Atmospheric pollution is known to induce corrosion effects biology essay

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corrosion effects on various materials. For Greece, stone deterioration could emerge severe costs in thecase of damaging cultural monuments. This workaims to investigate the corrosion process on materialsof archaeological importance (marble, limestone, andsandstone) in the Greater Athens Area (GAA) byusing sophisticated geoanalytical methods togetherwith dose–response functions for selected materials, in order to derive corrosion maps for GAA in theperiod 2000–2009. Also, a corrosion trend analysis isperformed, which can be a very helpful tool for theprediction of potential risks to monuments of culturalheritage due to atmospheric pollution. The corrosioneffects on the selected materials are generally weak. Nevertheless, increasing corrosion trends are found inthe eastern regions of GAA for all sheltered materialsand in the northern parts of GAA for unshelteredmarble. The technique is finally applied to 12locations in GAA, which include some of the mostimportant archaeological monuments of Athens, andprovides comprehensive results for the estimation ofthe impact of atmospheric corrosion on the structuralmaterials of these archaeological sites. Keywords Air pollution . Corrosion of materials . Dose–response . Archaeological sites . Athens . Greece1 IntroductionIt is well established that atmospheric pollution causesvarious problems to human health, such as chronicdiseases (Becker et al. 2002; Bell et al. 2011; Kampaand Castanas 2008; Lechón et al. 2002; Wang et al. 2008; Wanner 1990; Yang and Omaye 2009), itcontributes to forest decline and plant elimination(Bussotti and Ferretti 1998; Bytnerowicz et al. 2007; Oszlanyi 1997; Paoletti et al. 2010), and in manycases, it presents significant corrosion effects onvarious materials like metals, plastics, wood, buildingmaterials, and cultural heritage monuments

(Graedeland McGill 1986; Johansson 1990; O’Brien et al. 1995; Schuster and Reddy 1994; Van Grieken et al. 1998). Many of these materials need special attentionbecause of their great social, historical, and economicalvalue (Bell et al. 2011; Graedel and Leygraf 2001; Kucera and Fitz 1995; Kucera 2002; Mirasgedis et al. 2008; MULTI-ASSESS 2005; Screpantia and deMarco 2009). After the adoption of the Conventionon Long-Range Transboundary Air Pollution withinthe United Nation Economic Commission for Europein 1979, a series of International CooperativePrograms (ICP) was initiated for assessing the effectsof atmospheric pollutants on several materials ofmajor interest (Kucera 2002; Kucera et al. 2007; Mikhailov 2001; MULTI-ASSESS 2005; Tidblad etal. 1998, 2001; Tidblad 2009). For a long time, sulfur has been considered as themain pollutant; nevertheless, many researchers haverecently concluded that nitric oxides and ozone, together with favorable meteorological parameters, such as temperature, relative humidity, and precipitation, play an important role in the corrosion effectsdeduced on materials (Johansson 1990; Kucera andFitz 1995; Lan et al. 2005; Lipfert 1989; O’Brien etal. 1995; Roots 2008; Schuster and Reddy 1994; Screpantia and de Marco 2009; Tidblad et al. 1998; Van Grieken et al. 1998). To study these effects, dose–response functions (DRF) for corrosion onmaterials have been derived and applied (Kucera2002; Kucera et al. 2007; Mikhailov 2001; MULTIASSESS2005; Tidblad et al. 1998; Tidblad et al. 2001). These scientific tools represent the relationshipsbetween climate and air pollutants on the onehand and the resulted deterioration of structural materialson the other; they have been mainly used by the ICPon Materials for more than 20 years to determine themass loss/increase of the materials under corrosionattack in sheltered and unsheltered locations with verypromising results. These DRFs have been adopted inthe present work for a quantitative analysis of thematerials under investigation. For Greece, a nation synonymous with ancientcivilization and cultural heritage formore than 2, 500 years, the protection and preservation of such monuments aremore than a national necessity (Mirasgedis et al. 2008; Moropoulou et al. 1998). Athens, the cradle ofcivilization, has numerous such historical monuments. This work is, therefore, focused on the corrosioneffects on materials of archaeological value, i. e., marble, limestone, and sandstone, which are dominantin ancient monuments in the metropolitan area ofAthens; the study also aims to quantify the potentialrisks to these materials from their diachronic exposureto the atmospheric pollution of the city undersheltered and unsheltered conditions. The above aims are implemented by producingannual DRF maps over the Greater Athens Area(GAA) in the period 2000–2009 for each of theselected materials. The results show weak corrosionfor all materials, with greater spatial variations formarble. These corrosion maps can be considered auseful tool in predicting corrosion effects over theregion and can thus give to the Directorate ofConservation of Ancient Monuments, Ministry ofCulture and Tourism, the necessary informationabout the degree of corrosion of the culturalheritage monuments in GAA. Corrosion trends arealso calculated for the selected materials by usinglinear trend analysis for the corresponding DRFvalues. For all the materials under investigation, anincreasing corrosion trend is observed in the east ofGAA, except for unsheltered marble where thegreatest corrosion rate occurs in the northern regionof GAA. These corrosion trend maps thus serve asa potential protection tool for materials of importantarchaeological value (Graedel and Leygraf 2001; Kucera and Fitz 1995; Tidblad et al. 1998; Tidblad2009). The above techniques are applied to someimportant cultural heritage monuments in GAA, inorder to provide a quantitative estimation of theatmospheric corrosion effects on the materials ofthese monuments. 2 Materials and MethodsThe mandatory parameters used in this study are themean annual ambient temperature (temperature indegree Celsius), the mean annual relative humidity(RH in percent), the total annual precipitation (PR inmillimeter), the mean annual time of wetness (TOW, defined as the time fraction of the days with T > 0°Cand RH > 80%), and the mean annual concentration ofSO2 (in micrograms per cubic meter). For thecalculation of the mean annual TOW, daily values ofambient temperature and relative humidity have beenused. The annual values of these parameters weretaken from various monitoring stations within GAA. Table 1 presents these stations. This monitoringnetwork includes 18 environmental monitoring stations(air pollution and meteorology) operated by the Ministryof Environment, Energy and Climate Change(DEARTH network), the 2 meteorological stations ofthe National Observatory of Athens (NOA), and the 10hydrological–meteorological stations operated by theNational Technical University of Athens (HOATable 1 The monitoringstations in GAA ID Station Longitude (deg) Latitude (deg) Altitude (m abovemean sea level)network). The location of all the above stations is shownin Fig. 1. Due to technical problems and/or lack of data, some of the collected data series were incomplete forsome years and stations. To obtain a complete dataseries for the problematic meteorological and/or airpollutant parameter(s) at each station of Table 1, thekriging geostatistical analysis was applied to thewhole region of GAA (as depicted in Fig. 1) for theparameter(s) in question and the year(s) presenting thegap(s), using the ArcGIS 10 software. This way, thevalues of the parameters for those years, which hadmissing data at some stations, were identified and thegaps were filled. Kriging/Cokriging is an advancedgeostatistical tool that generates an estimated surfacefrom a scattered set of points. The procedure assumesthat the distance or direction between sample pointsreflects a spatial correlation that can be used toexplain variation in the surface. The kriging tool fitsa mathematical function to a specified number ofpoints, or all points within a specified radius, todetermine the output value for each location. Theresult of the kriging method gives optimal andunbiased estimates. Table 2 gives a list of all data used in this study(measured and computed by kriging). Though meteorologicaldata were available at many locations inGAA in the period of 2000–2009, additional precipitationdata at other locations than those of Table 2only started in late 2005. Table 3 shows the additionalannual precipitation values used in the present workfrom the HOA network. As in the case of air pollutantand meteorological data in Table 2, the krigingmethodology was also applied to precipitation stationH2 in year 2006 to replace the missing value and tofill the gaps at the stations of Table 1 (see derivedvalues for the DEARTH and NOA stations in thesecond rows of Table 2 for years 2006–2009). For sheltered materials (marble, limestone, andsandstone), the DRFs were calculated for the wholeperiod of investigation. Table 4 presents thecorresponding DRFs used in this study. In theliterature, there also exist DRFs for limestone andsandstone with equations that include the concentrationof ions (H+, Cl−) in the precipitation or theconcentration of particulate matter (Lan et al. 2005; Kucera 2002; Kucera et al. 2007; MULTI-ASSESS2005; Tidblad 2009); these specific DRFs were nottaken into account in this work as measurements ofthe concentration of ions are not available in GAA. By using the DRFs of Table 4, the geostatisticalprogram ArcGIS 10 was applied to the whole area ofGAA to derive corrosion maps for every selectedmaterial and each individual year as well as for thetotal period of investigation. These maps indicate theDRF values in all GAA, including the selected sites ofarchaeological interest, which are presented in Table 5, together with the main material that these monumentsare made of. Thus, for the whole period underinvestigation, the degree of corrosion could be determinedfor the 12 archaeological sites from the predictedDRF values (by means of mass increase for limestoneand sandstone and of surface recession for marble). In the next step, the linear trends of both shelteredand unsheltered materials for all years in the period ofinvestigation were derived at each archaeological site. The corrosion (DRF) trend is expressed as massincrease/surface recession per year for each material. Following the geostatistical technique for producingDRF maps above, DRF-trend maps over GAA werealso derived. These maps can determine the degree ofthe risk for corrosion attack on the selected materialsin GAA due to the dominant air pollutants and theclimatology in the area. Having finalized the DRF and DRF-trend maps formarble, limestone, and sandstone in GAA, specialattention was paid to the corrosion effects at the 12sites of Table 5, where some important culturalheritage monuments exist. Table 6 presents the DRFtrends at the archaeological sites of Table 5 for marble(in micrometers per year) and limestone/sandstone (ingrams per square meter per year). 3 Results and Discussion3. 1 SO2 Concentration Profile in GAAThe sulfur dioxide database formed from measurementsand data gap filling (using kriging analysis) resulted in a complete SO2 mapping over GAA. Asone can see from the dose–response functions(Table 4), this gas pollutant plays a significant rolein the corrosion impact on stone materials. For theperiod 2000–2009, maximum SO2 concentrationswere found at Patission station (#D14 in Table 2)and Piraeus-1 station (#D15) for all years, showing apeak in 2003 with concentrations of 42. 88 and31. 2 μg m−3, respectively. For the whole period, minimum SO2 concentration was observed in the eastof GAA, with values of about three to four timessmaller than those at the stations mentioned before; anexception was year 2009 when the situation wastotally different and the SO2 concentration becamehighest at Koropi station (in the SE of GAA, #D18 inTable 2), having a value of 18. 05 μg m−3, the sametime that the SO2 concentration was about 14 μg m−3at Patission and Piraeus stations and half of that at theother sites of GAA. By comparing the mean concentrationvalues of SO2 over the whole GAA, one canobserve a negative (decreasing) trend for the specificpollutant since in 2000 its mean concentration was~19 μg m−3 and in 2009 only half of that. 3. 2 Materials Behavior and Corrosion Trends3. 2. 1 Marble (Sheltered–Unsheltered)In the case of marble, which is the predominant materialused in ancient monuments in Greece, the DRFmapping of GAA reveals some very interesting results. For the sheltered locations, following the SO2 concentrationprofile, atmospheric corrosion has led tomaximum surface recession (SR) at Patission station(#D14) for the period 2000–2008, with an SR value abouttwice the average of all stations of Table 1, showing alsoa secondary maximum at Piraeus-1 station (#D15)after 2006. In general, the marble corrosion is weak, with greater values of SR of about 1–1. 5 μm in thenorthern–northwestern areas of GAA, comparing tovalues of about 0. 3–0. 6 μm in the southern–southeasternregions of GAA (except from year 2000 onwardswhen corrosion becomes greater in south–southwestGAA and smaller in north–northeast GAA). For unsheltered places and starting from 2006, marblecorrosion is about three to four times greater for thewhole area under investigation than for the sheltered ones(about 3. 7 μm for the maximum and 2 μm for theminimum SR values). In 2009, as is shown in Fig. 2, thecorrosion seems to move eastward. Taking, therefore, into consideration the archaeological sites of Table 5, it is seen that marble corrosion is almost constant atall locations, but Panathinaiko stadium (#11 in Fig. 2)is affected the most and Dimitra’s Sanctuary (#7 inFig. 2) the least by atmospheric pollution, with SRvalues of 2. 71 and 2. 42 μm, respectively. For the corrosion trends, some differences existbetween sheltered and unsheltered marble. For the sheltered material, an increasing corrosion trend in theeast and a decreasing corrosion trend in the south(having also a secondary minimum in the center ofAthens) are observed. For Patission (#D14) andPiraeus-1 (#D15) stations, where marble corrosionwas previously determined to reach its maximum, thecorrosion variation per year is decreasing. For theunsheltered marble, with relative data correspondingto the period 2006–2009 as mentioned before, thetrends are the same as for the sheltered, but three tofour times greater. The important difference comparedto the sheltered case is that the greatest corrosiontrend occurs now in the north of GAA, while thegreatest SR decrease is observed in the south of GAA. At Patission station (#D14), the corrosion trend isagain decreasing. By applying kriging analysis, prediction of thecorrosion trend for the archaeological locations ofTable 5 was possible. For sheltered marble, as isshown in Table 6, an almost constant decreasecorrosion rate for all sites occurs (−0. 04 μm year−1). For unsheltered marble, the situation changes sincethe annual DRF variation is still decreasing at all places, but not at the same rate. So, at Pnyx (#2 in Table 6) themarble DRF decreases with a rate −0. 06 μm year−1, while at Dimitra’s Sanctuary (#7), it decreases with arate −0. 19 μm year−1. The corrosion trend over GAA, including the 12 archaeological sites, is presented inFig. 3. Here, dark blue areas in west and south GAAcorrespond to decreasing DRF rates (as shown e. g. atDimitra’s Sanctuary, #7 in Fig. 3), while red-coloredareas, such as the eastern part of GAA, correspond toan annual increasing trend of marble corrosion. Nearthe historical center of Athens (including the archaeologicalplaces of Acropolis, Pnyx, Kerameikos, Ancient Agora, and Akadimia Platonos, #1, #2, #5,#6, and #8 in Fig. 3, respectively), the trend is slightlydecreasing. Limestone corrosion has a more smooth variation withinGAA than marble, showing a difference of ~60%between the observed maximum and minimum valuesof mass increase (MI) for the whole period underinvestigation. The maximum corrosion effects on limestone, occurring from the corresponding DRF, areobserved in western GAA (year 2000), moving tonorthern GAA (years 2001–2007) and then to easternGAA (years 2008–2009), while the minimum is in theeast (year 2000), the south–southwest GAA (years 2001–2005) and in the center of Athens (years 2006–2009). The corresponding corrosion map for sheltered limestonein GAA for 2009 is presented in Fig. 4 for all thearchaeological locations of Table 5; the blue areas correspond to minimum and the red areas to maximumMI values. As far as the corrosion trends are concerned, Fig. 5presents the corrosion trend map for the period 2000–2009 in GAA for sheltered limestone. The annualvariation is small, with the red areas in Fig. 5representing an increase of limestone’s MI trend inthe east of GAA, while the blue areas in the north of GAAcorrespond to negative corrosion rates with time. For thearchaeological locations of Table 5, a negative corrosiontrend is observed, with an average decreasing rate inlimestone’s MI of about −0. 01 g m−2 year−1. 3. 2. 3 Sandstone (Sheltered)Sandstone behaves in almost the same manner aslimestone for the total period and all areas of GAA. The only difference is that the MI values are about10–20% greater than the respective values forlimestone at each site. The corrosion trend forsandstone follows that of limestone, with the maximumSR (increasing corrosion) observed in the eastGAA and the minimum (decreasing corrosion) in thenorth GAA. As for the DRF trend, as one can seefrom Table 6 it is again decreasing for all the locationsof archaeological importance of Table 5, with analmost identical profile with sheltered limestone. 4 ConclusionsAthens consists of many archaeological monuments, with the majority of them consisting of marble, limestone, and sandstone. Since atmospheric pollutionhas been proved to cause corrosion effects on thesematerials, this work was focused on presenting aquantitative method for determining the potentialrisks from corrosion on marble, limestone, andsandstone over the Greater Athens Area, in order topreserve and protect the cultural heritage monuments. The use of experimental data from a wide network ofmeteorological stations, together with dose–responsefunctions for each material to quantify corrosioneffects and sophisticated analysis methods (kriging), resulted to corrosion maps for the three materials insheltered and unsheltered conditions. So, annualprofiles for the corrosion behavior for each materialwere deduced. For the sheltered marble, an increasing corrosiontrend in the east and a decreasing one in the southwere observed in GAA for the period 2000–2009. Forthe unsheltered marble, the trends were identical withthose of the sheltered, but with three to four timesgreater absolute values. For the sheltered limestone, an increasing corrosion trend in the east and adecreasing one in the north were observed in GAAfor the same period. For the sheltered sandstone, analmost identical profile with that for the shelteredlimestone was found in GAA for 2000–2009. Also, corrosion trends were evaluated for the period2000–2009 for the materials under investigation, leadingto the production of corrosion trend maps overGAA, which can be used as a guide to predict corrosionimpact on the archaeological sites in GAA. Acknowledgment The authors would like to thank theHydrological Observatory of Athens (hoa. ntua. gr) for providingsome of the precipitation data used in this study.