport sector. These pollutants create problems on the local scale, but they are also transported in the air over long distances.

One of the international organizations and institutions which study these effects is the UN ECE Convention

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of Long Range Transboundary Air Pollution (CLRTAP) under which operate the International Cooperative Program on effects on Materials including Cultural Monuments (ICP Materials), that started in 1985. This is one of several effect-oriented International Cooperative Programmes (ICPs) dedicated at studying the harmful effect of air pollution on materials. It was initiated in order to provide a scientific basis for new protocols and regulations developed within the Convention on Long-range Transboundary Air Pollution.

To reduce the harmful effects of pollutants on human health and the environment, the European Directive 1999/30/EC has been issued relating to limit values for sulphur dioxide, oxides of nitrogen, particulate matter and lead in the ambient air. These limit values have been established with reference to health and ecosystem effects but not to effect on building materials and cultural monuments. The European cultural heritage is very large and costs billions of euro



to be maintained. It is important to understand that such materials, from which the cultural monuments are created, are sensitive to pollution at even lower levels than biological systems.

The costs for deterioration and soiling of different materials due to air pollution are huge and the damage to culture targets seriously endangers the cultural heritage. Effective policy-making requires environmental impact assessment, cost benefit analysis and risk management. All these techniques need a serious scientific basis to support the assessment and the calculation of the effects of pollution.

In this study a methodology has been applied to estimate the real surface of the selected monuments and the materials from which they are created, in percentage. Subsequently, the ICP Materials doseresponse functions have been used in order to evaluate the corrosion and soiling effects of air pollution on the monuments, and in the next study to calculate the costs of the damage due to the deterioration of the materials that the monument is made of. Air pollution data for 2009-2010 have been used.

The Methodology [1]

The methodology applied consists of a real in-thefield inventory. The dimensions of the monuments was identified by direct examination, images, photos, drawings and other data available in literature and from the internet sources. The dimensions of monuments allowed to calculate their surface by valuating the surface covered by windows, doors, etc.

The nature of the materials employed was determined by direct examination of the building façade or using the literature sources. The proportions of materials was roughly evaluated in percentage. The dimensions of each monument were taken using the literature sources, images and proportions. When this information was not available, the height of the building was estimated by counting the number of floors and attributing them an individual average height of 3 m. A control of this arbitrary height of 3m per floor was performed using a laser beam measurement and the error did not exceed - 10% (Paris (3)).

The determination of the length of the façades

was obtained by measurements on the available city maps. Having height and length, the surface was easily deduced. The surface of the apertures (windows, doors), classically considered by architects equal to half of the total surface of the façades, was deduced from the surface materials of the monument.

The height and length of the Parthenon were obtained from the official technical documents available and from the literature data.

Dose-Response Functions

Europe. It was established that the target for 2020 y. corresponds to n=2.5. Considering the background corrosion rates during the first year of exposure taken from the UN/ECE Mapping Manual, the estimated tolerable corrosion rates calculated from Equation (2) are almost identical to the tolerable levels established from maintenance intervals (corrosion depth before action/tolerable time between maintenance). It was decided that the target for 2050 y. corresponds to n=2.0. In Table 1, the tolerable corrosion rate for the first year of exposure for limestone is indicated for the 2020 and 2050 targets. The tolerable corrosion rates given in Table 1 are those used for further assessment of target levels and are thus considered a conservative lower estimate of the tolerable level. We may calculate the The most recent development of dose-response functions for corrosion in the new pollution situation in Europe has been developed in cooperation with the EU project MULTI-ASSESS based on data obtained in the ICP Materials multi-pollutant exposure program. The degradation of limestone is expressed as surface recession (R, μ m). This function includes a range of pollution and climate parameters (Portland limestone):

 $\mathbf{R} = 4.0 + 0.0059[SO_2]RH_{60} + 0.054Rain[H^+] +$ $+ 0.078[HNO_3]Rh_{60} + 0.0258PM_{10}$ (1)

Stock at Risk

We need a uniform approach for policy-makers that might indicate them the target levels of corrosion. When the UN/ECE Mapping Manual is applied to

| Material | Background corrosion | Background corrosion depth (BCD) | Factor for acceptable corrosion | Tolerable corrosion rate per year |
|-----------|----------------------|-------------------------------------|------------------------------------|--------------------------------------|
| Limestone | | 3.2 μm | 2020 target (2.5 times BCD) | 8.0 µm year ¹ |
| Limestone | | 3.2 μm | 2050target(2.0 timesBCD) | 6.4 µm year ¹ |

 TABLE 1
 Tolerable corrosion rate based on background corrosion rates and the targets for 2050 (n=2.5) and 2020 (n=2.0)
 Source: [1]

(2)

tolerable levels, the tolerable corrosion rate, first year exposure ($K_{tol})$ can be calculated as:

$$\mathbf{K}_{tol} = \mathbf{n} \times \mathbf{K}_{b}$$

where n is a factor and Kb is the background corrosion rate, first year exposure for corresponding acceptable pollution concentrations from the tolerable corrosion rate using the dose-response functions. From the tolerable corrosion rates indicated in Table 1 and the real measured or estimated corrosion rates we may establish if a specific site may be classified as tolerable or exceedence (risk) site.

The Parthenon in the Acropolis, Athens

The Parthenon [2] (Coordinates: N370 58' 15".132, E23' 43' 34".248) was included in the UNESCO CH list in 1987. The Acropolis hill (acro - edge, polis - city), so-called "Sacred Rock" of Athens, is the most important site of the city and constitutes one of the most



FIGURE 1 The map of the Acropolis with the monuments and periods of creation (Orange: Monuments of the 5th century BCE; Rose: Monuments of the 4th century BCE; Blue: Hellenistic and Roman monuments) Source: [2]

recognizable monuments of the world. The monuments on the Acropolis reflect the successive phases of the city's history. It is 3.045 ha. Types of main external materials used in percentage: limestone - pentelic marble - (95%), porous stone, sandstone.

The Parthenon is the most important and characteristic monument of the ancient Greek civilization and still remains its international symbol. It was dedicated to Athena Parthenos (the Virgin), the patron goddess of Athens. It was built between 447 and 438 B.C. and its sculptural decoration was completed in 432 B.C. The sculptural decorations of the Parthenon are a unique combination of the Doric metopes and triglyphs on the entablature, and the Ionic frieze on the walls of the cella.

As indicated before, in order to valuate quantitatively the loss of materials due to the air pollution and to make an economic assessment, it is important to know the surface dimensions of the studied monument. From the literature we found the general external measures of the monument. The rest was valuated using the ratios between known and unknown dimensions of the temple. For this reason, we evaluated and calculated the surface of the external (visible) part of the Parthenon. Many original parts of the Parthenon are lost. And now the Temple is without roof and internal cell (naos) where the God's statue was originally situated (Fig. 2). Four columns are broken. The most important parts of the Parthenon still existing are the columns, the lintel, the tympanum.

Columns: their surface is not smooth but fluted (Fig. 3). The columns are 10 m high and their diameter is 1.9 m. The columns are not cylinders but the lower part is around 30% larger than the upper one. In order to find the column circumference we used a section of it and then applied the AutoCAD software. This way, the circumference of a column was found to be 7.05 m. The surface of one column is 10 m (h) x 7.05 m. = 70.5 m². In the temple we have 47 columns.



The Parthenon view from North-East Source: [2]



FIGURE 3 Scheme of a Greek temple Source: [2]

Four of them are broken and we considered that they are 50 % lost. The surface of the columns is: 43 columns x 70.5 $m^2 = 3031.5 m^2$; 4 columns x 35.2 $m^2 = 140.8 m^2$. Total surface of the columns is = **3172.3 m**².

- Lintel: the short sides of it are relatively integral. They are 29 m long and 3.5 m. high. The East side is 29 m (1) x 3.5 m. (h) = 101.5 m². The West side is 29 m (1) x 3.5 m. (h) = 101.5 m². The North side is relatively integral and is 69.2 m (1) x 3.5 m (h) = 242.2 m². The South side is damaged and 29 m. are lost, so it is 69.2 -29 = 40.2 m x 3.5 m. = 104.7 m². The total surface of the lintel is **549.5 m²**.
- Tympanums (triangles): The East side is relatively integral and is 29 m. (1) x 4.2 m. (h) / 2 = 60.9 m². The North side is very damaged. Using the rations between the integral east part end remaining pieces from the north one we calculated it as around 15 m². So the total surface of the tympanums is: 60.9 + 15 = 75.9 m².
- The total surface of the Parthenon is: Columns = 3 172.3 m²; Lintel = 549.5 m; Tympanums = 75.9 m². Total visible surface of the Parthenon is 3 798.1 m².

The Dose/response function which we used to calculate the recession of the limestone material (see equation 1) for the Parthenon indicates that the corrosion depth after one year of exposure is **5.60 \mum**. Table 1 shows that this result is lower than the tolerable corrosion rate per year for the 2020 target, which is 8.0 μ m year⁻¹ for limestone. This result is very close to the tolerable corrosion rate per year for the 2050 target, which is 6.4 μ m year⁻¹. On the other hand, the calculated corrosion rate for the Parthenon is almost two times as high as the background corrosion depth indicated in Table 1 (3.2 μ m). This means that in 2009-2010 the corrosion depth in the Parthenon was almost two times as high as the background corrosion rate, which is due to air pollution, but it is steel in the range of tolerable corrosion rate for the 2020 target.

The Façades in the Centre of Paris

The banks of the Seine (Coordinates: N48 51 30 E2 17 39) have been included in the UNESCO List of the World Cultural Heritage (Fig. 4) since 1991 [3]. We should consider that many important monuments are situated in this area.[See Report 68 (1)]. This study consists in the evaluation of the stock of materials at risk of degradation (corrosion, soiling) due to atmospheric pollution, between the Sully Bridge on the eastern side, and the Pont-Neuf on the western side. It includes the lle Saint Louis, the Ile de la Cite´ and the right bank of the Seine facing these two islands (Fig. 4). This sector is the very centre of Paris. The territory inscribed on the UNESCO List, extends towards West as far as the Eiffel Tower. This study includes roughly one-third of this territory and contains buildings dating from the



FIGURE 4 Satellite view of the centre of Paris Source: [3]

XVII and XVIII centuries, Haussmannian buildings (end of XIX century), as well as important monuments like Notre Dame and Sainte Chapelle, dating from the Middle Ages. Quays and bridges were not taken into account in this evaluation.

The authors methodology to calculate the surface of the monument consisted in a real in-the-field inventory, façade by façade, building by building, and monument by monument, based on the Paris Map at the scale of 1:2 000. They determinated the nature of the materials employed by direct examination of the building façade (Lutetian Parisian limestone, rendering/ mortar/ plaster, painting, brick, metal, modern glass) and their proportions were roughly evaluated in percentage. They estimated the height of each building by counting the number of floors and attributing them an individual average height of 3 m. A control of this arbitrary height of 3 m per floor was performed using a laser beam measurement: the error does not exceed - 10%. The determination of the length of the facades was obtained by measurements on the Paris Map. Having height and length, the surface was easily deduced. This entire surface was attributed to the constituting materials according to their proportions. The surface of the apertures (windows, doors), classically considered by architects equal to half of the total surface of the facade, was not deducted because it compensates for

the roughness of the façade (sculptures, decoration, balconies, ...). In summary, the total calculated surface was attributed to the constituting materials and half of this surface was arbitrarily attributed to the modern glass of the windows. Only the street facing, external façades were taken into account due to their direct exposure to pollution from traffic and the inaccessibility of interior private courts.

The authors decided to measure the surfaces of historical monuments directly in the field, according to the same methodology employed for private buildings. In the Ile de la Cité, the quantity of historical monuments and official buildings is very high. On the right bank of the Seine, three important monuments exist and in the Ile Saint Louis there are only two historical Monuments.

In total, the measurement of the length of each construction on the map of Paris, the counting in the field of the number of floors and the characterization and evaluation of the respective proportions of the constituting materials were performed on the façades of 525 buildings and monuments in the Centre of Paris, giving an excellent statistical value to the results presented below.

The total surface in m^2 of the **525** façades of buildings and monuments of the studied area, and the distribution of the different materials in these façades are given here below on the basis of a 3m mean height. The surface of modern glass is arbitrarily estimated as half of the total surface of the façade. The two historical monuments of the Ile Saint Louis have their façade entirely in limestone, covering 768 m², and the other six, in the Ile de la Cité accounting for 71,586 m².

With these results, the authors demonstrate that the main material present in the façades in the Centre of Paris is the Lutetian limestone (roughly 76%), followed by painting (15%) and then by rendering (7%). Brick (1%) and metal (0.02%) play a very minor role. Thus, limestone dominates in the lle de la Cite' and on the right bank facing it, due to the presence of many important monuments and Haussmannian buildings, whereas painting and rendering are more important in the lle Saint Louis, where buildings are dating from the XVII and XVIII centuries.

Total Paris Centre: 525 façade = $200,305 \text{ m}^2$, length of 11,203 m Limestone: 15,933 m² (76%) Modern glass



FIGURE 5 Geographical distribution of the percentage of limestone in the façades of buildings and monuments of the studied area, on a grid with cells of 100 m x 100 m (floor mean height=3m) Source: [3]

(estimated): 100,152 m² (50%), others 47,247 m² (24%). (Monuments): **72,354 m²** - 100% Limestone.

The geographical distribution, on a grid of $100m \ x$ 100m cells, of the total surface of the façades, of the surface in limestone and of the percentage of limestone in the façades, is given in Fig. 5. This confirms more in detail that limestone is mostly in the western part of the studied area.

The main risk for buildings and monuments in the centre of Paris is air pollution due to traffic, causing the soiling of façades by deposition of black carbonaceous particles, especially in the parts sheltered from rain, and the surface recession of these façades by erosion-dissolution in the parts exposed to the rain. The Dose /response function which we used to calculate the recession of the limestone material (see equation 1) for Paris Centre indicates that the corrosion depth after one year of exposure is 5.75 μ m.

Table 1 shows that this result is lower than the tolerable corrosion rate per year, which is 8.0 μ m year ⁻¹ for the limestone 2020 target. This result is very close to the tolerable corrosion rate per year for the 2050 target, which is 6.4 μ m year ⁻¹. On the other hand, the calculated corrosion rate for the Paris Centre is almost two times as high as the background corrosion depth

indicated in Table 1 (3.2 μ m). This indicates that in 2009-2010 the corrosion depth in the Paris Centre was almost two times as high as the background corrosion rate, which is due to air pollution, but it is steel in the range of tolerable corrosion rate for 2020 target.

Conclusions

The present study gives results from the quantitative census of materials in monuments based on a real in-thefield inventory, and on direct examinations, applying maps, images and other documents at the available scales.

The type of materials used in the monuments was determined by direct examination of the building façade, and their proportions was roughly evaluated in percentage. Different types of limestone were used in the construction of the studied monuments.

The dimensions of the monuments were identified using direct examination, images, photos, drawings and other documents available in literature and from the internet sources. The dimensions of monuments then allowed to calculate their surface by valuating the surface covered by windows, doors, etc.

As limestone is the dominating material, the doseresponse function for limestone was calculated in order to determine the corrosion of the materials used for constructing the monuments.

Using the pollution data for 2009–2010, the estimated recession rate for both sites does not exceed the 2020 target for limestone (2.5 times the background or 8.0 μ m year⁻¹), but is very close to the 2050 target (2.0 times the background or 6.5 μ m year⁻¹). However, the calculated corrosion rate for both sites is almost two times as high as the background corrosion depth indicated in Table 1 (3.2 μ m).

[1] S. Doytchinov, A. Screpanti, G. Leggeri, C. Varotsos: Pilot study on inventory and condition of stock of materials at risk at (UNESCO) CH sites. UN ECE ICP Materials Report 68, November 2011, prepared by the sub center of stock of materials including CH at risk.

[2] C. Varotsos, University of Athens, Faculty of Physics, Dept. of Applied Physics, Laboratory of Upper Air. Bldg Phys 5., 15784 Athens, GR, Private Communication.

[3] J. Watt, S. Doytchinov, R.A. Lefèvre, A. Ionescu, D. Fuente de Ia, K. Kreislova and A. Screpanti (2009): Stock at risk, pp 147-187, in *The effects of air pollution on cultural heritage*, Watt J, Tidblad J, Kucera V and Hamilton R, Eds., Springer, New York, USA.