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THE EFFECTS OF AIR POLLUTION ON THE STATUE OF SAINT GEORGE AND THE DRAGON IN CLUJ-NAPOCA, ROMANIA

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Abstract

The study presents the effects of air pollution on a historical symbol of Cluj-Napoca. The statue of Saint George and the Dragon is a copy made in 1904 by Kalman Lux. The original statue built in 1373 by two metalworkers Martin and George from Cluj, is in Prague, Czech Republic. The pedestal of the statue was built using the "Baciu Limestone" due to its famous white color. The "Cluj Limestone" is a white-yellow Cenozoic limestone, with high water uptake and porosity, which allows large amounts of water to easily be stored within the limestone. According to the emissions inventory provided by The Regional Agency for Environmental Protection from Cluj-Napoca for the years 2004-2010 the emission values of SO_2, NOx and SPM decreased comparing to the years 1992-2002, and the ammonia values were relatively constant. The results indicate the presence of a black layer of different thickness on the surface of the samples which consists mainly of new formed gypsum. The sample extracts indicate a dominance of phthalates, and the pyrolysis has identified substances characteristic for the products of incomplete combustion of carbonaceous materials.

Keywords: *Air pollution; Baciu Limestone, Black crust; Cultural heritage; SO_2; NOx; SPM*

Introduction

Black and irregular surfaces coloring can be observed on numerous historical stone building and stones [1-9]. Limestone buildings located in polluted urban environments show significant signs of decay. The rate of decay depends on the textural/fabric properties of the carbonates, on the pollution fluxes and on the environmental setting (air pollution, meteorological and micro-climatic conditions).

Effects of acid deposition on monuments by natural weathering or by manmade pollutants are well known [10]. Recently, the interest in materials damage has included the effects of acid precipitation, in addition to the effects of gaseous and particulate air pollution.

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This paper presents the effects of air pollution on the surface of the building material (limestone) used for the pedestal of the statue “Saint George and the Dragon” from Cluj Napoca city, Romania.

Located in the heart of Transylvania, Cluj-Napoca (hun:Kolozsvár; ger: Klausenburg), also named "The Treasure City", contains treasures of ancient and modern architecture. Cluj-Napoca has approximately a thousand years old, which is reflected in the diverse cityscape and at the monuments from past centuries.

The “St. George and the Dragon” statue in Cluj (made in 1904 by Kalman Lux) is a replica of the statue built in 1373 (by two metalworkers, Martin and George from Cluj) and initially was located in Saint George Square (which is now known as “Lucian Blaga Square”). In 1960 was moved to the small square in front of the Reformed Church of Calvin on Mihail Kogalniceanu Street, which was considered to be a more suitable location (Fig. 1).

The original statue from Prague was built in 1373 by sculptors Cluj Martin and George, sons of the painter Nicolae from Cluj, by request of Emperor Charles the IV century, the King of Boemia, upon the marriage of his son Sigismund of Luxemburg with Marie de Anjou, daughter of the Hungarian King Ludovic the Great. The original statue was moved in time to different locations of Hradčany Castle in Prague, and now is located in the Third Court, near a small fountain (Fig. 2).

Fig. 1. Location of the Statue of Saint George, and the Dragon in the Cluj city center and the main source of air pollution (cars)

Fig. 2. Saint George Slaying the Dragon at Prague Castle, Prague, Czech Republic

The pedestal of the statue from Cluj was built using the “Baciu Limestone” (due to its famous white color) which is in fact a Cenozoic (Upper Eocene) limestone that was quarried in Baciu, near Cluj, thus the name “Baciu Limestone” as described by [11].

As a result of the high porosity (30.55-32.26 %) which was established earlier [12], large amounts of water can be easily stored within the limestone, making it softer and "easier shaped”. After drying out, the limestone increases markedly in hardness. The authors also regard an infiltration of dissolved $CaCO_3$ from the overlying limestone when it is exposed as the main reason for this process.

According to [11], the bioclastic and oolitic limestones were used predominantly in the construction of historical buildings. They reflect primary the deposition on a shallow tropical

carbonate platform established in the Transylvanian basin during the Cenozoic (Upper Eocene - Lower Oligocene).

The deposition environment was influenced by episodes of terrestrial (siliciclastic) input from the hinterland locality.

Quartz, feldspar grains, and clay minerals were admixed to the carbonate sediment and are responsible for the white to yellowish color of the limestone, its technical characteristics, and different types and degrees of weathering. Clay minerals in particular strongly influence the weathering stability. The presence of finely dispersed swelling clay minerals in the micritic matrix of limestones (mudstones, wackestones, and packstones) makes these limestones highly sensitive to water uptake and increased weathering. This effect can be commonly observed in geological young limestone such as the Tertiary limestone described here.

R. Koch et al. [11] describes that the chemical influences of acids or bases, commonly result in dissolution of cementing agents and in single grains. Carbonate minerals such as calcite and dolomite can be affected by dissolution. The concentration of these cations (Ca^{2+}, Mg^{2+}) will control the type of crust formed at the surface. The anions for the crusts come from air pollution produced by the local industry. Carbon dioxide leads to the formation of carbonate crusts, SO_4^{2-} to gypsum crusts, and NO_3 - to efflorescence of nitrates. The formed minerals have different hygroscopic characteristics that strongly influence the rate of decay of a rock.

Natural stone is widely used as building stone, primarily because of its appearance and quality. However, it is particularly susceptible to deterioration principally through the effects of chemical dissolution. Even unpolluted rain contains carbon dioxide creating a weak carbonic acid which is able to dissolve calcite, the main mineral component of limestone. This natural acidity of rain is further increased by reactions with other atmospheric pollutants such as sulfur and nitrogen oxides, which results in the increasing rate of limestone dissolution. The quality of the urban air has greatly improved, however, the increasing vehicular traffic and the associated rise of atmospheric carbon and nitrogen oxidescompounds [13] continues to pose a threat to our built heritage.

Glossary of stone decay features mentions that the potential for stone surface change is shown by field trials, in which small limestone tablets affixed to buildings in exposed and sheltered locations, exhibit a range of features arising from the action of different weathering processes.

The rate of decay depends on the textural properties of the carbonates, on the pollution fluxes and on the environmental setting (air pollution, meteorological and micro-climatic conditions). The impact of acid deposition on the weathering of carbonate stone has been recognized for long time. Recently, the role of the acid and acidifying air pollutants has become a considerable concern at both national and international level. This concern has been centered mainly on its secondary reactions with acid deposition and serious damage to historical monuments.

In their work *A. Humberto Bravo et al.* [10], is mentioned that there are three classes of mechanisms involved in the stone damage by air pollution:

a) *Aqueous dissolution reactions of calcium carbonate*. Carbonate stones (limestone and marble) are particularly susceptible to acidic precipitation due to the dissolution of calcium carbonate with hydrogen ions in aqueous solutions. These solutions can be deposited by rain, dew, mist or fog.

b) *Gaseous deposition processes*. There are some important gaseous pollutants, like sulfur dioxide, that contributes to rain acidity and leads to the formation of commonly observed gypsum in surface crusts.

c) *Particle deposition on stone surfaces*. Some particulate pollutants may catalyze some processes to make them more effective to produce a more accentuated damage on the stone surface.

The first of these factors have been studied extensively and the carbonate stone recession has been assessed from several viewpoints, such as: weight loss, chemical analysis of run-off solutions, direct measurement of recession, etc. Although this is not the only mechanism responsible for deterioration of carbonate stone, its knowledge is crucial to understand how it affects the integrity of this material, an important characteristic in the construction industry.

In order to understand the environmental stress for monuments, it is necessary to establish which are the pollutants that influence the environmental stress.

The emissions inventory provided by *The Regional Agency for Environmental Protection from Cluj-Napoca* for the years 2004-2010 indicate that the emission values of SO_2, NO_x and suspended particulate matter (SPM) decreased, comparing to the years 1992-2002, and the ammonia values were relatively constant (for 2005 the amount of ammonia emitted was 4588.495 tons, and in 2010 the amount was 5554.40 tons).

Materials and Methods

Samples

The samples (named SG) were collected from the pedestal of the statue, and consist in limestone fragments which presents a layer of black crust on the surface, which were compared with a sample of unaltered limestone, named PL (pure limestone). Thin and polished sections were prepared from all samples for studying.

The micropetrographical analysis of polished sections included the identification of carbonaceous particles in reflected monochromatic light at λ = 546 nm and in a fluorescence arrangement, the determination of their morphology, and the degree of thermal transformation based on the light reflectance measurement, according to [9, 14, 15].

Carbonaceous particles, light reflectance and fluorescence properties were determined with UMSP 30 Petro OPTON-ZEISS microscopes in monochromatic light (λ = 546 nm), with immersion objectives (magnification 40x and 100x), and an OLYMPUS BX51 reflected light microscope with the CRAIC system and immersion objectives 40x and 100x. Chemical analysis of the organic compounds in deposits on chosen building materials from Cluj, included three methods: *determination of total and noncarbonated carbon*, *sample solvent extraction* followed by *GC/MS* and *analytical pyrolysis*, i.e., *thermal disintegration of sample combined with GC/MS*.

Results and discussions

Mineral and morphologic characterization

The optical microscope analysis of the thin sections (Fig. 3) revealed that the black crust layer is approximately 0.01mm and in the sample there are perfectly shaped as ooides, which is characteristic to this type of limestone.

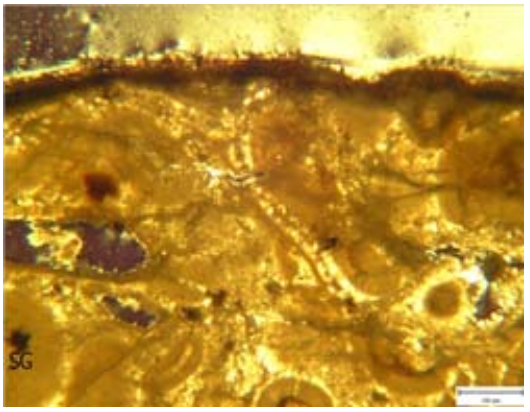


Fig. 3. On the surface of S.G. sample a very thin black layer can be observed

The Scanning Electron Microscope (SEM) analysis shows a re-sedimentation layer on the surface of the S.G. sample (Fig.4), which occurred probably due to the effect of acid rain, comparing to the unaltered sample named P.L. (Fig. 5) which has perfectly shaped ooids and calcite crystals on the surface of the sample.

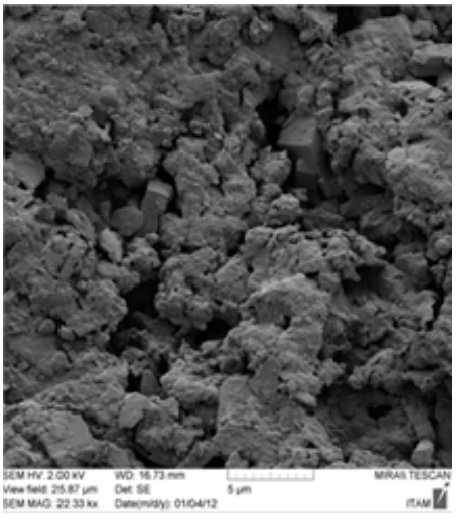


Fig. 4. The surface of the S.G. sample

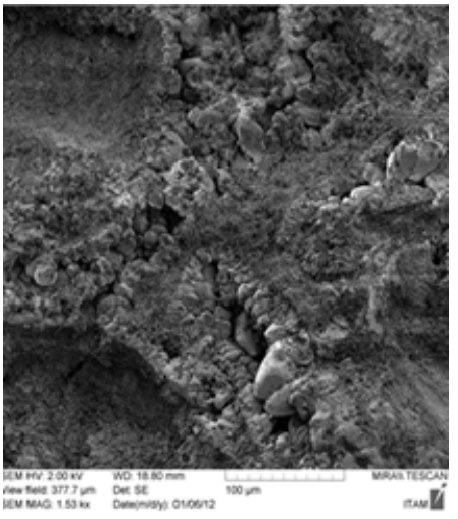
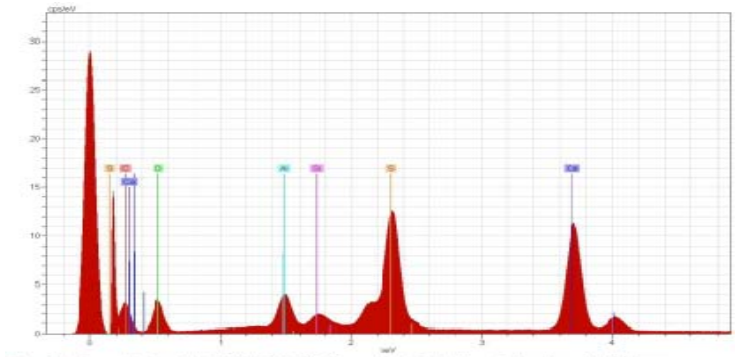


Fig. 5. The surface of the P.L. sample

Energy-dispersive X-ray spectroscopy (EDX) analysis (Fig. 6) shows a concentration of silicon and aluminum, which can be explained by the quartz and feldspar minerals present in the composition of the limestone. The high concentration of sulfur is believed to indicate the presence of the gypsum based black crust.



SG_gold 23 Data: 14/03/2012 10:57:37 HV: 15.0 kV Puls th.: 10.57 kcps

Spectrum: SG_gold 23

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]	Oxide	Oxid. C [wt.-%]	Error [%]	K fact.	Z corr.	A corr.	F corr.
Carbon	K-series	0.00	0.00	0.00	CO2	0.00	0.0	0.000	0.873	16.134	1.000
Calcium	K-series	3.06	10.23	7.25	CaO	7.16	0.0	0.027	0.986	1.156	1.000
Silicon	K-series	2.41	8.06	8.15	SiO2	8.63	0.1	0.026	0.925	1.200	0.977
Sulfur	K-series	17.47	58.44	51.80	SO3	73.03	0.6	0.213	0.906	1.122	0.999
Aluminium	K-series	3.53	11.82	12.45	Al2O3	11.18	0.2	0.035	0.639	1.372	0.993
Oxygen	K-series	3.42	11.45	20.34	O	-49.95	0.0	0.006	0.918	5.761	1.000
	Total:	29.90	100.00	100.00							

Fig. 6. EDX spectrum of the S.G. sample

Determination of organic compounds from the deposits. Carbon content and GC/MS

Total C (C_d) is composed of non-carbonate C and carbonate C. The carbonate C is linked to the limestone, however strange is a low carbon content (total carbon content as well as carbonate content) in the samples. Non-carbonate C may have a number of different and simultaneous origins, including the atmospheric deposition of pollutants, biological weathering and the decay of protective organic treatments. *GC/MS analysis* (Table 1) was used for the identification and determination of substances soluble in organic solvents. Di-ethylphthalate, di-isobutylphthalate, di-n-butylphthalate, and di-(2-ethylhexyl)phthalate dominated in bulk depositions, formed 35-49% of the total extract. Phthalates are used as plasticizers in production of plastics, and thus widespread in the environment [16]. Other groups were fatty acids (12-27%) and n-alkanes (8-17%) which originate from terrestrial organic matter (waxes and cuticles) and from the cell membranes of microorganisms.

Table 1. Identified compounds (mass percent) in the extracts of the samples using GC-MS

Compound	S.G.	Compound	S.G.
di-epi-cedrene	0,09	di-n-butyl phthalate	24,26
4-ethoxy-2-hydroxyoctanophenone	0,10	alkane - C20	0,60
2,6-di-tertbutyl-p-benzoquinone	0,22	isopropyl palmitate	0,36
alkane - C16	0,18	alkane - C21	0,57
diethyl phthalate	12,75	oleic acid $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	3,05
isopropyl laurate	0,14	stearic acid $CH_3(CH_2)_{16}COOH$	1,22
alkane - C17	0,38	alkane - C22	0,70
pristane	0,25	4,4'-diisopropylidenediphenol	1,10
ethylhexyl benzoate	0,51	alkane - C23	0,57
myristic acid $CH_3(CH_2)_{12}COOH$	2,37	alkane - C24	0,53
alkane - C18	0,33	alkane - C25	1,41
phytane	0,34	di(2-ethylhexyl) phthalate	5,61
isopropyl myristate	0,63	alkane - C26	0,80
pentadecanioc acid $CH_3(CH_2)_{13}COOH$	1,83	alkane - C27	0,77
diisobutyl phthalate	5,67	alkane - C28	1,33
alkane - C19	0,32	alkane - C29	1,22
hexadecanoic acid $CH_3(CH_2)_{14}COOH$	17,47	Sum of unknown compounds	12,30

Py-GC/MS

Toluene (not included in the pyrograms) (Table 2) was present in the highest quantity in the pyrolysis. Benzonitrile is an indicator of incomplete combustion [15, 17].

The distribution of n-alkenes/alkanes (C10-C12) [15] is an indicator of combustion of plant matter.

Table 2. Identified compounds (mass percent) in the pyrolysates at 700°C of the sample using Py-GC-MS

Compound	S.G.	Compound	S.G.
benzene	18,02	butylbenzene	0,23
toluene	70,90	alkene - C11	0,68
pyridine		alkane - C11	0,15
xylene		nonaldehyde	0,20
styrene	5,28	methylindene	0,63
benzaldehyde		alkene - C12	0,19
alkene - C10	1,45	alkane - C12	0,39
benzonitrile	0,61	decanaldehyde	0,14
C3 benzene	0,68	Uknown	0,01
indene	0,44		

Results of petrographic analysis of samples of black crust

The black crust on the statue of Saint George and the Dragon (sample S.G.) is composed of basic mineral material with small amount of carbonaceous particles on the outside part (Fig. 7-10).

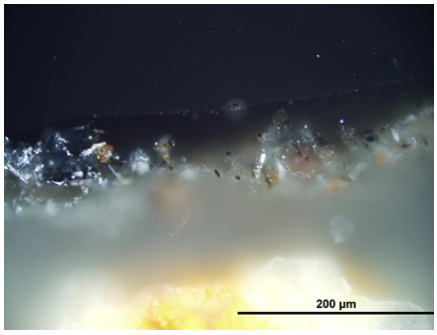


Fig. 7. Massive char fragment and plant organism residues. Reflected white light, immersion objective.

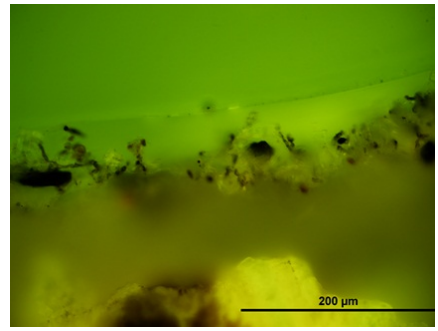


Fig. 8. Massive char fragment and plant organism residues. Reflected blue light, immersion objective.

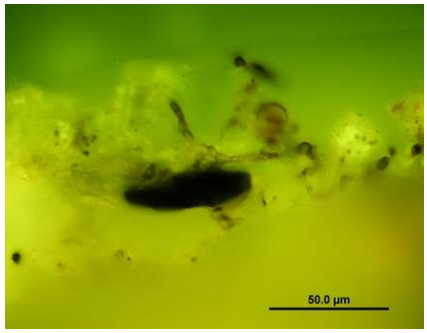


Fig.9. Massive char fragment and plant organism residues. Reflected white light, immersion objective.

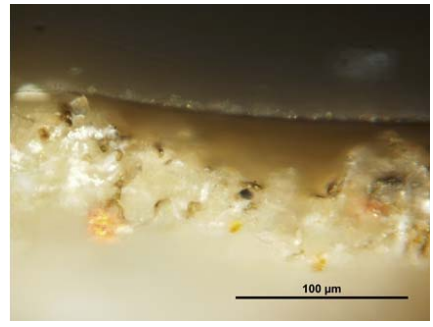


Fig. 10. Residues of plant organism. Reflected white light, immersion objective.

On the surface, there is a thin lamina containing a few bigger particles of massive char (up to 50μm) with high reflectance (Rr = 1.5 – 3.8%), small portion of soot and more residues of plant tissues and organs with chain structure too.

Conclusions

In conclusion, the porosity, as well as the mineralogical content (perfectly shaped ooides, which are characteristic to this type of limestone) of the analyzed sample of stone make it very susceptible to several types of decay, supported by air pollution.

The sample went through a series of tests: preparation of thin sections, optical microscope, Scanning Electron Microscope, EDX, organic compounds from the deposits, and petrographic analysis of samples of black crusts.

The optical microscope analysis of the thin sections revealed that the black crust layer is approximately 0.01mm thick. The microscopic analysis also detected that the sample is composed of basic mineral material with small amounts of carbonaceous particles on the outside part. The thin black layer shows a re-sedimentation of the calcite, which is most likely due to the effect of acid rain.

EDX analysis shows a concentration of silicon and aluminum, which can be explained by the quartz and feldspar minerals present in the composition of the Baciu limestone. The high concentration of sulphur is believed to indicate the presence of the gypsum based black crust. The extract yields in GC/MS analysis of the studied samples were small. Di-ethylphthalate, di-isobutylphthalate, di-n-butylphthalate, and di-(2-ethylhexyl)phthalate dominated in bulk depositions formed 35-49% of the total extract. Phthalates are used as plasticizers in production of plastics, and thus widespread in the environment. Another group of the identified substances were fatty acids (12-27%) and n-alkanes (8-17%). The fatty acids and n-alkanes (typically with odd-over-even preference) originate from terrestrial organic matter (waxes and cuticles) and from cell membranes of microorganisms.

All of the above mentioned analyses concluded that the air pollution can induce decay defects into the rock structure.

Acknowledgments

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References

[1] C. Saiz-Jimenez, *Deposition of airborne organic pollutants on historic buildings*, **Atmospheric Environment**, **27B**(1), 1993, pp. 77-85.

[2] G.C. Galletti, P. Bocchini, D. C.-G. Chiavari, R. Mazzeo, *Chemical characterization of the black crust present on the stone central portal of St Denis abbey,* **Fresenius Journal of Analytical Chemistry**, **357**(8), 1997, pp. 1211-1214.

[3] S. Machill, K. Althaus, W.E. Krumbein, W.E. Steger, *Identification of organic compounds extracted from black weathered surfaces of Saxonean sandstones, correlation with atmospheric input and rock inhabiting microflora*, **Organic Geochemistry, 27**(1-2), 1997, pp. 79–97.

[4] E. Papamichos, S.A. Papanicolopulos, I. Larsen, *Mechanical properties and damage diagnosis of natural building stone*, **Fracture and Failure of Natural Building Stones – Applications in the Restoration of Ancient Monuments** (Editor S.K. Kourkoulis), Springer, 2006, pp. 71-92.

[5] F. Cappitelli, P. Principi, R. Pedrazzani, L. Toniolo, C. Sorlini, *Bacterial and fungi deterioration of Milan Cathedral marble treated with protective synthetic resins*, **Science of the Total Environment, 385**, 2007, pp. 172-181.

[6] A. Török, *Black crusts on travertine: factors controlling development and stability*, **Environmental Geology**, **56**(3-4), 2008, pp. 583-594.

[7] V. Cnudde, G. Silversmit, M. Boone, J. Dewanckele, B. De Samber, T. Schoonjans, D. Van Loo. Y. De Witte, M. Elburg, L. Vincze, L. Van Hoorebeke, P. Jacobs, *Multidisciplinary characterisation of a sandstone surface crust*, **Science of the Total Environment**, **407**, 2009, pp. 5417-5427.

[8] B.J. Smith, R. Prikryl, *Diagnosing decay: the values of medical analogy in understanding the weathering of building stones*, **Building Stone Decay: from Diagnosis to Conservation** (Editors: R. Prikryl and B.J Smith), Special Publication No. 271, Geological Society Special Publication, London, 2007, pag.1-9.

[9] I. Sýkorová, M. Havelcová, A. Zeman, H. Trejtnarová, *Carbon air pollution reflected in deposits on chosen building materials of Prague Castle*, **Science of Total Environment**, **409**, 2011, pp. 4606-4611.

[10] A. Humberto Bravo, A. Rogelio Soto, E. Rodolfo Sosa; A. Pablo Sánchez; J. Ana Luisa Alarcon, K. Jonathan, B. Jaimes Ruiz, *Acid deposition effects on archeological monuments in Mexico*, **13th World Clean Air and Environmental Protection Congress and Exhibition**, London, UK, August 22 - 27, 2004, www.umad.de/infos/cleanair13/pdf/full_15.pdf (accessed 17 July 2013)

[11] R. Koch, C.P. Răcătăianu, I.I. Bucur, *Examples of weathering and deterioration of Tertiary building stones at St. Michael's Church in Cluj Napoca (Romania)*, **Studia Universitatis Babeş-Bolyai, Geologia**, **53**(2), 2008, pp. 25 – 39.

[12] I.A. Maxim, V. Lucca, *Calcarele grosiere de pe teritoriul oraşului Cluj. Materiale de construcţie. Calcarele de la Baciu (Cluj)*, **Studia Universitatis Babeş-Bolyai**, Series II, Fasciculus 1, Geologia-Geographia, Cluj, 1960, pp. 7-63.

[13] P. Brimblecombe, *Environment and Architectural Stone*, **Stone in Architecture-Properties, Durability** (Editors S. Siegesmund, R. Snetlage) Springer Heidelberg, ISBN 978-3-642-14474-5, 2011, pag. 324-338]

[14] * * *, *Methods for the petrographic analysis of coal,* **ISO 7404,** *International Organization for Standardization*, 2009.

[15] I. Sýkorová M. Havelcová, H. Trejtnarová, P. Matysová, M. Vašícek, B. Kríbek, V. Sucky, B. Kotlik, *Characterization of organic matter in dusts and fluvial sediments from exposed areas of downtown Prague, Czech Republic*, **International Journal of Coal Geology**, **80**(2), 2009, pp. 69-86.

[16] M.J. Teil, M. Blanchard, M. Chevreuil, *Atmospheric fate of phthalate esters in an urban area (Paris-France)*, **Science of Total Environment, 354**, 2006, pp. 212– 223.

[17] J. Kaal, A. Martınez Cortizas, E. Eckmeier, M. Costa Casais, M. Santos Estevez, F. Criado Boado, *Holocene fire history of black colluvial soils revealed by pyrolysis-GC/MS: a case study from Campo Lameiro (NW Spain)*, **Journal of Archaeological Science**, **35**, 2008, pp. 2133-2143.

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