COMPARATIVE ASSESSMENT ON COLORIMETRIC CHANGE OF CALCAREOUS GEOMATERIALS EXPOSED IN URBAN AND PERIURBAN ENVIRONMENTAL CONDITIONS FROM IASI CITY – ROMANIA

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Rezumat. *Schimbările climatice, tot mai frecvent raportate în ultimele trei decenii, necesită o mai bună înțelegere a modului în care o serie de geomateriale calcaroase, intens utilizate la nivel local, reacționează la factorii de mediu, cu implicații directe în deteriorarea și degradarea unor suprafețe construite din piatră. O evaluare preliminară a impactului poluării asupra acestor materiale litice este reprezentată de monitorizarea modificărilor colorimetrice aparente. În același timp, scopul lucrării este de a evidenția modul în care poluarea atmosferică acționează asupra materialelor litice, în condiții de trafic auto urban intens, comparativ cu o serie de condiții periurbane din orașul Iași - România, în aceeași perioadă și în aceleași condiții meteorologice.*

Abstract. *Climate change, more frequently reported over the last three decades, requires a better understanding of how a series of limestone geomaterials, intensively locally used, react to environmental factors, with direct involvement in the deterioration and degradation of some stone built surfaces. A preliminary assessment of the impact of pollution on these lithic materials is the apparent colorimetric changes. At the same time, the aim of the paper is to highlight the way in which atmospheric pollution works in urban traffic intensities, compared to a series of periurban conditions in the city of Iasi - Romania, at the same period and the same weather.*

Keywords: calcareous geomaterials, stone built surface, CIE *L*a*b** colorimetry, atmospheric pollution, urban and periurban environment

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1. Introduction

As it is well known, increasing urban air pollution concerning many specialists and organizations or institutions in Europe that draw attention to the consequences of changing the quality of ambient air, both in terms of population health and urban, periurban or rural ecology and on the accelerated alteration of building surfaces, including built heritage [1-5]. Scientific data and research over the past few decades have confirmed that polluting trends will generate undesirable industrial, urban and transport emissions on the conservation state of historic buildings, which will pose a serious threat to architectural heritage surface made by natural stone [5-7]. The aim of the paper is to present a preliminary method to monitoring, diagnose and evaluate some aesthetic and colorimetric changes for a series of calcareous and porous indigenous geomaterials exposed simultaneously in an intense urban activity area with increasing auto traffic, respectively, in a periurban area, characterized by the presence of a palustrian habitat and a rich tree vegetation with obvious premises for improvement of the ambient air.

2. Materials and methods

The used samples are oolithical sedimentary calcareous stones (see Figure 1) [8], by *Sarmatian* geological age. These rocks was collected from Paun Repedea, Iasi County, which was for many years an important quarry to provide the natural stone necessary for construction of many local buildings [9]. We both performed the colorimetric study of these samples with the aid of Lovibond®RT300 spectrophotometer (Reflectance Tintometer D65/10°) and monitored the chromatic change. This colorimetric investigation was made in constant laboratory conditions, at t~21°C and relative humidity (RH) approximatively equal to 60%. The meteorological parameters were monitored using a LSI LASTEM station which contains sensors and characteristics for wind and relative humidity.

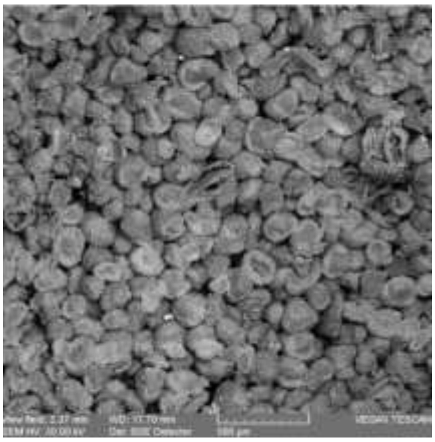

Fig. 1. Scanning electron microscope image (SEM 100×) on the oolithical sample taken from Paun – Repedea quarry, near Iasi City. [8]

3. Experimental part

The color change was determined for each coordinate (L^*, a^* and b^*) and compared to its initial value. The measurements were made for the same sample and in the same point. The total change of color (ΔE^*_{ab}) is given by this mathematical formula [8, 10-12]:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}\ ,\ \text{when:}$$

- ΔL^* is the change in light intensity: $\Delta L^* = L^*_n - L^*_{initial}$. In last equation L^* represents the lightness to darkness coordinate and varying from 0 (black) to 100 (white);

- $\Delta a^* = a^*_n - a^*_{initial}$ in which Δa^* is the chromatic change of the coordinates of a^* axis ($+a^*$ corresponds to red and $-a^*$ to green);

- Δb^* is the chromatic change of the coordinates of b^* axis ($+b^*$ corresponds to yellow and $-b^*$ to blue), considering the same math formula: $\Delta b^* = b^*_n - b^*_{initial}$.

After taken calcareous rocks from a pit located on the outskirts of Paun - Repedea village, in southern part of Iasi city - Romania, to allow the correct colorimetric investigations of the sample these were sliced having rectangular shapes with at least two planar surfaces. The aim of this cutting was to obtain a uniformity of the gravimetric deposition areas of the airborne particles [13].

The current urban environmental exposure area is located nearby the *Stone Bridge* (*Podul de Piatra*) (see Figure 2). This exposure area is located between the historical bridge and the south-eastern part of the intersection, having the geographical coordinates: 47.158035 N, 27.575451 E (see Figure 3) [8].

Fig. 2. *Stone Bridge* (*Podul de Piatra)* road junction Iasi, Romania. **a** - historical bridge; **b** – newer bridge; **c** –location of exposure area. [8]

To make this exposure we used six slices samples, marked from P1 to P6. The exposure time was divided in three periods: the first period called T1 during from October 10 to November 09, 2016 (*31 days*); the second called T2, from November 6, 2016 ÷ February 16, 2017 (*93 days*) and the third period called T3 during from February 23 ÷ August15, 2017 (*174 days*). Thus, for these samples, total exposure period was *298 days* and colorimetric change values before and after the three exposure periods are presented in Table 1.

Fig. 3. Exposure place for samples P1÷ P6, near *Bridge Stone* intersection, with location data: 47.158035 N, 27.575451 E [8].

Table 1. Total colour change values for sample P1 ÷ P6, before and after the three exposure periods, in *Stone Bridge* area.

Samples	Exposure periods														
	initial value			T1 - Oct. 10 ÷ Nov. 09, 2017				T2 - Nov. 16, 2016 ÷ Feb. 16, 2017				T3 - Feb. 23 ÷ Aug. 15, 2017			
	*L**	*a**	*b**	*L**	*a**	*b**	ΔE^*_{ab}	*L**	*a**	*b**	ΔE^*_{ab}	*L**	*a**	*b**	ΔE^*_{ab}
P1	69.14	5.22	19.15	69.47	5.44	19.84	**0.91**	60.24	4.39	16.50	**9.29**	67.13	4.56	18	**2.35**
P2	67.04	5.09	18.78	69.12	5.07	19.28	**2.14**	58.20	4.02	14.69	**9.80**	64.19	4.45	17.06	**3.39**
P3	69.05	5.12	18.43	69.26	5.63	20.70	**2.32**	58.38	4.28	16.01	**10.97**	66.41	4.76	18.38	**2.66**
P4	68.95	4.84	17.88	69.53	5.32	19.89	**2.15**	61.48	4.53	17.16	**7.51**	67.35	4.45	18.11	**1.67**
P5	68.73	5.13	18.87	68.65	5.22	19.57	**2.62**	60.31	4.45	16.78	**11.39**	*62.20**	*4.44**	*16.84**	***9.64****
P6	68.98	5.39	19.37	69.09	5.66	20.44	**1.11**	61.91	4.78	17.82	**7.26**	*62.29**	*4.75**	*17.65**	***6.94****

*Samples P5 and P6 were not exposed during T3 period and these values were obtained after some investigations and storage in the desiccator under constant laboratory conditions.

During the T1 period, 19 days of rain occur [8, 14]. Because of the weather conditions the samples were stored and dried in laboratory conditions during 96 hours. After this we collected the colorimetric data. Also, during the T2 period (because of mixed precipitations, rain and snow) the samples were investigated in laboratory conditions to obtain a new set of colorimetric measurements.

Analyzing the colorimetric data obtained after the first two exposure periods, it was observed that all of these six samples had total change of colour values (ΔE^*_{ab}) more than 5 units, above the limit at which each sample is considered to have a minimum color change can be discussed in relation to what determined that effect [10]. Therefore, the sample with the maximum value of the ΔE^*_{ab} = 11.39 (P5), together with the sample corresponding minimum value, ΔE^*_{ab} = 7.23 (P6), were withdrawn from the third exposure (T3) with the purpose to investigate color change on lithical surfaces, relative to atmospheric conditions specific to environmental pollution in that area [15].

Simultaneously with the location of samples P1 ÷ P6 in the urban area *Stone Bridge*, six other lithic samples, similar from a petrographic point of view, were exhibited from the same source of indigenous natural stone: Paun - Repedea village. These samples were cut using the same slicing process, resulting in rectangular surfaces, optimal for exposure to climatic and atmospheric factors [13]. These samples were marked from C1 to C6 and were located about 100 meters from the shore of artificial lake *Ciric II*, located in the periurban area of N - NNE of Iasi [47.182827 N, 27.604205 E] (see Figure 4).

Fig. 4. Exposure place for samples C1÷ C6 near shore of *Ciric* Lake, with geographical coordinate: 47.182827 N, 27.604205 E.

This lake has as its main destination part of the regularization of the Ciric River. Due to the presence of both the water surface and a habitat dominated by the tree vegetation, as well as the absence of intense car traffic, this area is attractive for the inhabitants of Iasi through the possibilities of recreation even if it is crossed by the road to the local airport that is in the development phase. The exposure cycles for the C1 ÷ C6 samples are similar to P1 ÷ P6 in order to obtain a series of comparative colorimetric data (see Figure 5 and Table 2) useful in assessing urban and periurban environmental conditions in the metropolitan area of Iasi, due to the capacity of porous lithic surfaces to become witness of atmospheric pollution [16, 17].

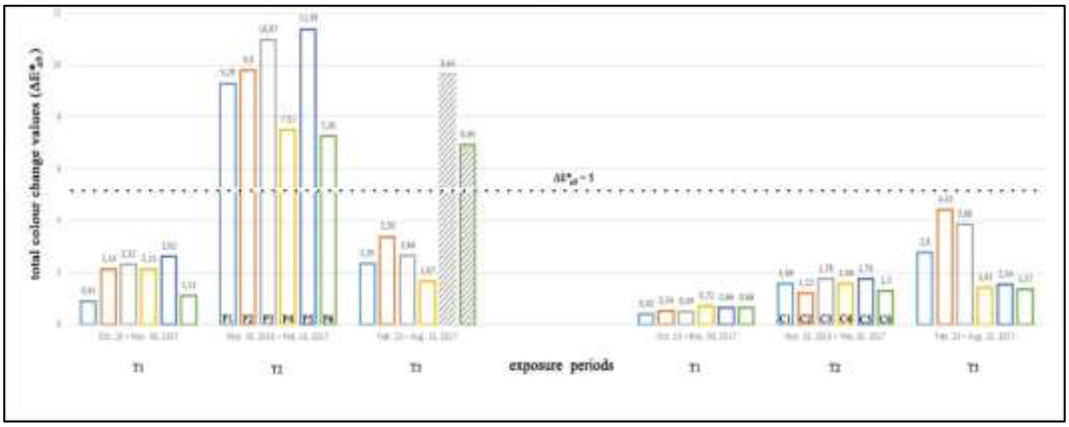

Fig. 5. Comparative graphical representation of the colorimetric data obtained in both exposure areas (*Stone Bridge* and *Ciric*), during the same exposure periods. **Obs:** The graphical representation for the P5 and P6 samples from the T3 period is marked differently because the samples were withdrawn after T2 for instrumental investigations and subsequently stored under laboratory conditions, being remade colorimetric measurements at the end of T3, along with P1 ÷ P4.

Table 2. Total color change values for C1 ÷ C6 samples, before and after the three exposure periods, in *Ciric* area.

Samples	Exposure periods														
	before			Oct. 10 ÷ Nov. 09, 2017				Nov. 16, 2016 ÷ Feb. 16, 2017				Feb. 23 ÷ Aug. 15, 2017			
	*L**	*a**	*b**	*L**	*a**	*b**	**Δ*E**ab**	*L**	*a**	*b**	**Δ*E**ab**	*L**	*a**	*b**	**Δ*E**ab**
C1	74.18	4.80	20.32	74.49	4.78	20.04	**0.42**	72.72	4.64	19.75	**1.58**	71.52	4.24	19.66	**2.80**
C2	73.05	4.69	20.23	73.45	4.68	19.88	**0.54**	72.05	4.52	19.55	**1.22**	68.91	3.98	18.81	**4.43**
C3	74.47	4.90	20.62	74.88	4.86	20.34	**0.49**	72.92	4.63	19.79	**1.78**	7.85	4.28	19.41	**3.86**
C4	73.80	4.57	19.79	74.45	4.50	19.48	**0.72**	72.42	4.35	19.05	**1.58**	72.63	4.20	19.05	**1.43**
C5	71.49	5.74	23.31	71.88	5.56	22.81	**0.66**	70.05	5.38	22.36	**1.76**	70.69	5.08	22.17	**1.54**
C6	73.64	4.73	19.76	74.12	4.53	19.36	**0.66**	72.54	4.43	19.16	**1.30**	72.65	4.24	18.94	**1.37**

Monitoring of meteorological parameters was performed during 05 Oct. 2016 ÷ 20 Aug. 2017, thus covering all three exposure periods. In the case of winds, both the direction and their intensity were recorded, their representation being shown in Figure 6. The atmospheric humidity data were obtained by processing over 61,000 percentages recorded at regular intervals (see Figure 7).

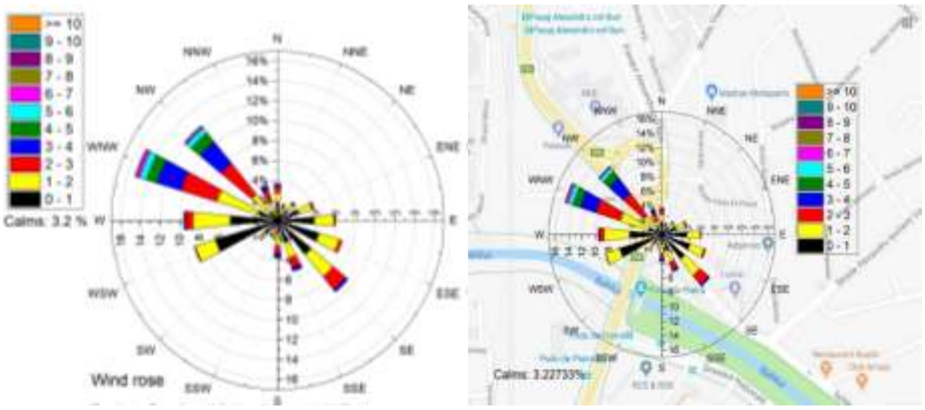

Fig. 6. The wind rose for T1, T2 and T3 periods, in *Stone Bridge* road junction, from Iasi - Romania.

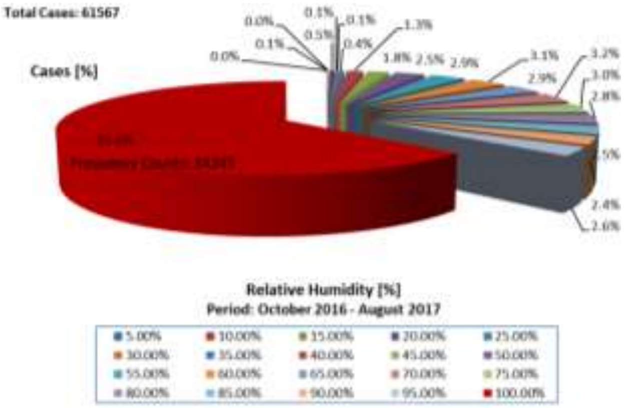

Fig. 7. Relative humidity during the period of October 2016 ÷ August 2017, in urban zone from Iasi city.

4. Results and discussions

As can be seen in the colorimetric data in Table 2, as well as in the graph in Figure 5, the samples P1 ÷ P6, recorded ΔE^*_{ab} values above 5 units, at the end of the exposure period T2, meaning that they exceeded the minimum threshold required for the exchange significant color [10] due to the gravimetric deposition of particles in the atmosphere, also confirmed by macroscopic and visual analysis, by the color change of the lithic surfaces visible before and after exposure (see Figure 8,a and Figure 8,b).

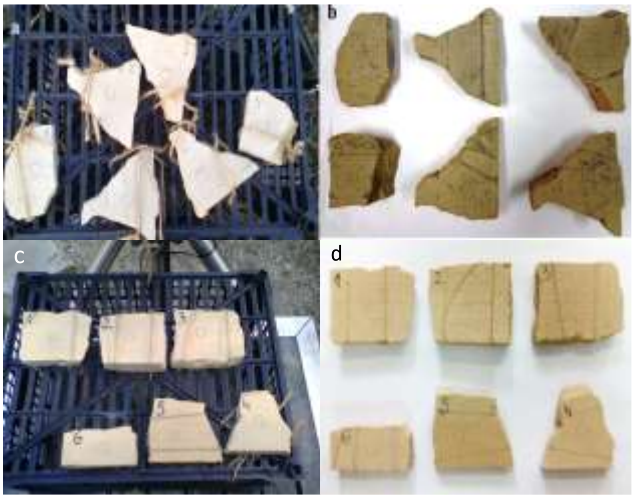

Fig. 8. Rock samples: **a**. P1 ÷ P6 initial calcareous surfaces, before exposure periods; **b**. P1 ÷ P6 surfaces after 124 days exposure; **c**. C1 ÷ C6 surfaces before exposure periods; **d**. C1 ÷ C6 surfaces after 298 days exposure days (pictures **b** and **d** are obtained in laboratory conditions).

Instead, after withdrawal of samples P5 and P6, samples P1 ÷ P4 experienced a regression of ΔE^*_{ab} values until the end of the T3 period, when about 300 days of exposure were achieved. A major factor in fluctuating evolution ΔE^*_{ab} of samples P1 ÷ P6 is the high share of days with relative humidity of 100%, meaning 34,245 data records (55.6%) out of a total of 61,567 (see Figure 7). The high relative humidity of the T1 and T2 periods is typical of the cold season from October to February, when it manifests with an increased frequency of rain, fog, hoarfrost and especially snow, which favors the transfer of particles from the atmosphere to the soil and to the built surfaces [18]. The quality of the urban environment in Iasi city is directly influenced also by the occurrence of the thermal inversion phenomenon, which maintains or pushes to the ground the existing pollutants at that time, which further led to the dark shades of the P1 ÷ P6 lithic surfaces exposed in the intensive traffic area of the *Stone Bridge* intersection [19].

Last but not least, it should be noted that the dominant presence of snow during the T2 period involved PM particles as well, which is confirmed by the specialized literature through the specific snowflake structure which allows for greater adhesion of many pollutants on the architectural surfaces in the ratio with drops of rain [20, 21]. The presence of PM particles in the urban area from Iasi city in the three exposure periods is confirmed by the public data of the National Air Quality Monitoring Network website (see Figure 9), which has a monitoring station in the immediate vicinity of the exposure area for samples P1 ÷ P6, having the following geographic coordinates: 47.156840N, 27.574813E [22].

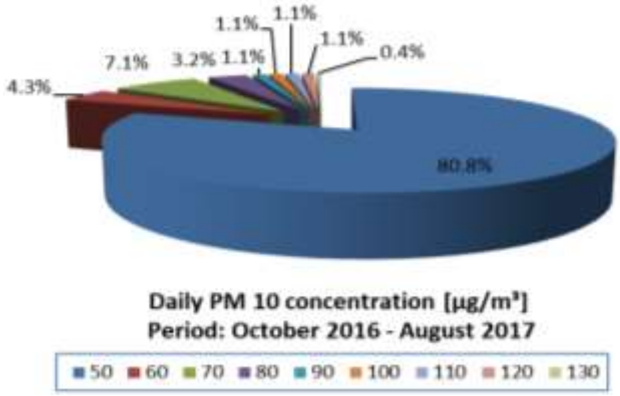

Fig. 9. Statistics of daily PM 10 concentration during the T1 ÷ T3 exposed periods, in *Stone Bridge* road junction area - Iasi City [22].

In Figure 9 it can observe the PM10 concentration shows that approximately 19% from daily averages have exceeded the legal limit value of 50 μg/m^3 but sufficient to be involved in the evolution of color exchange of investigated lithic surfaces from samples P1 ÷ P6, considering that many authors associate the presence of PM10 with the existence of intense windy periods [23], confirmed also by the data recorded by the meteorological station LSI LASTEM. In Figure 6 it is observed that the winds in this topoclimate are most time from the West - Northwest (WNW) to the South-East (SE), in concordance to other authors [19]. This wind direction corresponds to the following aspects favorable to the transport of pollutants and airborne to Iasi city, such as:

- the presence and development of the most important national road nexus with the west of the country, with a significant annual increase car traffic;

- the development of economic investments and a large periurban residential area in western part of Iasi city, which in turn generates various atmospheric pollutants (eg: Valea Lupului locality);

- the presence in this western area of some lands in the Bahlui riverbed, which are inappropriate for agricultural activities, being ultimately exposed to constant wind erosion.

On the other hand, the transition period from the cold season to the warm and then predominantly warm season, similar to the T3 period, favors the occurrence of short and intense rainfall with direct implications in regression of total color change values by the surfaces of samples P1 ÷ P4, through a washing phenomenon - *self-cleaning* [24, 25]; thus explaining the low final values of the total color exchange according to Table 1. With all these investigations and colorimetric measurements, can say that without some specialized intervention, some lithic surfaces even slightly blackened (such as those in Figure 8b) remain with an undesirable aesthetic aspect which will amplify over time without control and proper patrimony management [26]. Unlike the samples exposed in the *Stone Bridge* urban area, the low ΔE^*_{ab} values for samples exposed in the *Ciric* periurban area (C1 ÷ C6) can be correlated with the following aspects:

- the presence of a habitat with predominantly arboreal vegetation, which retains through the massive foliage an important part of the atmospheric pollutants [27];

- the water surface can favor the presence of aerosols with retention effect for airborne pollutants but without fully studied and elucidated of this phenomenon, as in the case of marine aerosols [28, 29];

- the impossibility of developing residential complexes within this perimeter due to the special utility status of this wetland;

- although the recreation area is crossed by the road to the locally small airport, car traffic is significantly lower than the one of the *Stone Bridge* intersection and therefore the worrying presence of specific gaseous pollutants it is not in discussion.

Finally, the porous limestone surfaces exposed in the *Ciric* periurban area remained without any undesirable effect of color change, even after the approximately 300 exposure days in T1 ÷ T3 periods (see Figure 8, c and Figure 8, d), which confirms that some architectural surfaces, in particular those of historical monuments, may have a status of a pollution witness (or pollution indicator) of the environment in which they are located [16,17,30].

Conclusions

Due to the porous character of indigenous limestone rocks from Iasi city area, there is a susceptibility (or receptivity) to the accumulation deposits on their surface, especially due to the abundance of atmospheric precipitations during certain cold periods of the year [31, 32], but there are some possibilities of partial self-cleaning effect, in few situations of reversible aesthetic and physical transformations [33]. Therefore, calcareous rocks from the Iasi city area, used in civil or historical constructions, are witnesses of atmospheric pollution, indicating the degree and/or duration of undesirable anthropogenic effects [17], while allowing preliminary assessment of the urban or periurban environment in which the respective construction are located.

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