Research on effects of bird excrement on metal materials copper and bronze

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ZKOUMÁNÍ PŮSOBENÍ PTAČÍCH EXKREMENTŮ NA KOVOVÉ MATERIÁLY MĚĎ A BRONZ

The presented study was aimed at understanding the effects of bird excrement on copper and bronze. The experiment used accelerated aging tests and focused on the impact of specific chemical components of droppings (uric acid, sodium nitrate, potassium dehydrate phosphate, potassium chloride and potassium sulphate). The effects of environmental conditions (relative humidity of 100 %, SO_2 pollution) and exposure duration were also studied. Pure copper sheets, copper sheets with a stable patina, as well as bronze sheets were contaminated by corrosive drops and then, after exposition, investigated.

The 3D digital microscopy showed the changes in surface colour and texture. Visual evaluation showed that the drops displayed visible changes within four weeks and that there are minimal differences between RH and RH + SO_2 exposure. SEM and SEM-EDS showed the change in surface texture and also identified the presence of fungi and dust particles.

Overall, bird droppings do promote the corrosion process of metals. A patina can act as a protective layer against corrosion for some time before it begins to deteriorate. A longer study is required to see more developed results.

Fig. 1 ***Flocks of birds in Trafalgar Square, London.*** *From: E. Finamore, Where Did Trafalgar Square's Pigeons Come From?, in: Londonist, July 2016. April 18, 2017, available on:* http://londonist.com/2016/07/where-did-trafalgar-square-s-pigeons-come-from.

1. Introduction

On visiting a historical monument, one will often discover another community enjoying the structure: birds. Birds, especially pigeons, can be a nuisance to urban areas. According to the theory of ideal free distribution, the suitability of a bird habitat is affected by several factors, including potential predators, food density, and cover. [1] These factors can often be found around monuments where food is abundant for tourists, and shelter for birds can be found within the structures themselves. Pigeon excrement can also be found on the surfaces of which they perch, causing aesthetic unsightliness as well as posing health risks to people. Aside from using nets, bird spikes, or gel to prevent birds from perching on surfaces, some cities such as London have incorporated laws to prevent people from attracting birds by disallowing feeding [2] [Figure 1] or by utilizing predators in the fight against pigeons [3]. Apart from aesthetic, economic, and health issues posed by bird droppings, excrement is also a key factor in causing the deterioration of materials.

It is known that the salts and uric acid in pigeon excrement affect materials differently depending on their susceptibility to the chemical compounds. There is an abundance of copper roofs and bronze statues in cities such as Prague, and suitable conservation efforts are required. The atmospheric effects on the deterioration of metal materials have been studied but there is a gap in research regarding the specific effect of bird droppings. The presented experimental study was aimed at

1 | Stephen Dewitt Fretwell – Henry L. Lucas, On Territorial Behaviour and Other Factors Influencing Habitat Distribution in Birds, *Acta Biotheoretica* XIX, 1969, No 1, pp. 16–36, available on: http://cescos.fau.edu/gawliklab/papers/FretwellSDandHLLucas1970.pdf

2 | Feeding Trafalgar's pigeons illegal, *BBC News*, 2003, November 17, http://news.bbc.co.uk/2/hi/uk_news/england/london/3275233.stm.

3 | Jana Pšeničková, Liberec nechce zabíjet holuby plynem, posílá na ně dravce, *idnes.cz*, 2017, April 11, https://liberec.idnes.cz/liberec-nechce-zabijet-holuby-plynem-posila-na-ne-dravce-pjh-/liberec-zpravy.aspx?c=A170411_104453_liberec-zpravy_jape, 19. 1. 2018.

gaining a better understanding of the corrosion processes taking place on copper and bronze surfaces exposed to pigeon droppings, using accelerated ageing for the simulation of climatic factors and uric acid (or a mixture of uric acid with individual inorganic salts contained in pigeon excrement) for studying the effects of the components of pigeon droppings.

2. Bird dropping characteristics – state of the art research

Few studies in the field of conservation have investigated the effect of bird droppings on materials. A study conducted in Spain determined that the droppings contained 4% soluble salts, including halite, sylvite, potassium calcium sulphate, aphthitalite, apatite group minerals, weddellite, and gypsum; the concentration of different ions determined in a water extract is summarized in Table 1.[4]

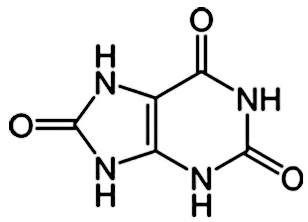

Fig. 2 ***Structure of uric acid.***

Table 1 ***Analytical concentration results of lixiviate (mg/l) (Gómez-Heras et al., 2004)***

Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	SO_4^{-2}	PO_4^{-3}	NO_3^-
935.0	831.8	507.3	139.6	2440.0	1563.3	786.4	263.6	10.0

An experiment conducted in Bologna, Italy and Norwich, UK studied the effect of uric acid on outdoor copper and bronze.[5] The scientists considered the fact that birds, unlike mammals, do not excrete urea as a major end-product of nitrogenous metabolism. Bird faeces are usually cream coloured and consist of two fractions: a clear liquid and a white part, generally viscous and mucoid, composed mostly of uric acid and other urates.[6] Uric acid is only very slightly soluble in water (64 mg L–1 at 310 K).[7] Biological degradation occurs in uric acid before and after excretion. Before excretion, the intestinal microbes transform uric acid into ammonia, short chain fatty acids, and carbon dioxide. Afterwards, external decomposition provides mainly ammonia, which is then nitrified. If this degradation is incomplete, urea and other intermediates are found.[8] Therefore, uric acid [Figure 2] and the compounds derived from biodegradation can cause damage to materials.[9] The scientists confirmed that uric acid chemically affects copper and bronzes in that the surface of the metal is modified and copper urates are formed and, furthermore, that the patina reacts with the acid, even though some degree of protection is created. Droppings leave tarnish marks on copper and water exacerbates the corrosion caused by bird droppings.[10]

Bassi and Chiatante[11] studied the role of pigeon excrement in the bio-deterioration of stone and they pointed out that pigeon excrement constitutes a highly favourable substrate for microbial growth. This study focused on the identification of microorganisms and effects of fungal species on lowering the pH value of the system. The composition of bird droppings is also dependent on whether the bird lives in an urban or rural environment. In a study from the University of Delaware[12] it was concluded that urban birds appeared to have both fungi and bacteria, whereas farm-grown birds showed more fungi than bacteria.

4 | Miguel Gómez-Heras – David Benavente – Mónica Álvarez De Buergo – Rafael Fort, Soluble salt minerals from pigeon droppings as potential contributors to the decay of stone based Cultural Heritage, *European Journal of Mineralogy* XVI, 2004, No. 3, pp. 505–509.

5 | E. Bernardi – D. J. Bowden – Peter Brimblecombe – H. Kenneally – L. Morselli, The effect of uric acid on outdoor copper and bronze, *Science of the Total Environment* 407, 2009, No. 7, pp. 2383–2389.

6 | Roger A. McNabb, Urate and cation interactions in the liquid and precipitated fraction of avian urine, and speculations on their physico-chemical state, *Comparative Biochemistry and Physiology, Part A: Physiology*, XLVIII, 1974, No. 1, pp. 45–54. – Paul D. Sturkie, *Avian physiology* (4th Ed.), New York 1986. – L.R. Drees – A. Manu, Bird urate contamination of atmospheric dust traps, *Catena* XXVII, 1996, pp. 287–94.

7 | Karel Verschueren, *Handbook of environmental data on organic chemicals*, New York 2001.

8 | E. Bernardi et al. (note 5).

9 | Ibidem.

10 | Ibidem.

11 | M. Bassi – Donato Chiatante, The Role of Pigeon Excrement in Stone Biodeterioration, *International Biodeterioration & Biodegredation* XII, 1976, No. 3, pp. 73–79.

12 | Gregory Lavenburg – D. Hall – J. Lewis – S. Wolfe – M. Strange, *Impacts of Bird Droppings and Deicing Salts on Highway Structures : Monitoring , Diagnosis , Prevention*, 1976 (December), 2011, s. 1–22.

The analysis performed on copper and bronze monuments in Prague showed the presence of moolooite (copper oxalate $Cu(C_2O_4)\cdot n(H_2O)$) and $(NH_4)_2Cu(SO_4)_2.6\ H_2O$ as a result of the effect of bird excrement.[13] The surface of copper and bronze corroded locally under the layer of these deposits and even the stable layer of protective patina is dissolved under the drops of bird excrement. Another study investigated the condition of the bronze sculpture [Figure 3 – statue of František Palacký, Prague] in the urban environment.[14] XRD analysis of the patina layer was performed and the resulting diffractograms indicated the presence of copper oxalate hydrate (moolooite) on the statue. This was attributed to the presence of a copious amount of bird droppings on the structure. The original green colour of natural bronze corrosion products, in areas affected by bird excrement, had been transformed into red run-off stains.

13 | Dagmar Knotková – Kateřina Kreislová, Atmospheric corrosion and conservation of copper and bronze, in: A. Moncmanová (ed.), *Environmental Deterioration of Materials*, Southhampton 2007, s. 107–143.

14 | Kateřina Kreislová – Dagmar Knotková – Alena Koukalová, *Posouzení korozního stavu plastik*, Praha 2010.

Fig. 3 ***Bird contamination on statue of František Palacký, Prague.*** *Photo: Kateřina Kreislová*

3. Experimental part – test procedures

Several tests were performed placing drops of different corrosive media (chemical components of bird droppings), all containing uric acid, on: 1) pure copper, 2) bronze plates and 3) copper with patina plates (roof samples from a Prague location). The pure copper specimens were prepared from normal cold-rolled laboratory grade ~100% Cu; the experimental plates measured 100mm x 70mm x 1mm and were treated before the experiment (by rinsing with distilled water, scrubbing with scouring powder, rinsing with distilled water, drying, brushing with a copper wire brush to remove existing patina, and rinsing once more with distilled water and then dried). The bronze experimental plates measured 75mm x 50mm x 5mm; the chemical composition of the bronze samples is specified in Table 2[15]. This type of bronze was chosen as it contains only 3% lead which is similar to historical bronze alloys. The samples of copper with patina were obtained from the Queen Anna's Summer Palace (Belvedere) roof in Prague, Czech Republic. The thickness of the copper samples ranged from 0.35 mm to 0.50mm (after its exposure of over 325 years). The thickness of the patina layer was within the range of 7–142 μm with an average value of 44 μm; the dominant compound of the patina was brochantite with other compounds such as cuprite and antlerite.[16] The sheets were cut to obtain specimens with the approximate dimensions of 100mm x 70mm to match the pure copper plates.

15 | Kateřina Kreislová – Alena Koukalová, *Hodnocení stavu měděné krytiny letohrádku Belvedér*, Praha 2012.

16 | Kateřina Kreislová – Hana Geiplova, Prediction of the long-term corrosion rate of copper alloy objects, *Materials and Corrosion* DXVII, 2016, No. 2, 2016, pp. 152–159.

17 | E. Bernardi et al. (note 5) – Gómez-Heras et al. (note 4).

Table 2 ***The chemical composition of the bronze experimental specimens (wt.%)***

Bronze Alloy	**Cu**	**Sn**	**Pb**	**Zn**	**Si**	**Ni**	**Fe**
Composition (% wt)	87.0	4.40	3.30	2.90	0.70	1.20	0.16

Each of the metal plates were numbered, weighed, and photographed. When not being studied, the metals were placed in a desiccator to remain dry. These materials were chosen in order to determine both the effects of components of bird droppings on copper versus those on bronze, and the effect of an established patina.

The tested corrosive media consisted of: 1) uric acid, 2) a mixture of uric acid and sodium nitrate, 3) a mixture of uric acid and potassium dihydrogen phosphate, 4) a commercial mixture with bird droppings, 5) a mixture of uric acid and potassium chloride and 6) a mixture of uric acid and potassium sulphate. The selected chemical compounds were based on the constituents of bird droppings mentioned in previous studies[17]. Pigeon droppings were also tested alongside the chemical compounds. Due to the limited time span, real bird droppings were not collected in sufficient quantity for testing, and only chemical analyses (pH, IEC and XRD) of the reference sample taken in Prague 4 were conducted. Material based on pigeon droppings, sold by a Belgian company as bait for fish, was purchased in the required amount and used for the experiment. During the study, the composition of this material was analysed [Table 3] and compared with the composition of the reference sample of fresh bird droppings taken in Prague on the balcony of a residential building [Table 4].

The tested corrosive media were applied to the metal specimens in the consistency of a paste [Figure 4]. For this purpose, suspensions of the substances in water were prepared. The solid compounds were first weighed on an analytical scale, then solid mixtures of uric acid with salts were prepared (1g of uric acid and 0.5 g of the individual salt) and then distilled water was added to prepare a paste. The pastes were applied as 'drops' to the metals in rows with a glass stirring stick. The approximate dry mass of each of the drops (excluding the bird droppings) was 0.002g. Similarly, purchased pigeon excrement was applied as "drops" in the form of a paste (suspension in water).

Table 3 ***The IEC and XRD results for the purchased bird droppings used in the experiment***

Anions	F^-	Cl^-	Br^-	NO^{3-}	PO_4^{3-}	SO_4^{2-}
mg/l	3.4	15.1	0.2	0.2	7.0	27.5
Cations	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
mg/l	10.1	0.2	28.5	6.5	24.1	
Minerals (XRD)	Magnesium Hydrogen Phosphate Hydrate	Weddellite	Calcite	Quartz		
Formula	$Mg(H_2PO_2)_2(H_2O)_6$	$CaC_2O_4(H_2O)_{2.4}$	$CaCO_3$	SiO_2		

Table 4 ***The IEC and XRD results for the reference pigeon excrement sampled in Prague (n.d. = not discovered)***

Anions	F^-	Cl^-	Br^-	NO^{3-}	PO_4^{3-}	SO_4^{2-}
mg/l	0.0	6.6	n.d.	n.d.	13.8	4.1
Cations	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
mg/l	5.4	18.0	12.0	1.7	1.3	
Minerals (XRD)	Magnesium Hydrogen Phosphate Hydrate	Weddellite	Aphthitalite	Quartz		
Formula	$MgNH_4PO_4\ (H_2O)_6$	$CaC_2O_4(H_2O)_{2.4}$	$K_3Na(SO_4)_2$	SiO_2		

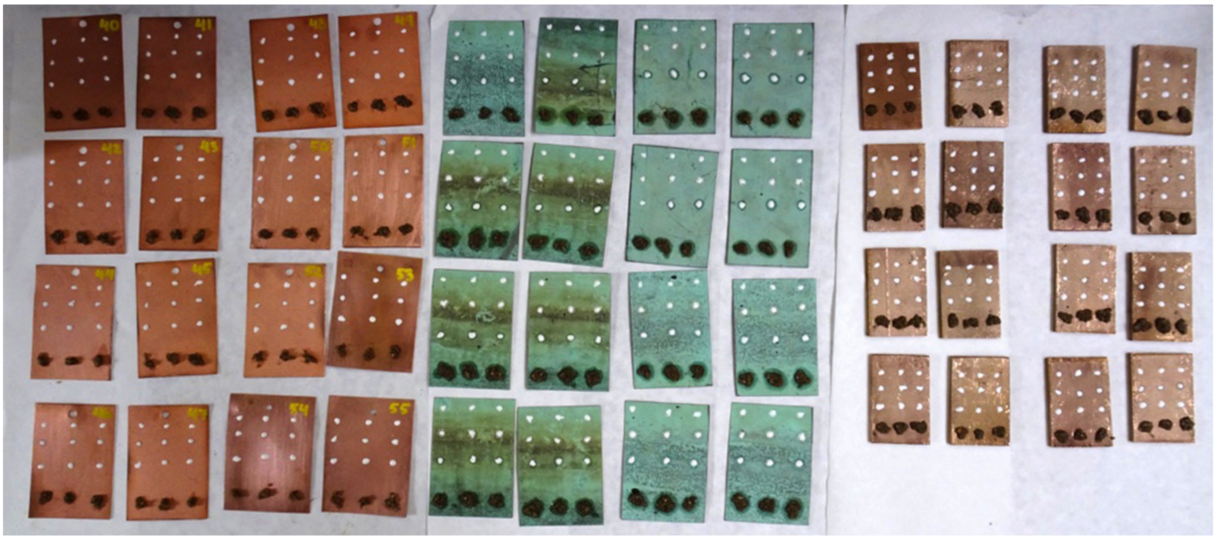

Figure 4 ***Copper, cooper with patina (Prague Belvedere roof), and bronze plates with the first four corrosive media applied.*** *Photo: Kristen Balogh*

The samples were exposed to two different environments. Two climatic chambers were utilized, each with 100% RH to accelerate corrosion. These chambers contained a bed of water at the bottom. The temperature was not modified and therefore reflected the temperature in the laboratory. The humidity and temperature were monitored and tracked throughout the experiment. The difference between the two chambers was that one was infused with SO_2 gas to mimic air pollution. Therefore, one half of the amount of samples was placed in each chamber. This part of the experiment was performed to determine the additional effect of SO_2 atmospheric pollution on the corrosion of the metals. The samples were removed at different time steps of exposure to track the rate of deterioration: 1 day, 1 week, 2 weeks, and 4 weeks (1 month).

The following procedures were utilized to analyse the results of the testing program. Ion Exchange Chromatography (IEC) was conducted on bird droppings used in the experiment and on referential real bird droppings collected from the balcony of a building in Prague. An IEC Dionex ISC 5000 was used with a conductivity detector to detect anions and cations. X-ray Diffraction (XRD) was conducted to identify the phase of a crystalline material in samples of bird excrement: a D8 Bruker was used with generator settings of 40mA, 40kV, Angular Range (2θ) 10-55°, Step size (2θ) 0.01°, Anode material Cu, spinning 15 rpm. [18]

The pH values of tested corrosive media removed from the metal surface after exposition were determined, as this data helped interpretation of the detected surface alterations. The drops were removed from the metal surface with a metal spatula, weighed, and then placed in a volumetric flask. 10mL of distilled water was added to each solution, the solutions were then filtered and the pH was measured using the pH meter.

At each sample extraction, the cleaned surface was observed using a Keyence VHX-5000 digital microscope. A fine-bristled toothbrush and cotton swab were utilized to remove the drops. Observation was conducted to investigate any visible corrosion products and any change of the surface morphology. Then the diffuse-reflected spectrophotometry method (Avantes equipment – AvaSpec-2048, AvaLight-Hal, and Ava Soft 8.0 software) was used to measure the colour differences that each of the solutions posed on the materials. During another step, the metal surfaces were again investigated by means of SEM with EDS. A scanning electron microscope (SEM) and Energy Dispersive Spectroscopy (EDS) helped to determine the elemental composition and morphology of the surface of the metals affected by the drops of corrosive media. The equipment used was the Quanta FEG 450 and Team software. For preparation, tape was applied and the sample was attached to the holder. Markings were used on the samples to aid in navigation among the different drop locations. These investigations were conducted only on the surfaces of the four-week samples.

18 | Alberto Viani, *XRD Analysis Report*, Telč 2017.

4. Results and discussion

The pH levels of the samples were first tested. As can be seen in Figure 5, the bird droppings used were more acidic than the fresh referential bird droppings (Prague). Overall, the samples are quite neutral.

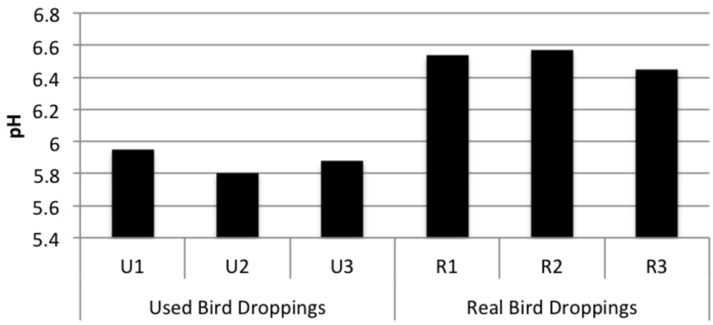

Figure 5 ***pH values of the bird-dropping samples.*** *Diagram: Kristen Balogh*

The evaluation of the surfaces of the samples was performed after the careful removal of the residual layers of the drops. These layers were partly washed down. The sample with bird droppings was entirely covered in mould and more blue crust could be seen [Figure 6].

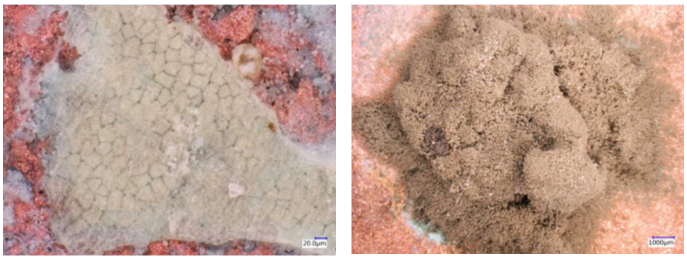

Figure 6 ***Copper with bird droppings covered in mould.*** *Photo: Kristen Balogh*

The effect of the chemicals simulating bird dropping was evident after 1 day of exposure in 100% humidity, the most visual changes were found on copper sheet contaminated by the following corrosive media: uric acid + sodium nitrate, uric acid + potassium chloride and uric acid + potassium sulphate. During 4 weeks' of exposure the development of corrosive products can be seen and after this period, a thin layer of dark corrosion products in the drop area with a ring of green products around the areas of these drops was observed [Figure 7]. In the case of the mixture of uric acid and potassium chloride, the surface of copper sheet was strongly etched.

As regards the samples with a stable layer of natural patina, the most aggressive effect was evident in the case of uric acid + potassium dihydrogen phosphate – after 1 day of exposure the patina was darker and white products formed on the boundary of the ring. In the case of the mixture of uric acid and potassium chloride the surface of copper sheet was strongly etched [Figure 8]. A similar effect was detected in the case of the deposition of uric acid and potassium sulphate, but only in 100% relative humidity conditions.

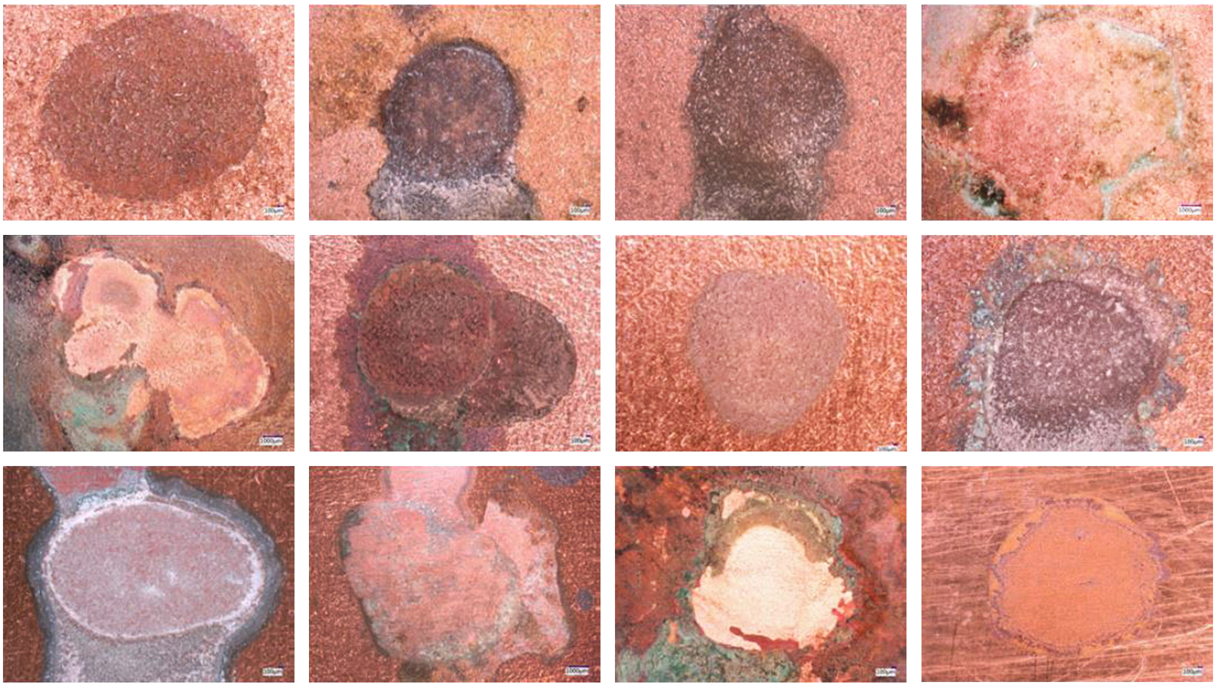

Figure 7 ***Copper under contamination after 2 weeks of exposition.*** *Photo: Kristen Balogh*

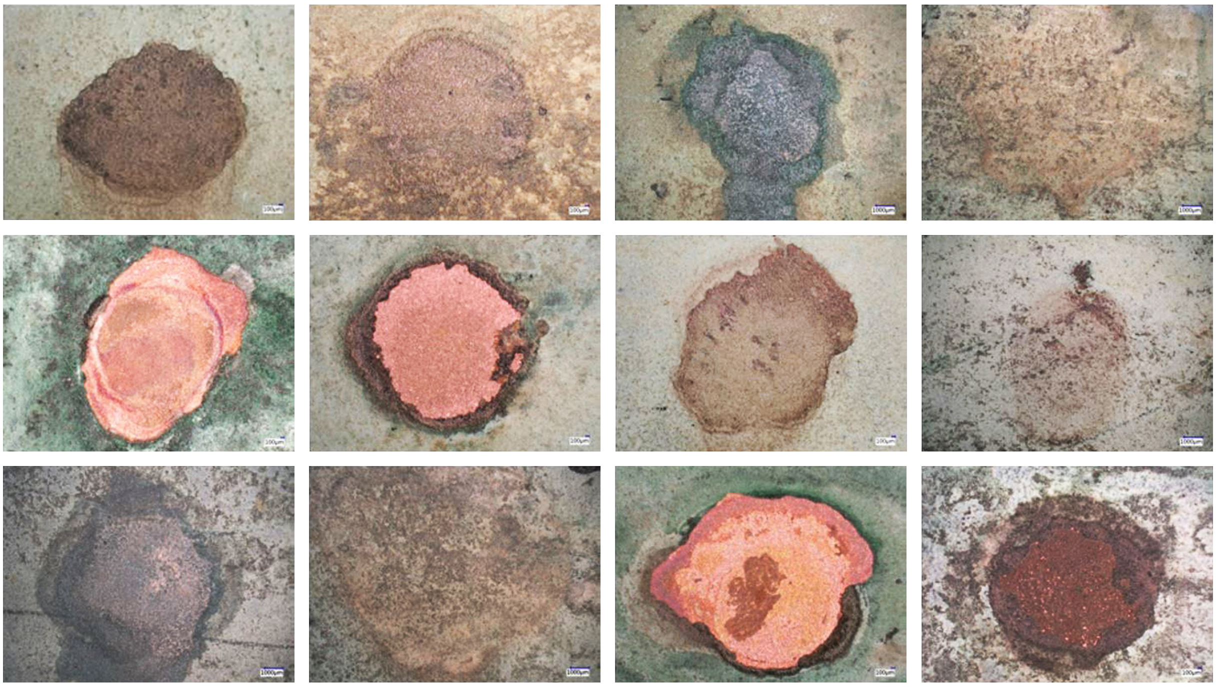

Figure 8 ***Copper with stable patina under contamination after 2 weeks of exposition.*** *Photo: Kristen Balogh*

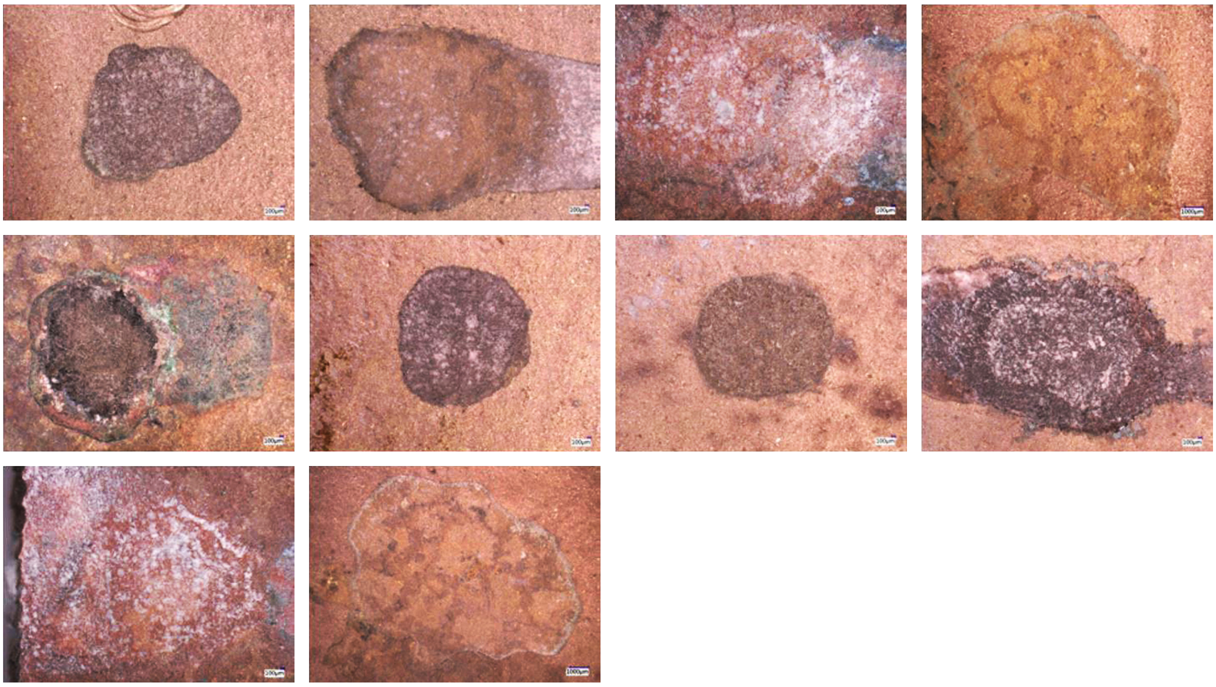

Figure 9 ***Bronze under contamination after 2 weeks of exposition.***
Photo: Kristen Balogh

The results of tests on bronze samples are very similar to those on copper sheet but less aggressive, probably due to the highly porous surface of casted samples [Figure 9]. Once again, the mixture of uric acid and potassium chloride on the surface of copper sheet had the strongest effect on the corrosion process.

Though the microscope gave a good visual representation of the colour transitions during the experiment, colourimetry allowed quantification of the colour changes. The change in colour was analysed for: 1) the inside and outside of each contaminant area, 2) inside the contaminant area between 2-week and 4-week samples, and 3) outside the contaminant area between 2-week and 4-week samples. The comparisons also allow the interpretation of the contribution of SO_2 pollution.

When comparing the total colour change (ΔE), there is no consistent pattern throughout all of the samples. The change between red and green (Δa*) shows more visible correlations [Figure 10]. The copper and bronze samples became greener, whereas the roof (patinated) in general became redder. It makes sense that uric acid + potassium chloride and uric acid + potassium sulphate became redder with the roof sample as the copper became exposed. Also, the uric acid + potassium dihydrogen phosphate of the roof samples becomes greener with the RH sample, which can be correlated with the blue-green colour that is evident after exposure. Bronze displays the least change in red/green among all three materials. There is no large difference between the RH and RH + SO_2 samples.

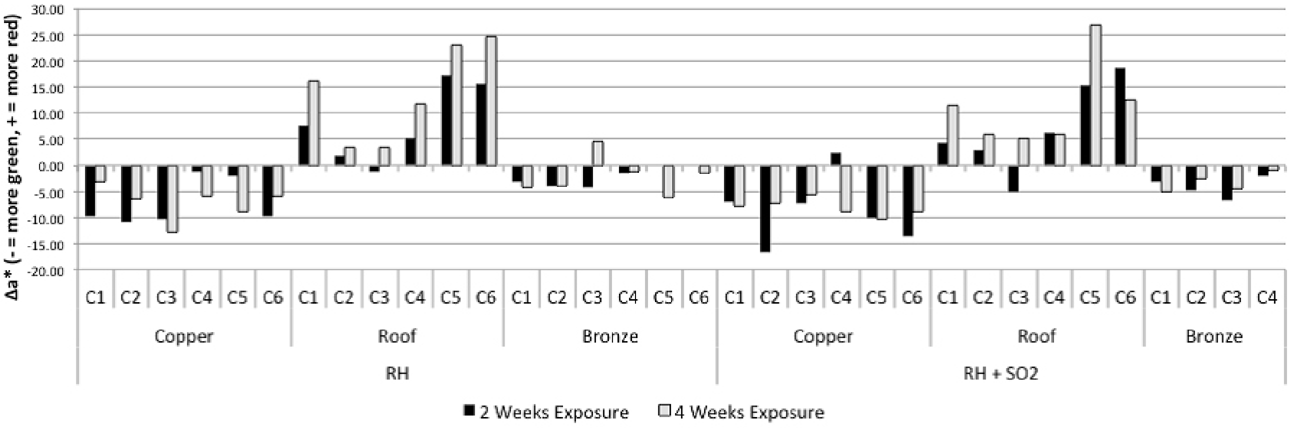

Figure 10 ***Difference in red and green between the inside and outside of drops. Contaminants: C1 uric acid, C2 mixture of uric acid and sodium nitrate, C3 mixture of uric acid and potassium dihydrogen phosphate, C4 Belgian bird droppings, C5 mixture of uric acid and potassium chloride, C6 mixture of uric acid and potassium sulphate.*** *Diagram: Kristen Balogh*

The morphology of all the samples exposed for 4 weeks were examined using SEM, with SEM/EDS also being used for qualitative investigation of the surface elemental composition. The surface of the uric acid + potassium chloride exposed at 100% RH is much more pitted and not uniform compared to that outside of the drop area [Figure 11, above]. Concerning the exposition 100% RH + 5 ppm SO_2, the contaminated surface was not as pitted as the RH exposed sample, but still it had a much rougher surface than the surrounding copper [Figure 11, below].

The patina of the roof sample has a rough appearance as compared to the copper samples. It is comprised primarily of brochantite [19], thus sulphur was detected together with other elements such as ferrous, silicon, aluminium representing dust particles. The nitrogen and carbon that are present are most likely from the uric acid itself [$C_5H_4N_4O_3$] and from other chemicals used for the dropping media; other elements represented additional chemicals.

The bronze sample surfaces were a lot less uniform, consisting of small fragmented layers. The exterior bronze surfaces primarily consist of copper. In some cases its other components such as tin, lead, zinc, silicon, nickel, and iron are present.

On samples of copper, copper with a stable patina and bronze too, chains of white spheres were visible throughout under the drops of uric acid exposed at 100% RH [Figure 12] – it is estimated that it is the growth of mould spore from the uric acids. After research into the different bacterial and fungal species found on bird droppings from previous studies [20, 21], it is presumed that these are the spores from either penicillium cyclopium or penicillium expansum.

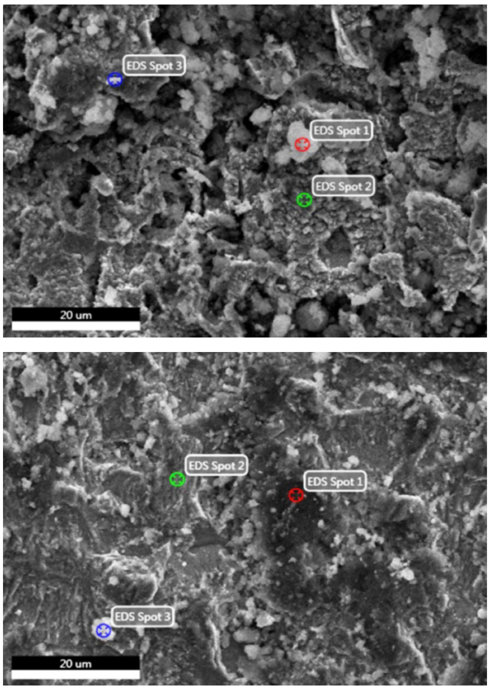

Figure 11 ***SEM image of the copper surface under drop of uric acid + potassium chloride exposed for 4 weeks in 100% RH*** *(above)* ***and 100% RH + 5 ppm SO_2*** *(below).*
Photo: Kristen Balogh

19 | Kreislová – Geiplova (note 17).

20 | Conidia, *Molds*, http://conidia.fr/en/molds/. retrieved June 24, 2017.

21 | He - Liu - Mustapha – M. Lin, Antifugal activity of zinc oxide nanoparticles against Botrytis cinerea and Penicillium expansum, *Microbiological Research*, 2011, No. 166, pp. 207–215.

5. Conclusions

The composition of bird droppings was determined using ion exchange chromatography (IEC) and X-ray diffraction (XRD). The anions found in the bird droppings used, ranging from the highest concentration to the lowest were: sulphate, chloride, phosphate, fluoride, bromide, and nitrate. The composition of media simulating the bird droppings was slightly different than that of real bird droppings because the emphasis was given to cations[22] instead of anions which are more significant in the corrosion process.

The microscopy and colourimetry provided a good analysis of the visual impact of the contaminants. The surfaces in all of the samples changed depending on the contaminant added. Some became cracked, whereas others became more fragmented and pitted than their surroundings.

Sometimes the contaminant acted as a protective agent and the surrounding metal tarnished. In most cases, the copper and bronze became a darker brown colour, most likely indicating the initial formation of posnjakite or cuprite. The turquoise colour of some of the contaminants most likely indicated copper (II) hydroxide. Performed tests showed that the long-term effect of bird droppings is very significant, especially in the case of a surface with a stable natural patina. The corrosion attack in test conditions of only high humidity (100%) is much more significant than in conditions of high humidity and low SO_2 pollution. The low concentration of SO_2 slightly inhibited the effect of aggressive chemicals simulating bird dropping except for the effect of chloride salt.

The mixture of uric acid + sodium nitrate created dark corrosion spots and a red area after two weeks' of exposure, and the surface was more eroded with red spots after four weeks [Figure 13]. This colour was also found on the statue of František Palacký due to the powerful effect of bird excrement [Figure 3].

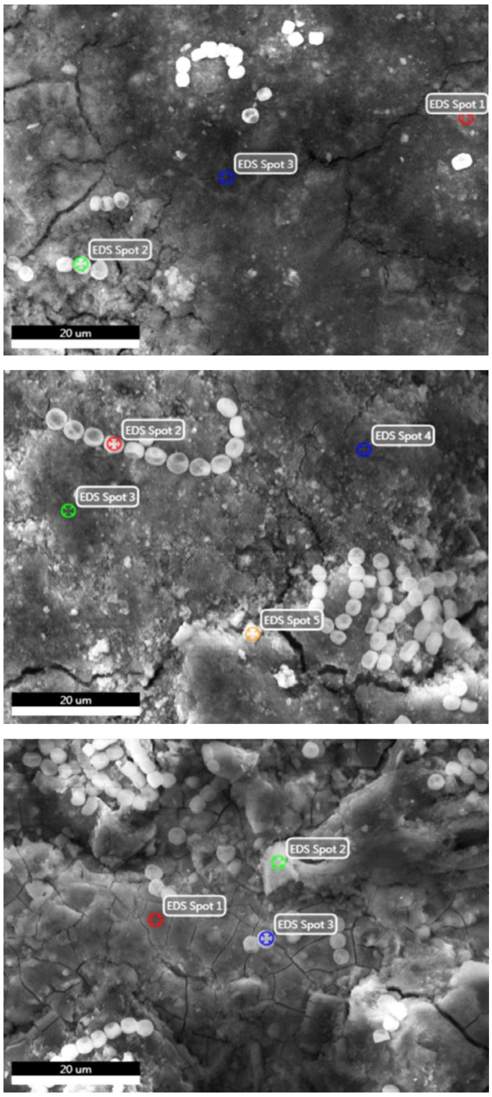

Figure 12 ***SEM image of the circular chain element on copper*** *(above)*, ***copper with stable patina*** *(middle)* ***and bronze*** *(below). Photo: Kristen Balogh*

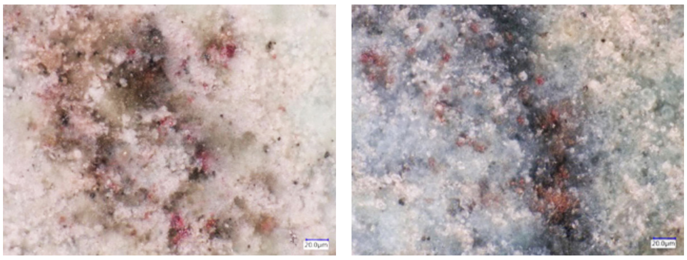

Figure 13 ***Layers of deposits and corrosion products in drops of uric acid + sodium nitrate and applied (Belgian) bird droppings after 4 weeks´exposure – eroded surface with red crystals.*** *Photo: Kristen Balogh*

Acknowledgements

This work was undertaken with support from the project No. LO 1219 under the Ministry of Education, Youth and Sports National sustainability programme I.

22 | E. Bernardi et al. (note 5).

RESUMÉ

ZKOUMÁNÍ PŮSOBENÍ PTAČÍCH EXKREMENTŮ NA KOVOVÉ MATERIÁLY MĚĎ A BRONZ

Studie se zaměřuje na zkoumání účinku ptačího trusu na měď a bronz a reviduje současný stav znalostí týkajících se vlastností mědi a bronzu a degradačních procesů souvisejících s působením ptačích exkrementů. Posuzovány jsou také předchozí studie týkající se vlivu exkrementů ptáků na různé materiály.

Za použití zrychlené zkoušky stárnutí byly zkoumány různé aspekty: vliv specifických dopadajících komponent na chemické složení a morfologii povrchů kovů, další účinky na životní prostředí a vliv doby trvání expozice. Čisté měděné plechy, měděné plechy s rozvinutou patinou stejně jako bronzové plechy byly podrobeny působení šesti rozdílných roztoků, které napodobovaly složení ptačích exkrementů: 1) kyselina močová, 2) kyselina močová a dusičnan sodný, 3) kyselina močová a fosforečnan draselný, 4) získané ptačí exkrementy, 5) kyselina močová a chlorid draselný, 6) kyselina močová a síran draselný. Kontaminované kovy byly umístěny do dvou komor: v první při pokojové teplotě a s relativní vlhkostí 100 %, ve druhé při pokojové teplotě a s relativní vlhkostí 100 % a s plynem SO_2, imitujícím atmosférické znečištění. Vzorky byly vyjímány v různých intervalech v rozpětí čtyř týdnů.

Výsledky iontově-výměnné chromatografie (IEC) a rentgenové difrakce (XRD) ukázaly různé chemické složení vzorků holubího trusu. Ptačí trus použitý v experimentu (belgická rybí návnada) se odlišoval od výkalů získaných odběrem ptačích exkrementů v Praze. Hlavními anionty v belgickém ptačím trusu byly sírany, chloridy a fosfáty, zatímco ptačí trus z Prahy se sestával především z fosfátů, a méně z chloridů a síranů. Belgický trus se primárně sestával z kationtů draslíku, vápníku a sodíku, zatímco pražský ptačí trus obsahoval především amonné, draselné a sodné ionty.

Z výsledků XRD vyplývá, že belgický ptačí trus obsahoval kalcit, křemen, weddellit a hydrát hydrogenfosforečnanu hořečnatého. Pražský ptačí trus obsahoval také křemen a weddellit, avšak zbytek sestával z afthitalitu a hydrátu fosforečnanu hořečnato-amonného.

Digitální mikroskopie ukázala změny v barvě a struktuře povrchu kontaminovaných kovových vzorků. Vizuální hodnocení ukázalo, že změny mohou být u vzorků pozorovány už v průběhu čtyř týdnů, a že mezi expozicí s relativní vlhkostí a s relativní vlhkostí obohacenou SO_2 jsou v tomto čase minimální rozdíly. Pomocí skenovací elektronové mikroskopie (SEM) a energiově disperzní spektroskopie (EDS) bylo určeno chemické složení, popsána morfologie povrchu kovů pod kapkami roztoků chemických sloučenin a byl též zjištěn růst spor plísně na některých vzorcích.

Celkově lze říci, že ptačí exkrementy podporují proces koroze kovů. Patina může působit jako ochranná vrstva proti korozi nějakou dobu, pak se její stav začne zhoršovat. Avšak aby bylo možné vidět podrobnější výsledky, bylo by zapotřebí delšího výzkumu.