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Approaching on Colorimetric Change of Porous Calcareous Rocks Exposed in Urban Environmental Conditions from Iasi – Romania

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Abstract. According to the scientific literature, the pollution phenomenon is strongly related by the urban activity from the last decades, with direct effects on the state of conservation of the stone constructions also. This paper presents a preliminary study on the colorimetric evolution of the lithic surfaces exposed under strongly traffic influence from the urban microclimate conditions. The analysed lithic surfaces are similar with the building stone from the structure of an historical monument (from 19th century), such as the *Stone Bridge* in Iasi - Romania, located in the immediate vicinity of the roadside loop with the same name. The colour change monitoring for the above-mentioned geomaterials aims at anticipating the effects of postponing the decongestion of car traffic and implicitly initiating the assessment of the effects of pollution over this historic monument, which is in an advanced state of deterioration and degradation.

1. Introduction

In the recent decades, the urban environment has undergone major changes, including cities such as Iasi (Romania), where the interaction between the atmosphere and historic stone monuments leads to the alteration of the lithic surfaces and the appearance of a new superficial layers [1] that ultimately affect the geomaterials [2] used to implement these objectives. Thus, taking into account the intensive use in local constructions of porous sedimentary indigenous lithic materials specific to the Iasi area [3], it is necessary to perform interdisciplinary studies, to monitor the colour changes of the surfaces affected by the atmospheric pollution by gravimetric deposition of airborne particles [4], given that for the scientific preservation of historical monuments the use of the same geomaterials as the original

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ones must be taken into account in all restoration interventions[5,6] but in an entirely different environment than the initial state [7,8].

The paper also presents the evaluation of the color changes of the lithic surfaces as a way to interpret the degree of pollution and its dynamics over time [9].

2. Materials and method

The lithic material exposed to urban environmental conditions is a sedimentary and oolithical calcareous rock (Fig. 1), form during the Sarmatian geological age, and was sampled from Paun – Repedea village, Iasi County.

CIE *L*a*b** colorimetric investigations were performed using a Lovibond® RT 300 (Reflectance Tintometer D65/10°) spectrophotometer, monitoring the chromatic deviation at the same measurement points in each specific work step.

Scanning Electron Microscopy (SEM) coupled with energy dispersive X-ray (EDX) allowed the recording of the micrographic analyzed area and recording the spectrum based on which to determine elemental composition for lithic materials. A scanning electron microscope model Vega II LSH – Tescan®, coupled with an EDX detector, model Quantax QX2 – Bruker - Roentec® was used (Fig. 1).

Colorimetric investigations were carried out in constant laboratory conditions, at a temperature of 21°C and relative humidity (RH) of 60%.

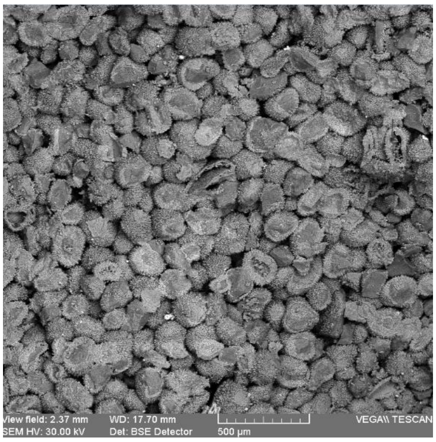

Figure 1. SEM image (100xbse) on oolithical calcareous sample surface.

3. Experimental part

The current urban environmental exposure area is located in the city of Iasi (Romania) in the immediate vicinity of a 19th century historical monument, called *Stone Bridge* (*Podul de Piatra*), which is located over the Bahlui River and borders South of a major and crowded road junction, bearing the same name: *Stone Bridge* (figure 2a and 2b). Thus, the sampling area is located between the historic building and the eastern part of the intersection, with the following geographical coordinates: 47.158035 N, 27.575451 E (figure 2c and 3).

For exposure to urban environmental conditions, six samples of calcareous rock, numbered P1 to P6, were cut using roughly rectangular shapes with at least two planar surfaces to facilitate fastening on support and to have a uniformity of the gravimetric deposition areas of the airborne particles, while allowing for colorimetric investigations before and after each exposure (figure 4).

Exposure of stone samples was performed in two distinct periods, as follows: Oct. 10 ÷ Nov. 09, 2016 (*31 days*) and Nov. 16, 2016 ÷ Feb. 16, 2017 (*93 days*). Taking into account that 19 days of precipitation were recorded in the first 31 days of exposure [10], the samples were withdrawn, stored and dried under laboratory conditions for 96 hours, after which the colorimetric measurements were carried out. Also, after the second exposure within 93 days, the samples were withdrawn and dried under the same laboratory conditions for a new set of colorimetric measurements (table 1).

Figure 2. *Podul de Piatră – Stone Bridge* Intersection from Iasi, Romania: a - older *(historical)* bridge; b – newer bridge; c – geographical position for exposure area.

Figure 3. Exposure place, near road junction, with geographical coordinate: 47.158035 N, 27.575451 E.

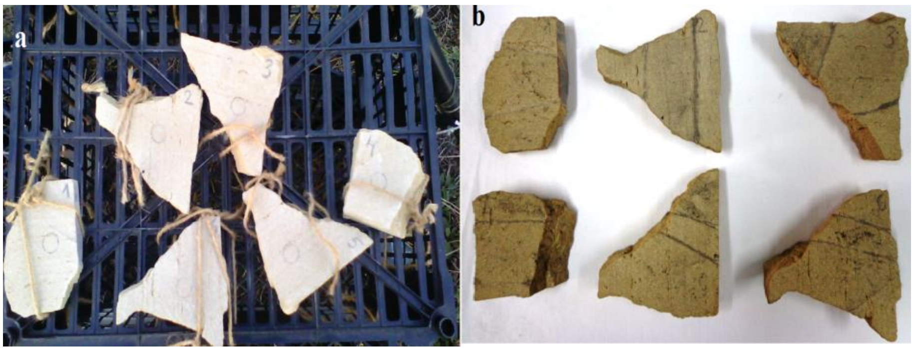

Figure 4. Lithical samples: a – fresh calcareous rocks, before exposure period; b – after 124 exposure days (right image is obtained in laboratory conditions).

Table 1. Colorimetric change after the two exposure periods.

Lithical samples	ΔE^*_{ab}	
	after 31 exposure days	after 124 exposure days
P1	0.91	9.29
P2	2.14	9.80
P3	2.32	10.97
P4	2.15	7.51
P5	2.62	**11.39**
P6	1.11	**7.26**

Concerning the colorimetric evolution, the colour change was measured for each coordinate (L^*, a^* and b^*), as compared to its initially value, on the same sample and in the same point, whereas the total change of colour (ΔE^*_{ab}) was calculated in accordance with the following equation [11-13]
$\Delta E^*ab = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$, in which:

- ΔL^* represents the change in light intensity in the respective point, at different time intervals, as compared to the initial value ($\Delta L^* = L^*_n - L^*_{initial}$), where L^* represent the lightness to darkness coordinate and varying from 0 (black) to 100 (white);
- Δa^* represents the chromatic modification of the coordinates of axis a^* ($+a^*$ indicating red and $-a^*$ green), from the same point, at different time intervals, as compared to its initial value ($\Delta a^* = a^*_n - a^*_{initial}$);
- Δb^* represents the chromatic modification of the coordinates of axis b^* ($+b^*$ means yellow and $-b^*$ blue) while respecting the same method of calculation ($\Delta b^* = b^*_n - b^*_{initial}$).

4. Results and discussions

According to literature and analyzing the results presented in Table 1, an excess of the minimum value for total color change ($\Delta E\ ^*_{ab} > 5$) [11] for each of the six samples is observed after 124 exposure days, which confirms the meeting of preliminary conditions of alteration of the lithic surfaces [4,7,8].

Thus, for the preliminary assessment of the atmospheric pollution conditions, elemental analysis by SEM-EDX technique was performed by two microprobes, taken from the sample with the minimum value of the color change ($\Delta E^*_{ab} = 7.26$, sample P6) and respectively from the sample with the maximum value ($\Delta E^*_{ab} = 11.39$, sample P5), the results obtained are presented in Figure 5 and table 2.

Also, analyzing the elemental compositions (table 2), the following aspects can be observed:
- increasing the presence of Si and Al elements on the surface samples (outside) as compared to the non-exposed inner part (inside) indicates the deposition of aluminosilicates from the street dust (both due to of peri-urban soils erosion and the increase of buildings progress with direct implications for the street dust form);
- the sulphur appearance on the sample surfaces, exposed to urban conditions, indicates the presence precursor conditions of $CaSO_4$ as a first effect of pollution[14,15], especially due to the biomass combustion and using Diesel engines;
- the occurrence of sodium and chlorine on the outer surface of the P5 sample indicates the uses of sodium chloride to defrosting the adjacent streets to the exposure area. The fact that these two elements do not appear on the surface of the sample P6 can be the explanation of the higher value of the total colour change, where: $\Delta E^*_{ab} = 11.39$ for P5 vs. $\Delta E^*_{ab} = 7.26$ for P6.

During the 124 days of exposure, there were 63 days of specific precipitation to the cold season in the temperate continental climate [10]. Besides the elemental chemical changes signaled on the exterior lithic surfaces, these conditions contribute to the colorimetric evolution previously presented. Also, a major role in the transport and subsequent deposition of atmospheric particles are the winds from this topoclimate, which is predominantly from the West - Northwest direction (WNW) to the South – East (SE), according to field measurements [10,16] (figure 6).

Table 2. SEM-EDX - elemental composition in percentage (inside vs. outside) for lithical micro-samples P5 and P6, after 124 exposure days.

Elements	Sample P5 (ΔE^*_{ab} = 11.39)				Sample P6 (ΔE^*_{ab} = 7.26)			
	% atomic		% weight		% atomic		% weight	
	inside	outside	inside	outside	inside	outside	inside	outside
Calcium	32.08	21.48	48.96	35.55	29.79	32.09	46.20	46.82
Silicon	12.90	14.14	13.80	16.41	12.33	19.47	13.39	19.91
Aluminum	0.97	1.65	0.99	1.84	1.23	1.76	1.29	1.72
Carbon	0.24	0.75	0.11	0.37	0.26	0.13	0.12	0.06
Iron	0.70	0.76	1.49	1.75	0.65	0.79	1.42	1.59
Manganese	0.37	0.31	0.77	0.70	0.30	0.00	0.61	0.00
Potassium	1.57	1.13	2.34	1.83	1.50	2.47	2.27	3.52
Magnesium	0.65	1.02	0.60	1.02	0.93	0.74	0.87	0.66
Sodium	0.60	1.84	0.52	1.74	0.87	0.94	0.77	0.79
Oxygen	49.93	55.52	30.42	36.68	51.31	40.85	31.76	23.79
Sulfur	0.00	0.59	0.00	0.79	0.00	0.33	0.00	0.39
Chlorine	0.00	0.53	0.00	0.77	0.00	0.00	0.00	0.00
Titanium	0.00	0.28	0.00	0.55	0.46	0.43	0.85	0.75
Phosphorus	0.00	0.00	0.00	0.00	0.37	0.00	0.45	0.00
Total	100	100	100	100	100	100	100	100

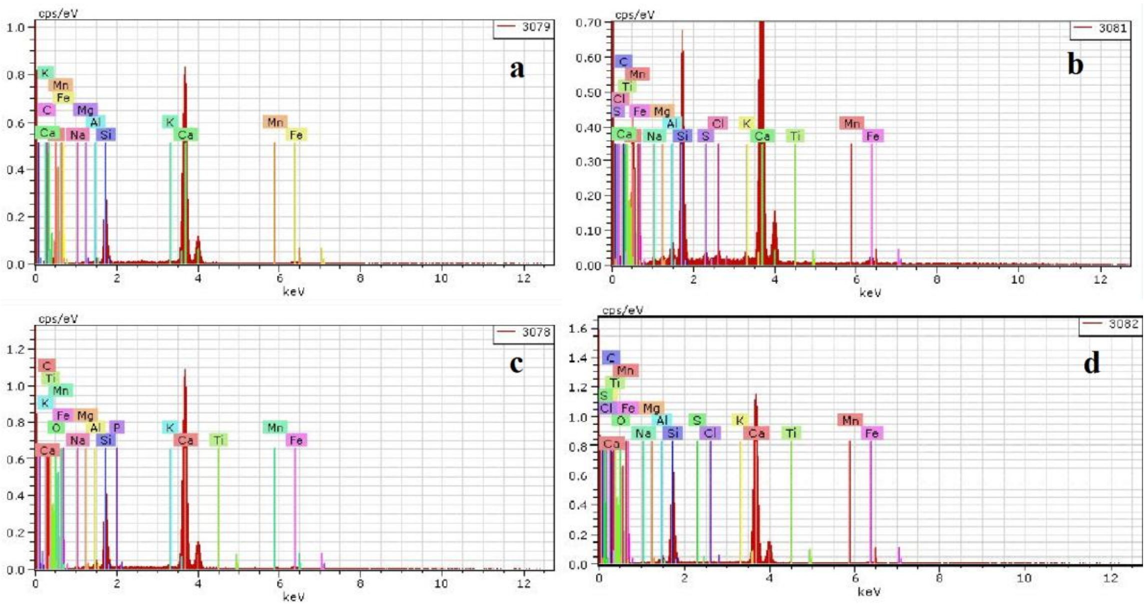

Figure 5. EDX spectral analysis for lithical micro-samples, after 124 exposure days: a – P5 inside; b – P5 outside; c – P6 inside; d – outside.

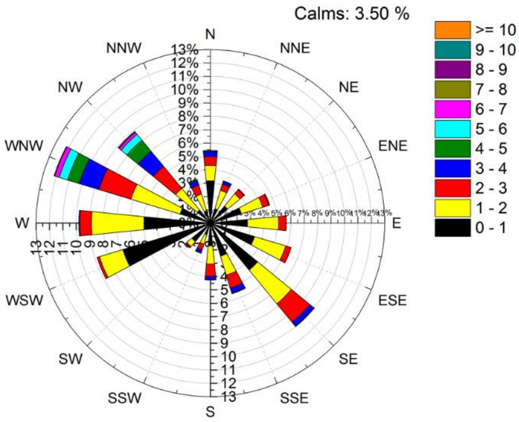

Figure 6. Wind rose for exposure periods, in *Stone Bridge* Intersection – Iasi, Romania.

5. Conclusions

Taking into consideration the fact that, starting with September 25, 2014, the Commission of the European Union calls on Romania to take measures to reduce air pollution, including in the city of Iasi [17] it is necessary to study all aspects of this issue due to the multiple unwanted effects, including historical monuments. Thus, the interdisciplinary researches carried out in the *Podul de Piatra* (*Stone Bridge*) Intersection [16] confirm the various forms or degrees of pollution with major implications on the Iasi community. Also, the colorimetric evolution - during only four months - of the lithic surfaces exposed in the current urban environment, characterized mainly by the increase of the road traffic, is an additional argument for the permanent monitoring and management of the respective topoclimate [18].

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